CAPACITIVE ENERGY STORAGE:
FILLING THE GAP

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Capacitive Energy Storage:
Filling the gap
DECLARATION

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Richard Fields

September, 2017
Abstract

Energy storage is a fundamental requirement for utilising clean but intermittent renewable resources, maintaining a resilient power grid and powering a multitude of portable electric devices and systems. The work presented in this thesis investigates methods of filling the performance gap between electrochemical capacitors (EC) (commonly known as supercapacitors) and batteries; the former often has high power capability but low energy density while the latter often has high energy density but low power capability. Three approaches towards this are taken during this work: first, capacitance balancing of a traditional electrical double-layer capacitor (EDLC) type EC device is attempted by electrode material asymmetry; this approach advances upon previous techniques in which cells have electrode material symmetry but electrode mass asymmetry. The benefits of capacitance balancing were found to be improved device energy density and reduced capacitance loss during long term operation. Second, a novel type of lithium ion capacitor (LIC) which uses a silicon based negative electrode is developed. Such a device was found to offer high power capability (23 kW kg⁻¹) while demonstrating an energy density of over 97 W h kg⁻¹, both values are per total electrode mass. Third, layer-targeted spray deposition was used to deposit multi-walled carbon nanotubes (MWCNTs) as specific locations within an electrode structure. It was found that spray depositing MWCNTs at the outer electrode surface may increase its power capability. A consequence of this targeted deposition may be a reduction in the current collector material alongside improvements in energy storage and power capabilities.
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# CONTENTS

## 1 GENERAL INTRODUCTION

1.1 Introduction 1

1.2 General Aims and Objectives 4

1.3 Outline and Thesis Structure 5

## 2 LITERATURE REVIEW

2.1 Introduction 8

2.2 Electrochemical Principles Related to ECs 8

2.2.1 Electrochemistry Fundamentals 9

2.2.2 Classical Electrical Energy Storage Devices 13

2.2.3 Electrolytes for ECs 19

2.2.4 EC Charge Storage Mechanisms 24

2.2.5 Summary and Conclusion 28

2.3 EC Configurations and Performance 29

2.3.1 EC Configurations 30

2.3.2 General Performance 34

2.3.3 Summary and Conclusions 37

2.4 Organic Electrolyte based EDLCs: Materials and Considerations 38

2.4.1 Electrode Materials and Associated Capacitance 39

2.4.2 Relationship between SSA, PSD and Capacitance 45

2.4.3 Cell Ageing and Mass Balancing 47

2.4.4 Summary and Conclusions 49

2.5 Investigations of Lithium Ion Capacitors 50

2.6 Design and Fabrication of EC Devices 55

2.6.1 General Components 55

2.6.2 Effect of Electrode Thickness 58

2.6.3 Methods for Active Electrode Material Deposition 59

2.6.4 Cell Containment 62

2.6.5 Summary and Conclusions 66
2.7 Conclusion and Outlooks

2.8 Research Aims

3 EXPERIMENTAL CONFIGURATIONS, MATERIALS AND CHARACTERISATION TECHNIQUES

3.1 Introduction

3.2 Experimental Configurations
   3.2.1 General Configurations
   3.2.2 Electrode Material Asymmetric Capacitance Balancing
   3.2.3 Silicon Based Negative Electrode in Lithium Ion Capacitors
   3.2.4 Multilayer Spray Deposition

3.3 Experimental Materials
   3.3.1 Electrolyte Salts and Solvents
   3.3.2 Active Electrode Materials
   3.3.3 General Components

3.4 Characterisation Techniques
   3.4.1 Nitrogen Sorption Measurement and Isotherm Analysis
   3.4.2 Scanning Electron Microscopy and Elemental Analysis
   3.4.3 Electrochemical Analysis Techniques

3.5 Conclusion

4 PHYSICAL CHARACTERISATION AND FABRICATION TECHNIQUES

4.1 Introduction

4.2 Active Material Physical Characterisation
   4.2.1 Active Material Observations by SEM and EDX Analysis
   4.2.2 Isothermal Response of Nitrogen Sorption
   4.2.3 Specific Surface Area from Isotherm Analysis
   4.2.4 Specific pore volumes from Isotherm Analysis
   4.2.5 Pore Size Distribution from Isotherm Analysis

4.3 Toyal Carbo® Observations by SEM and EDX Analysis

4.4 Tape Casting and Disk Cutting of Electrode Coatings
   4.4.1 Equipment and Configuration
4.4.2 Concentrated Slurry Preparation for Tape Casting 115
4.4.3 Tape Casting Deposition 117
4.4.4 Electrode Disk Cutting 117
4.4.5 Tape Casting Method Analysis 118

4.5 Electrolyte Preparation and Cell Containment 121
4.5.1 Equipment and Configuration 122
4.5.2 Electrolyte Preparation 122
4.5.3 Coin (‘Button’) Cell Fabrication 123

4.6 Conclusion 127

5 THE IMPACT OF ELECTRODE CAPACITANCE RATIO ON ASYMMETRIC ACC/PAC EDLC ELECTROCHEMICAL CAPACITORS UTILISING ORGANIC ELECTROLYTE 130

5.1 Introduction 130

5.2 Methodology 133
5.2.1 Materials and Experimental Control 133
5.2.2 Electrochemical Analysis and Key Performance Indicators 134
5.2.3 Cell Ageing 135

5.3 Electrochemical Analysis of AC Materials in both a Material and Mass Symmetric Cell Configuration 137
5.3.1 Cell Configurations - Material and Mass Symmetric Cells 137
5.3.2 Results and Analysis - Material and Mass Symmetric Cells 139
5.3.3 Conclusion - Material and Mass Symmetric Cells 148

5.4 Potentiostatic Ageing of Material Symmetric while Mass Asymmetric EDLC Cells 149
5.4.1 Cell Configurations – Material Symmetric but Mass Asymmetric Cells 149
5.4.2 Theoretical Insight – Material Symmetric but Mass Asymmetric Cells 151
5.4.3 Results and Analysis – Material Symmetric but Mass Asymmetric Cells 152
5.4.4 Conclusion – Material Symmetric but Mass Asymmetric Cells 162

5.5 Potentiostatic Ageing of Material Asymmetric (ACC/PAC) EDLC Cells 163
5.5.1 Cell Configurations – Material Asymmetric Cells 163
5.5.2 Theoretical Insight – Material Asymmetric Cells 164
5.5.3 Results and Analysis – Material Asymmetric Cells 165
5.5.4 Conclusion – Material Asymmetric Cells

5.6 The Impact of Mass Asymmetry on Potentiostatic Ageing of Material Asymmetric (ACC/PAC) EDLC Cells

5.6.1 Cell Configurations – Material and Mass Asymmetric Cells
5.6.2 Theoretical Insight – Material and Mass Asymmetric Cells
5.6.3 Results and Analysis – Material and Mass Asymmetric Cells
5.6.4 Conclusion – Material and Mass Asymmetric Cells

5.7 Discussion

5.8 Summary and Outlook

6 AN INVESTIGATION OF USING A SILICON BASED NEGATIVE ELECTRODE IN LITHIUM ION CAPACITORS

6.1 Introduction

6.2 Methodology

6.2.1 Experimental Overview
6.2.2 Materials and Experimental Control
6.2.3 Electrochemical Analysis and Key Performance Indicators
6.2.4 Pre-lithiation Technique – Formation Cycling

6.3 LIC Using a Graphite Based Negative Electrode

6.3.1 Theoretical Insight – LIC with Graphite Based Negative Electrode
6.3.2 Cell Configurations – LIC with Graphite Based Negative Electrode
6.3.3 Results and Analysis – LIC with Graphite based Negative Electrode
6.3.4 Conclusion – LIC with Graphite Based Negative Electrode

6.4 LIC Using a Silicon Based Negative Electrode

6.4.1 Initial Theoretical Insight – LIC with Silicon Based Negative Electrode
6.4.2 Cell Configurations – LIC with Silicon Based Negative Electrode
6.4.3 Results and Analysis – LIC with Silicon Based Negative Electrode
6.4.4 Conclusion – LIC with Silicon Based Negative Electrode

6.5 Comparison of Si and GC based LIC devices

6.6 Summary and Outlook
7 A STUDY OF MULTILAYER SPRAY DEPOSITION FOR COMPOSITE CARBON ELECTRODES

7.1 Introduction

7.2 Methodology

7.2.1 Experimental Overview
7.2.2 Materials and Experimental Control
7.2.3 Electrochemical Analysis and Key Performance Indicators

7.3 Spray Deposition of Electrode Coatings

7.3.1 Equipment and Configuration
7.3.2 Dilute Slurry Preparation for Spray Deposition
7.3.3 Spray Deposition
7.3.4 Spray Deposition Method Analysis

7.4 Multi-layer Spray Deposition of PAC Electrodes

7.4.1 Cell Configurations
7.4.2 Results and Analysis
7.4.3 Conclusion

7.5 Multi-layer Spray Deposition of Composite PAC/MWCNT Electrodes

7.5.1 Cell Configurations
7.5.2 SEM Analysis of MWCNT Dispersion in Spray Deposited Electrodes
7.5.3 Electrochemical Results and Analysis
7.5.4 Conclusion

7.6 Targeted MWCNT deposition in Multi-layer Spray Deposition of Composite PAC/MWCNT Electrodes

7.6.1 Cell Configurations
7.6.2 SEM Analysis of Targeted MWCNT Deposition in Spray Deposited Electrodes
7.6.3 Electrochemical Results and Analysis
7.6.4 Conclusion

7.7 Summary and Outlook

8 GENERAL DISCUSSION

8.1 Experimental Techniques and Characterisation – A Review
8.2 Impact of Electrode Capacitance Ratio on Asymmetric ACC/PAC EDLC Electrochemical Capacitors using Organic Electrolytes 315

8.3 Investigation of using a Silicon Based Negative Electrode in Lithium Ion Capacitors 317

8.4 Study of Multilayer Spray Deposition for Composite Carbon Electrodes 321

9 CONCLUSIONS AND FUTURE WORK 324

9.1 Conclusions 324

9.2 Future Work 326

10 REFERENCES 328

APPENDICES 346

Appendix 1 – Derivation of Energy Stored in Capacitor. 346

Appendix 2 – Review of pseudocapacitive materials. 347

Appendix 3 – Gravimetric coulomb capacity for a carbon electrode using the intercalative (lithium) charge storage mechanism. 349

Appendix 4 – Gravimetric energy density for an LIC based on an activated carbon positive electrode and graphitic carbon negative electrode 349

Appendix 5 – Gravimetric coulomb capacity for a silicon electrode using the intercalative (lithium) charge storage mechanism. 352

Appendix 6 – Gravimetric energy density for an LIC based on an activated carbon positive electrode and silicon negative electrode 353

Appendix 7 – Gravimetric energy density for an LIC based on an activated carbon positive electrode and an underutilised negative electrode. 354

Appendix 8 – Inference of specific surface area (SSA) from a pore size distribution (PSD) with the underlying assumption of slit shaped pores. 358

Appendix 9 – SEM Images of Activated Carbon Materials 359

Kynol 507-15 Activated Carbon Cloth 359
Sigma C9157 Powdered Activated Carbon 360
Appendix 10 – EDX Analysis of NXA-513 361

Appendix 11 – Variance in reference point for a silver quasi-reference electrode (QRE) incorporated into a coin cell device. 364

Appendix 12 – Calculating the quantity of lithium atoms in 1 g 1M LiPF6 EC/DEC 50/50 electrolyte. 364

Appendix 13 – Constant current charge-discharge (CCCD) of sample A of a lithium ion capacitor (LIC) with a graphite based negative electrode. 365

Appendix 14 – Constant current charge-discharge (CCCD) plots of silicon based LIC devices (3rd sample only) with increasing current density 366

Appendix 15 – Plastic stencil used for spray deposition 371

Appendix 16 – Planar SEM images of spray deposited electrodes. 372

Appendix 17 – EDX analysis of defects present in spray deposited electrodes 373

11.17.1 Electrode Site A 373
11.17.2 Electrode Site B 375

Appendix 18 – Analysis of spray deposited samples using IEC 62576 standards 380

LIST OF TABLES 384

LIST OF FIGURES 388

ABBREVIATIONS AND ACRONYMS 398
For formatting purposes:
Lists of tables, figures and nomenclature are presented at the end of this thesis.

Note:
The final page of this thesis contains nomenclature for ease of access.
1 GENERAL INTRODUCTION

1.1 Introduction

Energy storage is a fundamental requirement for having an advanced technological society, where energy production is decoupled from immediate energy consumption. The ability to do this is an absolute necessity for utilising clean but intermittent renewable resources, maintaining a resilient power grid and powering a multitude of portable electric devices and systems. There are seven main energy storage categories: mechanical flywheels, compressed air, thermal capture, pumped hydroelectric, flow batteries, electrostatic capacitors and solid state electrochemical energy storage. As of 2010, pumped hydroelectric represented 99% of static energy storage installed worldwide [1] while solid state electrochemical devices, such as lithium ion batteries, represent the majority of portable energy storage [2, 3]. In particular, it is portable energy storage which has facilitated the rise of portable computing and is expected to play a prominent role in supporting mankind’s transition away from fossil fuelled cars [4].

The field of solid state electrochemical energy storage focuses around two devices, electrochemical batteries, commonly shortened to just batteries; and electrochemical capacitors (ECs). These two devices have a common feature in that energy storage takes place at an electrode-electrolyte interface with electron and ion transportation being indirectly associated, but their energy storage methods differ. In a battery, electrical energy is stored by the conversion of energy through reduction-oxidation (redox) reactions at the positive and negative electrodes. In contrast, an EC does not utilise any redox reactions; instead, energy is stored in the form of electrostatic attraction between electrons and ions at the electrode-electrolyte interface, subsequently forming an electric double layer (EDL) in the electrolyte.

While the primary purpose of these devices is energy storage, it is also necessary to consider power, the rate at which energy can be transferred. To broadly compare the capabilities of each device, a gravimetric Ragone plot (shown in Figure 1.1) is used to visually express the differences in device energy storage and power capability [5]. Disregarding lithium primary batteries which cannot be recharged, it is quite obvious that rechargeable batteries such as those using nickel-metal hydride and lithium-ion chemistries occupy the high-energy region of the plot while ECs
occupy the high power region. Of key importance is that at no point do regions intersect and thus a gap becomes apparent in which a high energy, high power device may possibly exist.

![Graph showing capacitive energy storage](image)

Figure 1.1  Gravimetric energy and power capabilities of commercially available electrochemical and capacitor devices. Dashed lines indicate RC time constant; red and green areas indicate batteries. From ref [6].

The gap between batteries and ECs is one which has been of great interest in recent research [7, 8] but it has been one which is difficult to fill. Apart from an energy-power related gap, there are other notable differences such as cycle life, cost and upscaling, all of which need to be addressed. The cycle life of a lithium ion battery is in the order of $10^3$ cycles [9], comparatively poor considering that ECs can achieve $10^6$ cycles [10]; to represent this clearly, note that a mobile phone or laptop battery, ‘modemly’ non-removable, is often charged and discharged on a daily basis and, as such, has little chance of surviving 5-10 years’ worth of use before the battery is unusable and the device is discarded. As such there has been particular emphasis in research of not only seeking high energy/high power devices, but ones which also achieve long cycle lives [11].

A cost analysis has put the current energy specific price of a battery between 200 to 4,000 US$ kWh$^{-1}$ [2, 12] whereas an EC with comparable energy storage would cost ten times more; instead, EC devices find advantage in their power specific price which, at $\sim$15 US$ kW^{-1}$, is
one-fourth that of batteries [12]. As of 2014, EC sales are less than 3% of lithium-ion battery sales [13]; this significant difference in sales can be understood by considering the intended applications; batteries are good at powering portable products for extensive periods of time while ECs similarly used could provide power for one tenth of the time at best. As such, the majority of EC applications relate to providing rapid bursts of energy to perform emergency tasks [14] or providing short power boosts to augment other power provision systems [15].

It can be theorised that there are in fact three approaches to bridging the gap between batteries and ECs: the first would be to improve the power capabilities of batteries; the second would be to improve the energy storage capabilities of ECs and the third would be to search for an energy storage device which operates on novel principles associated with neither of the two previous devices. The third option sounds extremely implausible and the first option is already under investigation but poor electrical conductivity and slow ion transport, particularly at the positive electrode; are being found to be insurmountable power limiting factors [16, 17, 18, 19]. The second option has received little interest in the past but recent advances in understanding phenomena such as nanomaterial-electrolyte relationships [20] and pseudocapacitance [21] have led to renewed hope that it may be a viable method for filling said gap. Thus, it was decided to pursue the second option for the work entailed as it is believed this holds the most promise for a substantial breakthrough.

In addition, by considering a broader picture, it is clear to see that batteries and EC devices are not necessarily in competition with one another. Instead, these devices can complement each other by operating in parallel to build an energy storage and provision system which excels in all areas. At the present point, ECs are the weaker part of such a system due to their low energy density and non-constant voltage during discharge and as such limit their development; thus, by improving EC performance it would certainly better facilitate their implementation. Such implementation could take the form of utilising ECs in electric vehicles to harvest energy by regenerative breaking, increasing drive range [22]; and to reduce power demands on the battery, hence improving cycle life [23, 24].

Other novel applications which could also utilise improved EC energy storage are satellite based synthetic aperture radar (SAR) [25], a form of ranged observation; and the temporary storage of energy from intermittent renewable resources [26], taking great advantage of the long cycle life of ECs. Futurological considerations have also led the author to theorise that improved ECs could also play a significant role in autonomous technology. Modern distribution centres
are presently trialling electric vehicles to move packages from storage to shipping [27, 28]; while battery technologies have long recharge time, improved ECs could possibly provide adequate runtime and a shorter recharge time, possibly refining operation dynamics. This consideration could apply to a myriad of systems in which large groups of electric devices provide short bursts of service interspaced with rapid recharging. A further example could be the development of a drone collective for use in construction to move material from one location to another, possibly replacing cumbersome lifting equipment and reducing build time.

1.2 General Aims and Objectives

It is necessary to clearly establish the general aims and objectives of this thesis, a concise sheet of these has been provided in supplement A. These have been developed from a general understanding of EC devices and the issues they may face. Concisely, there are three key aims (KAs):

1. Improve the cycle life performance of EC devices.
2. Improve the mass specific energy density of EC devices.
3. Improve the mass specific power density of EC devices.

Although some varieties of EC can theoretically reach millions of cycles, in some cases unwanted chemical reactions may occur. Hence, the first aim requires a thorough understanding of how cycle life performance is affected over time. This can be achieved by understanding the factors which impact cycle life performance, such as electrode or electrolyte degradation, followed by assessing how these factors can be altered or modified to improve performance. A similar approach must be taken for improving the mass specific energy and power densities of EC devices. In the former case, it will be necessary to establish how energy is stored by EC devices; in the latter case, it will be necessary to establish how energy is transferred to and from EC devices.

Thus, to achieve such tasks it is necessary to review state-of-the-art scientific literature relating to this field; this will be primary objective one (PO1). Further primary objectives to this are: the establishment of sound hypotheses for which the scientific method can be applied (PO2), establishment of experimental configurations and procedures which will enable these hypotheses to be tested (PO3), to acquire appropriate experimental materials (PO4), to conduct characterisation of these materials (PO5), and to conduct experiments which test the hypotheses at hand (PO6).
In addition to this, the author proposes the creation of secondary objectives for this project. One secondary objective is the replication, where possible, of techniques used at the industrial scale as opposed to the laboratory scale (SO1). The author believes the inclusion of this secondary objective will enable the rapid transferral of knowledge from the academic community to commercial enterprises. Note: this does not imply that fundamental research will not be conducted, merely that where possible research techniques will be adapted to match those used in industry (e.g. using standardised coin casings for EC device containment).

A further secondary objective is to develop advanced research techniques or methods which can aid other researchers or industrialists in this field (SO2). This may possibly take the form of combining two prior research techniques into a single approach, perhaps reducing research time and cost. It is the author’s belief that significant improvements in the field of electrochemical energy storage are still to be made, any additional techniques which aid these improvements would be certainly appreciated by the scientific community.

The aims and objectives mentioned above provide an initial direction for this thesis, but detailed research aims will be produced at the end of the literature survey. These aims will be specifically tailored towards meeting the general aims and objectives mentioned in this section.

Broadly speaking, the general aims stated at this section’s introduction can be achieved by following the scientific method. This is a widely-accepted method of acquiring or improving human knowledge; it consists of systematic observation, measurement and experimentation to formulate, test and possibly modify hypotheses. Ultimately, the aim of this method is to provide others with the ability to predict the outcome of situations under similar conditions. It is this ability which has enabled mankind to achieve wondrous advances such as modern medicine and materials. One apparent flaw of this method is the necessity for human input, we are intrinsically presumptuous beings which does not fit well with the objectivity required to implement the method. As such, the investigation entailed will endeavour to represent work in a fair and unbiased manner; contradictions in prior research are to be sought out and expanded upon where possible, whilst conclusions shall be truthfully based upon repeated experimental results, regardless of performance.

1.3 Outline and Thesis Structure

The work included in this thesis has been conducted as follows: a literature review was performed (Chapter 2) with the intention of finding possible avenues for EC improvement. It
starts with a brief overview of the electrochemical principles related to EC devices followed by descriptions of possible EC device configurations and performance related to commercial and hypothetical devices.

Following on from this in the literature review, a detailed review of organic electrolyte based EDLC type EC devices was produced; this particularly focused around the use of the salt tetra-ethylammonium tetrafluoroborate (TEA⁺BF₄⁻) combined with the solvent acetonitrile (ACN) as the electrolyte. Note: this electrolyte is standard across industry, helping to meet objective SO1. Electrode materials, and their associated capacitance, were discussed alongside the relationship between specific surface area (SSA), pore size distribution (PSD) and capacitance. Finally, the phenomena behind cell ageing and the concept of electrode mass balancing were introduced with an emphasis on two electrodes (full cell) devices.

The subsequent section of the literature review has been dedicated to investigations into lithium ion capacitors (LICs). These are a type of hybrid device which combines aspects of traditional EDLC and battery electrodes. Of note was their potential to achieve significantly higher energy densities compared to traditional EDLC devices. The final study of the literature review is centred around the design and fabrication of EC devices. This study will cover the general components of EC devices, methods for active material deposition (i.e. electrode fabrication) and cell containment methods of EDLC type EC devices.

Upon completion of the literature review, a series of conclusions were produced alongside developing an outlook on possible research avenues. This culminated in the production of specific hypotheses (PO2) and research aims; the former would guide the topics of research in the subsequent chapters and the latter would provide broader direction and context within said research.

The third chapter of this thesis entails the design of experimental configurations, acquisition of suitable materials for experimentation and consideration of characterisation techniques required for the research proposed to be completed. The primary intention of this chapter was to meet objectives PO3 and PO4 but a secondary intention was to meet objective SO2. Based around the designs and considerations of the previous chapter, the fourth chapter details the physical characterisation (e.g. sorption and SEM analysis) of experimental materials and descriptions of fabrication techniques (e.g. electrode fabrication and electrolyte preparation). This chapter was developed to meet objective PO5.
Chapter 1: General Introduction

Beyond this are three chapters which describe the experiments designed and conducted to test hypotheses created at the end of the literature survey. The first group of experiments (Chapter 5) are designed to assess capacitance balancing in material asymmetric EDLC type EC devices; this could culminate in devices which operate at higher voltages and capacitance, both of which are parameters relating to energy storage capability. Alongside higher voltages there is also the potential for a higher degree of electrochemical stability, possibly improving cycle life of EC devices.

The second group of experiments (Chapter 6) have been focused around the development of LIC type EC devices. Specifically, a novel silicon based electrode was used as the negative electrode. This offered the potential for improving energy storage performance alongside improvements in power capabilities.

The third group of experiments (Chapter 7) attempt to introduce highly conductive additives to an otherwise standard electrode, in a targeted manner. This was achieved through spray deposition of active electrode material. This work offered the possibility of maximising device power capabilities whilst minimising the quantity of conductive additives required, potentially improving performance across a wide range of EC devices.

Ultimately, a general discussion of the work presented in this thesis will be conducted. This will attempt to draw all the findings of the work entailed into succinct conclusions and highlight areas of potential future work.

It will be of great interest to see whether there are improvements to be made in electrochemical capacitor energy storage technology. This is an area of profound significance to mankind’s future prospects; improvements could lead to drastic changes in the way we interact with, and operate within, our world. I sincerely hope that you enjoy the forthcoming journey with me through such a fascinating field as much as I have.
2 LITERATURE REVIEW

2.1 Introduction

To identify possible avenues for improving the performance of electrochemical capacitors (ECs) it is necessary to conduct a review of prior work and literature related to this field. A good starting point in doing this must be to acquire an understanding of how solid state electrochemical energy storage devices, specifically batteries and capacitors, operate in general; without basic knowledge, the production of high quality research is not likely.

From this broader viewpoint, a detailed appreciation of different EC configurations can be made thus leading to a discussion as to what properties they possess and why. One requirement of this will be to assess suitable materials and investigate if any material properties are more desirable than others. Beyond the fundamental charge storage and material behaviour of ECs, it is also of interest to review how such devices are fabricated, packaged and tested. This may lead to deeper insight as to how the gap between them can be filled whilst also achieving objective PO1 (see Section 1.2).

Evidence found throughout this review, and the conclusions drawn from it, will help build hypotheses as to what improvements could be made to EC device performance. The final step in this chapter will be to devise experimental setups which can test and validate any hypotheses drawn from the review.

2.2 Electrochemical Principles Related to ECs

The first step in reviewing ECs is to define the electrochemical terms and principles required to distinguish solid state electrochemical energy storage devices (EcESDs) and partly related electrostatic energy storage devices (EsESDs). By starting at the fundamentals of charge, it is possible to discuss the nature of electrodes and electrolytes including the role they play in electrochemical and electrostatic cells; advanced topics such as the electrical double layer, pseudocapacitance and intercalation can be subsequently approached and understood. Building upon this knowledge will allow for discussion of possible EC configurations, performance and fabrication methods.
2.2.1 Electrochemistry Fundamentals

**Charge and Electricity**

Electrical charge $Q$, measured in coulombs (C), is a fundamental property of matter which causes it to produce, and be affected by, electromagnetic fields. It can be either positive or negative in polarity; particles of opposing polarity attract one another whilst particles of same polarity repel. The most basic quantity of charge is the elementary charge $e$, the magnitude of charge carried by a single proton or electron and is equal to $1.602 \times 10^{-19}$ C.

According to quantum mechanics, electrons occupy discrete energy levels in an atom or crystal lattice; if a large number of possible energy levels minutely differ they are described as an energy band. Collectively, these bands form an electronic band structure which describes the range of energies an electron may and may not have. Using thermodynamics, it has been possible to theorise an energy level at which an electron will be present 50% of the time, this is termed the Fermi level [29]. The first bands encountered above and below this level are known as the conduction and valence bands, respectively; in the conduction band, electrons are free to be moved between adjoining atoms whilst in the valence band electrons are considered bound to individual atoms.

In some materials, such as metals and carbons, the valence and conduction bands overlap; in practice this means that at all times there are electrons available for conduction, such materials are said to be naturally conductive. The electrical potential difference $\Delta \Phi$ between two points is commonly referred to as voltage $V$ and measured in volts (V). Upon the application of a voltage between points, electronic charge can flow, this flow constitutes an electric current $I$ measured in amps (A). The amount of electrical charge which flows in a constant current over a period of time $t$, measured in seconds (s), can be calculated as per equation (2.1).

$$ Q = I t \quad \text{(2.1)} $$

Commonly, there is a resistance $R$, measured in Ohms (Ω), to this flow of electronic charge. This is primarily due to two factors, the first being impurities creating imperfections in the lattice structure of a material and the second being ‘vibrational’ disturbance of the lattice caused by heat when above 0 K [30]. Simplistically, as electrons flow from one point to another they ‘bump’ or ‘rub’ against these imperfections thus losing energy i.e. resisting the free motion of
Charge between said points. The relationship between \( V \), \( I \) and \( R \) is simply described by Ohm’s law, shown below as equation (2.2).

\[
V = IR
\]  

(2.2)

It is important to appreciate that the voltage between two points is a measure of the total energy transferred per second when a unit of charge flows from one point to the other. If a resistive circuit is completed between these points, a current will flow and impart electrical energy upon components of this circuit, thus doing work. The amount of work, quantified as energy \( E \) and measured in joules (J), imparted by charged particles \( Q \) (C) moving between two points is directly proportional to the voltage between them, as described below:

\[
E = QV
\]  

(2.3)

The rate at which work can be done is known as power \( P \) and measured in Watts (W). Work can be achieved in many ways but two are particularly important in electric energy storage devices, namely: the transmission of electric energy and the conversion to or from electric energy. The rate at which both forms of work can be achieved is described by the term power. In electrical energy transferal, power is proportional to current flow and voltage between points as described as per the first and second terms of equation (2.4) below.

\[
P = IV = I^2R
\]  

(2.4)

The conversion to or from electric energy can be described by substituting equation (2.2) into the second term of equation (2.4) thus giving the third term of equation (2.4). An important aspect of this equation is that power becomes squarely dependent upon current while only proportional to resistance. This equation has significant implications which will become apparent when considering the energy storage efficiency of EC devices.

While energy can be expressed in Joules, it is quite common in electrochemistry related to energy storage devices to use the unit watt-hour (W h). This unit is also an expression of energy and is defined as the quantity of energy transferred if the power output of a device is 1 W for 1 hour. As 1 hour is equal to 3,600 seconds, it turns out that 1 W h is equal to 3,600 J. This is an
important consideration which finds heavy use throughout the subsequent sections of review and research.

**Electrodes and Cells**

The fundamental components of electrochemical and electrostatic devices are the electrodes. These are electrical conductors which make contact with non-metallic parts of the circuit e.g. electrolytic or dielectric materials. A full-cell comprises two (or sometimes more) electrodes, a cathode at which reduction reactions occur and an anode at which oxidation reactions occur. These respectively define where electrons are entering or leaving a full cell. It is important to note that inconsistencies commonly arise from the use of these terms: they are not representative of an electrode’s polarity (i.e. positive or negative) but instead indicate how this polarity is currently changing.

In the research and development of electric energy storage devices it will be necessary to assess how electrodes perform against various currents and voltages. This assessment can be done in one of two ways, the first method is to use a three electrode setup, as in Figure 2.1 (A); and the second method is to use a two electrode setup, as in Figure 2.1 (B).

![Figure 2.1 Illustration of different electrode setups where (A) is a three electrode setup and (B) is a two electrode setup.](image)

In a three electrode setup current flows through a counter electrode and working electrode, a potential is sensed between the working electrode and a reference electrode which enables the user to identify the electric response of a single electrode (half-cell). This is useful if a wide variety of different electrode types are to be compared, the reference electrode can provide a static point of reference from which the performance of other electrodes can be fairly evaluated. Note that an electric current is not usually passed through the reference electrode.

A two electrode (full-cell) setup differs from the prior setup by short circuiting the counter and reference electrodes such that the voltage sensed is between the working electrode and counter electrode. In applying this method, it is not possible to distinguish the performance of
a single electrode, instead it is better used to represent the electric response of a real world device. Both methods will be considered for the upcoming work upon gathering a better understanding of the previous work in this field.

To allow electronic charge transfer between electrodes, they are connected by an external circuit. It must be considered that electronic charge flows in both directions at the same time; an electron carries negative charge while the absence of an electron, commonly known as an electron hole, carries positive charge. As electrons flow one way around a circuit, electron holes flow the other way.

Important characteristics of electrodes to note are their electronic conductivity, hardness, form, size and chemical corrosion resistance [31]. Electronic conductivity and chemical corrosion resistance should be as high as possible but hardness, form and size vary between applications. Generally, EC electrodes are made of a current collector, a deposited active material, a conductive additive, and a binder [32].

**Ions and Electrolytes**

Electrolytes play a vital role in ECs, they facilitate ionic charge transfer to and from electrodes while prohibiting electronic charge transfer through the electrolyte solution. To better understand their role in ECs let us first consider ions, the fundamental component of an electrolyte. An ion is an atomic or molecular particle which has a net electrical charge. This is due to an imbalance of protons to electrons; a deficit or excess of electrons defines if an ion is positively or negatively charged, respectively. As mentioned previously, charges of opposing polarity electrostatically attract one another. In the case of ions with opposing polarity, this electrostatic attraction may result in an ionic bond; 3-D arrays of the bonded ions are referred to as an ionic compound, or more commonly, a salt.

One matter of confusion is this area are the terms cations and anions. As in the prior case of anodes and cathodes, these terms do not refer specifically to ion polarity but instead as to how this polarity has changed; cations lost electrons (oxidised) while anions gained electrons (reduced). For the remainder of this work, polarity of ions will be stated as either positive (+) or negative (−) with the sign convention referring to oxidised forms as being positive relative to a prior state [33].

An electrolyte solution is thus one in which a salt has dissociated into its constituent ions, so enabling free movement of said ions through either a liquid solution or the defects in the
crystal lattice of a solid. This movement can be characterised by an ionic conductivity, measured in siemens per meter (S m⁻¹), a measure of how rapidly charge can move throughout an electrolyte.

While ionic conductivity is of great importance, there are other features of an electrolyte which must be considered. The electrochemically stable potential window (ESPW) of an electrolyte essentially describes the potentials relative to a reference electrode, above or below which undesirable chemical reactions will occur; these typically degrade cell performance and reduce cycle life. The possession of a wide temperature range, often termed the thermal window, is also desirable from an applications perspective; this is generally and simply defined by the freezing and boiling points of the liquid electrolyte [34].

2.2.2 Classical Electrical Energy Storage Devices

While the matter of importance in this work is ECs, it has been found that they may incorporate aspects of both EcESDs and EsESDs. For this reason, it is first necessary to appreciate how these other devices work. Electrochemistry is the study of how electric charge and chemical change relate, electrostatics is the study of how stationary electric charges interact. Additionally, it is common in electrochemistry to use the term faradaic, a process which involves the production of, or a close association with, electricity. EcESDs and EsESDs are best embodied by two types of energy storage device: electrochemical batteries and electrostatic capacitors.

Electrochemical Batteries

An electrochemical battery, often abbreviated to just battery, contains a cell in which faradaic reactions may occur at both electrodes when a voltage is applied between electrodes. This electrochemical reaction takes place at the electrode-electrolyte interface and can take the form of electronic charge consumption, which releases an ion, or ion consumption, which releases an electronic charge. The reactions which produce and consume electrons are formally known as reduction and oxidation reactions, or simply redox reactions. It should be noted that the polarity of the consumed or produced pair is the same e.g. electron consumption may release a negative ion. To facilitate this, electrons flow between electrodes via an external circuit while ions flow between electrodes via the electrolyte.

The cell in a battery has a desire to reach electrochemical equilibrium. Upon closing the external circuit, a current is formed which enables electrochemical reactions to occur; this current subsequently induces the release of electrical energy. Conversely, if the flow of electrons
is reversed by the application of external voltage between electrodes, such that the reaction is driven away from electrochemical equilibrium, electrical energy will be stored. An example of a battery’s charge-discharge operation is displayed in Figure 2.2 as a plot of voltage versus time; note how at mid charge and mid discharge the voltage plateaus to differing near constant levels.

![Cell potential diagram](image)

**Figure 2.2** Schematic representing relationship between charge and voltage for an ideal battery and for a capacitor under constant current charge/discharge. TOC: Top of Charge, EOD: End of Discharge. Adapted from ref [10].

In practice this voltage quasi-plateau ideally makes up the majority of a charge-discharge cycle and as such, it is simple to describe the energy being transferred to and from a battery by equation (2.3). Since the voltage is relatively constant, the maximum quantity of stored charge, known as a coulomb capacity (A h), is directly proportional to the maximum quantity of stored energy. This energy is often valued in terms of watt-hours (W h), discharge power multiplied by the discharge time in hours, or simply the battery voltage multiplied by its coulombic capacity.

In order to assist in appreciation of this concept, a schematic of the charge-discharge processes in a common lithium ion battery is shown in Figure 2.3. This schematic presents the positive electrode as lithium transition-metal oxide (TMO) and the negative electrode as graphitic carbon (GC), the electrolyte is based on a lithium conducting organic solvent. The electrodes are prohibited from electronically short circuiting by the use of an electronically insulating separator. Figure 2.3 clearly demonstrates the core charge-discharge principles, during charge electrons and positive lithium ions transit from the TMO to the GC and during discharge electrons and positive lithium ions transit back to their origins on the TMO.
Let us study the power aspects of a battery. From equation (2.4) it can be seen that power is directly proportional to resistance. The electrical resistance of a battery varies on three key factors namely: electrochemical reaction rate, electrode electronic conductivity and electrolyte ionic resistivity.

A certain process of thought is required to better contemplate battery resistance. Let us consider a pristine electrode, one which has not yet reacted, interfacing a balanced electrolyte, one which has no excess charge. If a large concentration of electronic charge were to suddenly form at the electrode interface, a rapid electrochemical reaction could occur producing a high concentration of ions at the electrolyte interface. This high concentration of ions would desire to diffuse throughout the bulk electrolyte but would be hindered by ionic resistivity to migration. Subsequently, an excessive concentration of ions may remain close to the interface, this would slow the reaction process and resist further electronic charge transfer to the electrode.

This thought can also be inverted so that a sudden concentration of ions forms at the electrolyte interface, resulting in electronic charge which may not be able to move away/towards fast enough due to the electrodes electronic resistance. It is important to note that an electrode-electrolyte interface is not generally planar [35]; it may be required that ions diffuse a short distance through a solid crystal lattice or pore structure before reaching the liquid electrolyte phase, thus producing further resistance [36].

Modern rechargeable battery materials are typically like the type used in the preceding battery example. The electrochemical reactions implemented in such a battery (i.e. the storage
and release of lithium ions) require a significant quantity of energy. A modern rechargeable battery can store large amounts of energy and can achieve gravimetric energy density values approaching 150 W h kg⁻¹ [10]. Unfortunately, this same electrochemical nature, which is enabled by diffusion of ionic charge to reactions sites [16, 17, 36, 19], is what significantly inhibits a battery’s power capabilities to less than 1 kW kg⁻¹ and energy efficiencies to ~77.5% [10]. Consequently, batteries commonly find use in applications which require low power rates but long run times.

**Electrostatic Capacitor**

As previously mentioned, electrostatic capacitors best embody the principles of EsESDs (electrostatic energy storage devices); a type of energy storage device which utilises electrostatic attraction to store electric potential energy. This is the older, and possibly simpler, energy storage device when compared to EcESDs (electrochemical energy storage devices). It was first developed in 1745 and relies on potential energy being stored in an electrostatic field rather than through chemical reactions. In its most basic form, the device consists of two parallel electrodes in close proximity but separated by a dielectric material, an electronic insulator which allows the transmission of electric fields. A schematic of such a device is presented in Figure 2.4.

A fundamental aspect of the charge-discharge process in a capacitor, exemplified in Figure 2.2, is that it does not occur at a constant voltage. Electronic charge which arrives at an electrode cannot travel through the dielectric separator, due to its electronically insulating properties, and as such it accumulates at the electrode-dielectric interface. The accumulation of opposing charge at opposing electrodes results in a voltage forming between them; as the state of charge (SOC) increases or decreases the voltage also increases or decreases, respectively.
Figure 2.4 Schematic of charge-discharge processes in a common electrostatic capacitor. In a charged state the presence of an electrostatic field, denoted by field lines, is what leads to stored electrical charge.

\[ C = \frac{Q}{V} \]  

(2.5)

This phenomenon is known as capacitance \( C \) (F) which can be described as the ratio between charge transferred and the consequent voltage between electrodes as per equation (2.5). It is important to note that this does not occur in batteries because charge can transfer between electrodes via the electrolyte system, inhibiting the accumulation of excess charge on the electrode. For a typical parallel electrode capacitor, the capacitance is determined by three main factors: electrode separation distance \( D \), electrode surface area \( A \) and dielectric permittivity \( \varepsilon \), their relationship is defined below as:

\[ C = \frac{\varepsilon A}{D} \]  

(2.6)

A material's dielectric permittivity is generally taken relative \( (\varepsilon_r) \) to the permittivity of vacuum \( \varepsilon_0 \). The dielectric permittivity is a term used to indicate the ability of a material to resist the formation of electric fields; this occurs through the storage of charge generated by the field. This resistance to the formation of electric fields enables more charge to be accumulated at each electrode before a breakdown of the dielectric’s insulating property occurs. If a breakdown does occur, then charge can avoid the external circuity and transfer directly from one electrode to
the other, thus prohibiting further charge accumulation. This concept defines a capacitor’s maximum voltage. In practice, a dielectric gap is not a perfect insulator [37] and current will leak between electrodes over time, thus causing self-discharge.

Energy storage of a capacitor does not follow the simplistic nature of that in a battery. An electrical field is formed during charge storage; this field not only opposes the loss of charge but also the gain of it. Thus, as the electric field gathers in strength so does its opposition to charge transfer, consequently; a larger amount of energy is required for transfer to occur. To calculate the energy stored it is therefore necessary to consider charge transfer in infinitesimal steps and integrate the energy which is required in each of these steps. The amount of energy transferred to a capacitor is directly proportional to its capacitance and squarely proportional to the change in voltage, as per equation (2.7). The full derivation of this equation can be found in Appendix 1.

\[ E = \frac{1}{2} CV^2 \]  

(2.7)

The power capability of a capacitor is also not as straightforward as that of a battery. If a capacitor is discharged at constant current, then the power output will decrease over time due to also decreasing voltage. To achieve a constant power output, it is thus necessary to increase current proportionally to the decrease in charge, but this has a problem. In equation (2.4) power is stated as directly proportional to resistance and squarely proportional to current, the equation also describes the rate at which electrical energy is lost due to resistive heating. As such, if current is increased to maintain a specific power output then energy loss is squarely proportional to this increase.

One consequence is the requirement for a non-zero voltage at which further discharge is no longer viable; a device’s non-zero voltage (minimum operating voltage) depends heavily on its ability to handle large voltage and current variations. A major implication of this is that not all the energy stored by a capacitor can be used in applicable practice.

Integrating the energy stored from maximum voltage \( V_{\text{max}} \) to \( \frac{1}{2} V_{\text{max}} \) leads to the conclusion that 75% of the total energy is stored in the voltage window from \( V_{\text{max}} \) to \( \frac{1}{2} V_{\text{max}} \). As such it is preferable [38] for energy storage of a purely capacitive device to be stated as:
Chapter 2: Literature review

2.2.3 Electrolytes for ECs

Ionic Liquids

The first electrolyte discussed, and possibly purest, is an ionic liquid. This a solution of ‘near room temperature molten salts’ which behaves similar to common liquids. This can happen when at least one ion has a delocalised charge, one which is not associated with a single atom or bond, and an organic component; together these prohibit the formation of a stable crystal lattice [41]. The most important aspect of an ionic liquid’s fluidity is that it enables free ion movement throughout their bulk, and as such, charge can be transferred to and from an electrode. As most work in the field of electric energy storage operates around room temperature [42], only specific molten salts are applicable and can thus be classified as room temperature ionic liquids (RTILs). Due to the complex chemical nomenclature of RTILs only the acronyms will be presented in this work; full names can be found in the list of abbreviations and acronyms presented on the final page.

RTILs are the newest category of EC electrolyte. They are generally characterised by low melting points, large thermal windows and very low vapour pressures and as such are non-flammable with decomposition temperatures above 400 °C. The investigated RTILs for EC applications contain positive ions based on imidazolium and pyrrolindinium with BF\textsubscript{4}, TF\textsubscript{4}, TFSI\textsuperscript{-}, FSI\textsuperscript{-} and PE\textsubscript{6}\textsuperscript{-} as negative ions [43].
Importantly, RTILs can display ESPWs of up to 6 V and good ionic conductivities of 14 mS cm\(^{-1}\) but it has been noticed that these properties do not necessarily complement each other in the same electrolyte [43]; an example of this is EMI-TFSI which features a respectable ~10 mS cm\(^{-1}\) conductivity but an ESPW of only 4.1 V when evaluated at a platinum electrode [44]. Interestingly, the high ESPW values are only exhibited when using flat glassy carbon electrodes. Upon application of the high surface area electrodes required to achieve high capacitance values the ESPW drops significantly [43, 34]; an example of this is PYR\(_{14}\)-TFSI in which the ESPW drops from 5.5 V to 4.2 V [45]. It is believed by the author that this phenomenon is due to the relation between RTIL ions and the complex surface textures that arise in high surface area electrodes.

A prominent aspect of electrolytes are ion size and shape. A smaller ion can penetrate deeper into a porous network, thus increasing accessible surface area, and achieve a closer approach to the electrode surface, thus reducing the charge separation distance and increasing capacitance [46]. Consider that a relatively flat, yet long and wide ion may access electrode pores of a narrow slit (letterbox) shape while more bulbous ions may not. Qualitatively considering RTIL positive ions, imidazolium based ions appear to possess quite a slim structure, possibly due to the associated imidazole ring, while pyrrolidinium based ions appear rather more rounded and angular [47, 48]. Having said this, it should also be noted that RTILs lack solvation shells and have been found to access pores approaching their largest ionic dimension [49].

One drawback associated with RTILs is high density, commonly in the range of 1.2–1.5 g ml\(^{-1}\) which makes them heavier to implement than other electrolytes [43]. Additionally, the known toxicity of RTILs varies from low to extremely hazardous [50, 51]; this issue is compounded due to the large combination of cations and anions with which RTILs can be made [43, 34, 52], toxicity could vary dramatically even between similar chemistries. Another consideration is cost; only recently have companies started producing high purity RTILs and as such their cost remains high [43].

**Solvent based Electrolytes**

The second category of electrolyte is like RTILs, but instead, the salt requires solvation by a solvent for liquidity to be attained. Upon dissolution, the salt receives liquid charge-carrying properties like the RTILs mentioned above, thus allowing ionic conduction and enabling charge to be moved to and from electrodes. Electrolytes which utilise solvents are arguably the most commonly used [34], with the primary solvents in use being aqueous (water based) or organic
(carbon based) solvents. These are the foundations for the aqueous electrolytes and organic electrolytes most commonly used in EC devices [10].

For a salt to be placed in solution, a solvent of an appropriate chemistry is required to overcome the electrostatic attraction between ions in the salt. When dissociation occurs, solvent molecules become trapped and orientated in the electrostatic field of an ion, thus forming a series of ‘shells’ surrounding it [53], as depicted in Figure 2.5.

![Schematic of ion solvation shells formed of dipolar solvents. Note, some ions have only one solvation shell. Adapted from [54].](image)

Figure 2.5  Schematic of ion solvation shells formed of dipolar solvents. Note, some ions have only one solvation shell. Adapted from [54].

The inner most shell experiences the strongest electrostatic force; the solvent molecules at this point would be tightly bound, thus possessing some semblance of order. Beyond the strong influence of an ion’s electrostatic field, the long-range order of solvent molecules would be undisturbed. As there are two distinct regions of differing order the transition between these regions is disordered. This transition, termed the structure-broken region, has been found to cause electrolyte solutions, particularly those based on water, to have lower viscosities than their pure solvent counterparts [53].

Aqueous electrolytes, such as acids (e.g. sulfuric acid, H₂SO₄) and alkali (e.g. potassium hydroxide, KOH) have ionic conductivities approaching ~1 S cm⁻¹, an order of magnitude or at least twice that of organic or RTIL electrolytes [10]. Other beneficial properties of aqueous electrolytes include high relative permittivity [34, 55, 56], a component of capacitance, and that aqueous ions are typically extremely small, between 0.1 and 0.4 nm [10, 34]. Additionally, aqueous electrolytes are considered of low cost and environmentally friendly [10, 57], particularly related to environment harming RTILs and organic solvents.

Despite numerous beneficial properties there is a major limitation. The ESPW in aqueous electrolytes is traditionally limited to ~1.2 V, above which an electrochemical breakdown of water occurs [58]. This value not only limits the energy storage capability, as per equation (2.7),
but also means that multiple cells in series are required to achieve high operating voltages demanded by some applications [59].

For this reason, there has been a transfer over recent years to the use of organic solvents, commonly propylene carbonate (PC) and acetonitrile (ACN). These solvents permit an ESPW of between 2.3 V and 2.8 V [34, 58] which, as per the square dependency of voltage in equation (2.7), leads to significant improvements in energy storage capability. It is not often mentioned that traditional EDLC cells based on organic electrolytes should dwell at ~2.3 V and only increase to high voltages for short periods [58]. Extended periods at high voltage can be detrimental to long term device performance; this becomes clear when examining a product guide for a recent (2009) commercial EDLC based EC [60], reasons and implications will be further considered in section 2.4.3.

The transfer from aqueous to organic–solvent-based electrolytes has also been facilitated by reasonable ionic conductivity. Tetra-ethylammonium tetrafluoroborate (TEA⁺BF₄⁻) a commonly used salt with organic solvents, has ionic conductivity values of 11 and 60 mS cm⁻¹ when solvated in PC and ACN, respectively [10]. While not as impressive as aqueous electrolytes, these values have been found to enable sufficient ion transfer rates required for high power capabilities.

TEA⁺BF₄⁻ based organic electrolytes are considered of higher cost than aqueous electrolytes [10]. This is partly material-cost-related but also due to the need for thorough solvent drying and assembly under inert atmospheres; it has been found that 1M TEA⁺BF₄⁻ containing 14 parts per million (ppm) of water has a ESPW of 3.8 V while the same electrolyte containing 40 ppm has an ESPW of 2.7 V [32], one can safely presume that preparation of this electrolyte in an ambient atmosphere will result in an electrolyte of substandard quality. In addition to this, the solvents and salts used are also considered toxic and as such, non-environmentally friendly; thus fabrication in an isolated environment is preferred [10].

As the system of TEA⁺BF₄⁻ in ACN is a common electrolyte in EDLC EC devices [34, 10], it was deemed appropriate to pursue the ion shape and size in more detail. Simulations of these ions were conducted using molecular modelling software Spartan15 (courtesy of Andrew Dunn). Simplistic ball-and-stick models of TEA⁺, Figure 2.6 (A); and BF₄⁻, Figure 2.6 (B); were calculated by finding the lowest energy conformer for bond lengths and angles. Ab initio Hartree–Fock molecular orbital calculations were conducted to find the lowest occupied molecular orbital (LOMO) structure and the highest occupied molecular orbital (HOMO)
structure; from these it is possible to state the probability of electron presence at a specific location and as such, produce an isosurface-based electron density map. Upon this isosurface, which represents the Bohr surface, it is possible to present the charge distribution of a molecule in the form of an electrostatic potential map where areas shaded red and blue represent lowest (electronegative) and highest (electropositive) electrostatic potential energy, respectively.

![Ionic ball-and-stick models](image)

**Figure 2.6** Ionic ball-and-stick models for (A) TEA\(^+\) and (B) BF\(_4\)^- with their corresponding electrostatic potential maps, (C) TEA\(^+\) and (D) BF\(_4\)^-. Areas shaded red and blue represent lowest and highest electrostatic potential energy respectively. Reproduced with permission of Andrew Dunne.

From these models it is possible to see that the effective geometry of bare (i.e. unsolvated) TEA\(^+\) and BF\(_4\)^- ions is not particularly spherical; this is interesting because it is common in literature for their dimensions to be expressed as a radial value. This may be justified for bare BF\(_4\)^- ions due to their high order of symmetry, but qualitatively does not fit well with bare TEA\(^+\) ions. In the case of a solvated ion it is believed that the solvent shell will provide additional sphericity, thus providing further justification for stating dimensions in radii values, but the shape and content of the solvation sphere (if any) is unknown.

While the majority of publications are in wide agreement that the bare diameters of TEA\(^+\) and BF\(_4\)^- are 0.67 and 0.46 nm, respectively [61, 62, 63], a widely cited paper by Chmiola et al. [64, 65, 66, 67] states that the bare diameter of BF\(_4\)^- is 0.33 nm with no direct reference as to where this value came from. It also appears that their ACN solvated diameter is disputable. Original molecular simulations produced by Kim et al. found that ACN-solvated TEA\(^+\) and BF\(_4\)^- have diameters of 1.30 and 1.16 nm [68], respectively. In contrast, more recent molecular simulations by Guang Feng found their diameters to be 1.58 and 1.2 nm, respectively [69]. Upon contacting Guang Feng it was found that the difference in BF\(_4\)^- value is considered minimal i.e. the solvation number, the number of solvent molecules with which an ion can combine, at this distance would be comparable. The differences in TEA\(^+\) diameter are also
considered acceptable and may have arisen due to improvements in computational accuracy or the use of a lower electrostatic screening threshold in the prior work.

**Solid- or Quasi-Solid-State Electrolytes**

The third, and least common category, is solid or quasi-solid-state electrolytes. As their names suggest, these electrolytes will maintain a fixed shape without external interference; a major advantage of this being that, unlike RTIL and solvent based electrolytes, they require minimal or no external packaging and are effectively liquid-leakage free. This category is commonly composed of polymeric materials which offer a range of possibilities. Solid polymer electrolytes (SPEs) can provide ion transportation through the polymer and require no liquids whilst gel polymer electrolytes (GPEs) utilise a polymer matrix swollen by a solvent; in the latter case ions transport through the solvent instead of the polymer phase. SPEs are notorious for their lower ionic conductivity, while GPEs offer reasonable performance but with a greater risk of structural damage and degradation [34].

### 2.2.4 EC Charge Storage Mechanisms

**The Electric Double-Layer**

A fundamental aspect of EC devices is the involvement of an electrical double-layer (EDL). The EDL is a surface phenomenon in which ions from an electrolyte are electrostatically adsorbed onto an electrode surface [70]. It is commonly formed at an electrode-electrolyte interface whereupon excess electronic charge is counteracted (screened) by the presence of ionic charge. A model schematic of the EDL phenomenon, which was first developed by von Helmholtz in 1879 [71], can be found in Figure 2.7 (A) and presents the double-layer of counteracting charges.

![Figure 2.7](image)

**Figure 2.7** (A) Helmholtz EDLC model and (B) structure of Stern EDLC model for an electric double-layer at a positive electrode where \( \Phi \) is electrode potential. Note, the term double layer refers to the model presented in (A) and not to the Stern and diffuse layers presented in (B).
Chapter 2: Literature review

The original EDL term used by Helmholtz described the double layer of charge which forms at a polarised electrode-electrolyte interface. An advanced model was built by Stern [72] upon EDL structural models proposed by Chapman [73] and Gouy [74] in which the electrolyte interfacial charge is split into two layers, the inner Stern layer and the outer diffuse layer, as illustrated by Figure 2.7 (B); the two layers are at times confused with the double-layer [75]. It has been suggested that the Stern model represents the EDL through the use of a triple layer model [70, 76].

Adopting Helmholtz’s original and simplistic definition allows us to envision the formation of an electric double layer capacitor (EDLC) in which an extremely thin, but not well understood [70] dielectric is present. The dielectric strength in such case is the point at which an electrode surface no longer maintains electrochemical stability, thus allowing charge to transfer across the interphasial region. An EDLC formed at a planar interface behaves similarly to an electrostatic capacitor and obeys equations (2.5), (2.6) and (2.7) thus exhibiting a charge-discharge process like that shown in Figure 2.2.

Whilst it is common to say that charge storage occurs at the electrode-electrolyte interface, it is necessary to clarify that the boundary is actually a 3-dimensional structure and as such should be described as interphasial. This boundary effectively behaves as a dielectric with a thickness between 0.3 to 0.5 nm; counteracting charges lie in extremely close proximity [77]. This distance between charges is represented by D in Figure 2.7 (A), but the location of the charges in the electrode surface is hard to define.

The models described above help us understand the capacitive response of the EDLC phenomenon but have certain limitations; the electrolyte cannot be highly concentrated, with the models typically breaking down at molar concentrations above 0.1 M, and only represents unconfined planar surfaces [20]. A plethora of advanced models have recently been developed to confront the limitations of traditional EDL models [20], while most are beyond the scope of this work a few are of particular interest and will be discussed in Section 2.4.2 when assessing “EDL capacitance” in highly porous electrode structures.

**Pseudocapacitance**

In addition to the EDLC phenomenon, pseudocapacitance and intercalation have been found to be of use in ECs. The word pseudocapacitance is used to describe the properties of an electrode which behaves like a capacitor in its electrochemical signature [78]. Its full definition
can be found in Conway’s influential book titled “Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications” [77] in which he states:

‘Pseudocapacitance arises at the electrode surfaces where a completely different charge-storage mechanism applies. It is faradaic in origin, involving the passage of charge across the double layer, as in battery charging or discharging, but capacitance arises in account of the special relation that can originate for thermodynamic reasons between the extent of charge acceptance (ΔQ) and the change of potential (ΔV), so that the derivative d(ΔQ)/d(ΔV) or dQ/dV, which is equivalent to a capacitance, can be formulated and experimentally measured by dc, ac, or transient techniques.’

Figure 2.8  Schematics of pseudocapacitive phenomena: (A) underpotential deposition of Pb onto Au; (B) redox pseudocapacitance of hydrogen ions inserting into RuO₂; (C) intercalation pseudocapacitance of Li into Nb₂O₅. Adapted from [79].

A particularly insightful paper by Augustyn et al. [79] builds upon Conway’s original work and defines three different mechanisms which contribute towards pseudocapacitance; underpotential deposition, redox pseudocapacitance and intercalation pseudocapacitance. Underpotential deposition, Figure 2.8 (A), occurs when metal ions form an adsorbed monolayer at a different metal’s surface well above their redox potential. Redox pseudocapacitance, Figure 2.8 (B), occurs when ions are electrochemically adsorbed through the surface or near surface of a material with naturally accompanying faradaic charge transfer. Intercalation pseudocapacitance, Figure 2.8 (C), occurs when ions intercalate into the tunnels or layers of a redox-active material accompanied by a faradaic charge transfer (ideally with no crystallographic phase change). Each of these occur due to the presence of different physical processes and material characteristics. It should also be noted that pseudocapacitive phenomenon are accompanied by the formation of an EDLC on the outer material surface.
A pseudocapacitive material can usually achieve higher gravimetric capacitance values than those of standard EDLCs (having both their own EDLC and pseudocapacitance); this may be due to its faradaic nature, reduced dielectric thickness, as ions are absorbed, or a combination of the two [21]. The power capabilities of some pseudocapacitance mechanisms are limited by the rate at which ions can diffuse into an electrode’s surface structure. On one hand, if the electrode is a thin film (i.e. of the order of a few nanometers), then performance is not limited by diffusion kinetics so allowing pseudocapacitance to be termed an intrinsic property. On the other hand, if an electrode is a thick film (i.e. greater than 20 nm), then ion transportation will be limited by diffusion kinetics and is thus termed extrinsic pseudocapacitance [80]. This applies particularly to materials which exhibit redox or intercalation type pseudocapacitance.

Based upon this finding, it has been deemed reasonable to assume that a material with an intrinsic pseudocapacitive property has a crystalline structure which enables deep and rapid ion transport, only if ions are below a certain size, to and from charge storage sites. In the case of a material with an extrinsic pseudocapacitive property, it is more likely to expect that surface defects and pore structure play an important role in ion transportation as an ordered subsurface crystalline structure may prohibit deep electrolyte penetration.

**Intercalation**

The phenomenon of intercalation, with no pseudocapacitive response, produces charge-discharge dynamics which operate at constant voltage. The term itself refers to a process in which a guest atomic or molecular species is inserted into a host lattice structure [81]. In principle, this concept is simple to understand; weak interlayer van der Waals forces of a 3-dimensional host lattice offer the possibility for guest species to be inserted without significant chemical interaction with the host lattice [82]. In practice, the intercalation phenomenon is exhibited by materials which possess a stable band structure whose electron occupancy can be changed over a wide range by guest intercalant species [83].

A common example of such a material is GC (graphitic carbon) combined with lithium as an intercalant, this material often plays the role of the negative electrode in a lithium ion battery. Figure 2.9 (A) presents a schematic drawing of the crystal structure of hexagonal graphite while Figure 2.9 (B) shows the formation of fully Li-intercalated graphite compound LiC_{6}. To achieve this state, lithium must travel in-between graphitic planes. This process occurs at around $10^7$ cm$^2$ s$^{-1}$, from which it has been deduced that if GC were produced with crystalline domain sizes around 45 nm, intercalation/deintercalation could occur in less than 0.2 milli-seconds [36].
2.2.5 Summary and Conclusion

This section introduced the basic understanding, notions and principles required to fully appreciate EC devices. Fundamental concepts of electrochemistry relating to EC devices has been covered; this included a discussion as to how electricity functions in both electronic and ionic systems and how these systems interact in and at an electrode. Testing of electrodes can be conducted in either half-cell or full-cell configurations but the extent to which these approaches affect results is yet to be discussed. Essentially, the fundamental metrics can be derived by knowing two values, the quantity of charge transferred in the form of a current and the voltage drop across which they are transferred. Voltage, and by alternative definition ESPW, appears to be a highly influential parameter and, as such, its maximisation should be sought.

EcESDs and EsESDs (i.e. batteries and capacitors) were discussed in depth. In a battery, electrical energy is stored through the conversion of energy by redox reactions at the positive and negative electrodes; in a capacitor, energy is stored in the form of electrostatic force fields which develop between the positive and negative electrodes. Additionally, the voltage of a battery remains relatively constant during charge/discharge while the voltage of a capacitor ideally has linear proportionality with SOC; this relationship is expressed as capacitance, which is commonly less than 10⁻⁶ farads in classical dielectric capacitors. In terms of energy density, batteries are significantly more capable, with some devices readily reaching 150 W h kg⁻¹ while capacitors languish at 0.1 W h kg⁻¹; however, in terms of power density, capacitors possess greater than 10 kW kg⁻¹, with batteries conversely languishing at 1 kW kg⁻¹ or less.

The three core electrolyte types in ECs have been identified and discussed. RTILs present ESPWs of up to 4.2 V (with high surface area electrodes) but generally possess limited conductivity, high densities and high toxicity. Solvent based electrolytes have been found to primarily consist of two categories, aqueous and organic electrolytes. Aqueous electrolytes
possess high power capabilities due to the presence of a structure-broken region surrounding ions but have ESPWs limited to around 1.2 V. Organic electrolytes possess ESPWs approaching 2.7 V, especially at high purity, but have been found to have rather mediocre conductivity, with acetonitrile being the best performer as solvent. In-depth attention was paid to TEA⁺ and BF₄⁻ ions solvated in ACN due their widespread use in EC devices; for the remainder of this work “bare” TEA⁺ and BF₄⁻ ion diameters will be stated as 0.67 and 0.46 nm, respectively, while ACN solvated TEA⁺ and BF₄⁻ ion diameters will be stated as 1.58 and 1.2 nm, respectively. Solid or quasi-solid-state electrolytes such as SPEs and GPEs were not considered in depth but appear to present great benefits where a leak free device is desired, but with a loss of power relative to liquid systems.

EC charge storage mechanisms were presented. This was done with single electrodes in mind; full-cell device configurations are yet to be discussed. The most common storage mechanism associated with EC devices is that of an EDLC in which ionic charge is electrostatically bound to an electronically polarised electrode. Due to the thin dielectric, high capacitance values can be achieved per electrode unit surface area; particular influences and contributors to EDLC capacitance will be discussed in the coming section. Pseudocapacitance appears to be a promising phenomenon through which capacitance values can be further increased. As it is Faradaic in origin, particular attention will be paid to its cycle life and energy density; power capability will also be of interest, particularly in the varying case of intrinsic/extrinsic pseudocapacitance. Non-pseudocapacitive intercalation i.e. the charge storage mechanism used batteries, also appears to be a promising energy storage phenomenon which may be incorporated into an EC device; it is not yet clear how its lack of capacitive response will function with an opposing capacitive electrode, this will be investigated. Due to its similarity in function to that of a battery it is believed this charge storage mechanism may present high voltage capabilities; as such, further investigation is warranted.

2.3 EC Configurations and Performance

From the comprehensive study of electrochemical principles related to ECs it is possible to fully compare EC performance, not only relative to classical devices, such as batteries and capacitors, but also between different EC configurations. It is now of interest to review EC configurations and what relative advantages/disadvantages they present. Comparisons will be made based upon the general performance of a range of configurations; ideally, these values will be derived from real world devices but this may not always be suitable. Beyond this initial
review it will be possible to investigate the specifics of each EC configuration with the intent of finding properties or phenomena of interest.

![Common EC configurations](image)

**Figure 2.10** Common EC configurations. (a) EDLC, (b) pseudocapacitor, (c) hybrid EDLC – pseudocapacitor (d) hybrid EDLC – intercalation (e) hybrid pseudocapacitor – intercalation. Adapted from [85], reproduced with permission.

Mistakenly, it is common that all EC devices are referred to as supercapacitors or ultracapacitors; these are actually trade names originating from the late 20th century and relate to commercial EDLC and pseudocapacitive based devices, respectively [10]. Instead of sensational trade names, during this work the appropriate scientific name, based upon the underlying storage mechanism, will be used to classify different EC devices.

### 2.3.1 EC Configurations

There are three primary classifications of EC storage devices: EDLCs, pseudocapacitors and hybrid capacitors. An EDLC-based EC (Figure 2.10 a) implements the EDLC charge storage mechanism at both electrodes, commonly being material symmetric in nature; this is the most highly developed and commercialised class of ECs [32]. A pseudocapacitor (Figure 2.10 b) uses pseudocapacitive charge storage (in addition to EDLC) at both electrodes, thus also being material symmetric in nature; despite utilising extremely well understood phenomena [21, 77] this variety of EC has not yet seen commercialisation for reasons to be discussed. A hybrid capacitor (Figure 2.10 c, d and e) is one which uses an asymmetric combination of EDLC, pseudocapacitive and/or battery related electrodes; presently there are limited commercial examples of such a device [32, 86, 87].
Figure 2.11 Schematic of charge-discharge processes in an EDLC based on activated carbon. During charge and discharge, ions are electrostatically adsorbed and released, respectively.

An EDLC based EC functions with both positive and negative electrodes behaving as individual EDLCs (Figure 2.11). Thus, each electrode-electrolyte interface presents itself as an individual capacitor; charge is not transferred across the interface due to dielectric separation, and a non-constant voltage-charge relationship occurs. As such, each EDLC electrode has capacitance as per Equations (2.5) and (2.6). Since the capacitance is thus related to surface area it is desirable to use materials which possess a high surface area, such as activated carbon (AC). It has been found that other properties of AC are also desirable, these are discussed further in section 2.4. Common varieties of suitable electrolyte have been tested with this EC configuration, their corresponding capacitance values will be discussed upon in-depth consideration of the specific materials the electrolytes interact with.

A pseudocapacitor functions with both positive and negative electrodes exhibiting pseudocapacitance (Figure 2.12). Due to their use of faradaic reactions they can achieve significantly higher capacitive responses while maintaining high power capabilities. Although the rate at which these faradaic reactions occur is often stated as ‘fast’, their speed is in fact heavily influenced by the type of pseudocapacitance exhibited [88, 89]. Pseudocapacitance typically arises in materials such as conducting polymers; transition metal oxides or carbons enriched with heteroatoms e.g. oxygen and nitrogen. In addition to electrode materials, pseudocapacitance can also originate from redox reactions of the electrolyte species but this is not currently common [21]. A brief review of these materials and the properties they exhibit can be found in Appendix 2.
Capacitive Energy Storage: Filling the gap

Figure 2.12  Schematic of charge-discharge processes in an extrinsic redox pseudocapacitor based on transition metal oxides. During charge and discharge, ions are electrochemically absorbed and released, respectively.

A hybrid capacitor is one which uses a combination of EDLC, pseudocapacitive and/or battery based electrodes. While many possible devices exist [86, 90], one device of notability is a lithium ion capacitor (LIC). As shown in Figure 2.13, a LIC device possess an EDLC based positive electrode and an intercalation based negative electrode; this intercalation electrode is operating in the same fundamental manner as that of a lithium ion battery (LIB). In such a device, it would be sensible to assume that only one electrode is capacitive in nature but this does not always appear to be true [91]. The state-of-the-art materials for the positive and negative electrodes of an LIC are AC and GC, respectively [86, 92, 91, 93]. The selection of electrolytes for use with LICs is limited to those which consist of lithium ions e.g. lithium hexafluorophosphate (LiPF6) in ethylene carbonate/diethyl carbonate (EC/DEC).

Figure 2.13  Schematic of charge-discharge processes in a carbon-carbon LIC hybrid device. During charge and discharge, negative ions are electrostatically adsorbed and released, respectively, while positive lithium ions are intercalated (absorbed) and released, respectively.
Chapter 2: Literature review

Only EDLC and pseudocapacitive electrodes experience a capacitive charge-voltage relationship. From this it can be deduced that only configurations (a), (b) and (c) from Figure 2.10 will exhibit a purely capacitive electrochemical response. In essence, both electrodes in these configurations behave as individual capacitors which are connected in series. Thus, it is possible to calculate the total cell capacitance $C_T$ based on the capacitance of each electrode, $C_{E1}$ and $C_{E2}$; as per equation (2.9). This has been proven experimentally to be true by Béguin et al. [94].

\[
\frac{1}{C_T} = \frac{1}{C_{E1}} + \frac{1}{C_{E2}}
\]  

(2.9)

In order to compare EC cells and devices it is necessary to define them by key performance indicators (KPIs), this can range from characterising the performance of a single electrode to the performance of a fully contained industrial device. Many of these metrics are discussed specifically, e.g. gravimetric KPI ($g^{-1}$). This is done to facilitate comparison between varying device, cell, and electrode configurations. In the case of a symmetric EC cell, $C_{E1}$ equals $C_{E2}$ and as such the capacitance at both electrodes would equal double that of $C_T$. In such a case it is also found that mass specific capacitance ($F g^{-1}$) of a half-cell will be four times higher than a full-cell [95] thus yielding equation (2.10).

\[
C_{Ts} = \frac{C_{Es}}{4}
\]  

(2.10)

Where $C_{Ts}$ and $C_{Es}$ are specific full-cell and half-cell capacitance, respectively.

An EC cell configuration broadly has the following requirements: a conductive path from electrode to external circuits must be made. This often takes the form of a dedicated current collector; the electrode material must be electronically conductive to enable charge transfer to and from storage sites, the electrolyte must be ionically conductive for the same reason, and both electrodes must not be in electronic contact, which can necessitate a nonconductive separating material. In addition to this, all EC cells must have some method of containment (i.e. packaging) which prohibits electrolyte escape; this containment should also provide a suitable amount of rigidity to ensure an electrode is not deformed beyond its mechanical stability [12]. The electrode, not considering material type or morphology, may be fabricated with varying
thickness, density and mass-loading per area; each of these factors has an impact on different KPIs.

2.3.2 General Performance

Before commencing a discussion on performance, let us consider how difficult it can be to accurately and rigorously compare performance. Research on EDLCs using AC electrodes and aqueous electrolytes was conducted in [96]; a symmetric AC based EDLC was tested with 1 M H₂SO₄ aqueous electrolyte. In this work they conducted cyclic voltammetry (CV) (Section 3.4.3) analysis and the results show that half-cell specific capacitance varies from ~300 F g⁻¹ at 0 V up to ~400 F g⁻¹ at a peak voltage of 1.2 V. They concluded that 368 F g⁻¹ is the average. As part of their conclusion and opening abstract, they stated that specific energy densities up to 20 W h kg⁻¹ were achieved. This value can only be produced by firstly using equation (2.7), which inappropriately assumes that all energy can be accessed in a capacitive device, and secondly by selecting their half-cell specific capacitance to be the maximum ~400 F g⁻¹. If the more appropriate equation (2.8) is used along with the average specific capacitance, then the specific energy density drops to 13.8 W h kg⁻¹; a decrease of over 30% from their stated value. As such, it has been deemed more appropriate to investigate general performance from a commercial device perspective, of which metrics are readily available and with testing methods clearly stated [97].

In Table 2.1 a performance review of all three EC categories has been conducted and presented, alongside classical energy storage devices. Broadly, it can be seen that EC devices fit midway between dielectric capacitors and batteries, with hybrid LICs representing the best EC device in terms of energy storage. The power density of EC devices is considerably higher than that of battery type devices. ECs incorporating elements of pseudocapacitivy achieve the highest power performance of this category; this is almost certainly due to the high ionic conductivity of aqueous (acid or alkaline) electrolytes. The exact power capability of a pseudocapacitive EC is heavily influenced by the type of pseudocapacitance exhibited [88, 89].
## Table 2.1 Comparison of typical classical capacitor, battery and EC characteristics.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Capacitor</th>
<th>Battery</th>
<th>EDLC</th>
<th>Pseudo-capacitor</th>
<th>Hybrid AC-Pseudo</th>
<th>Hybrid (LIC) AC-GC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode Materials</td>
<td>Al, Ta oxide</td>
<td>Lead acid, Ni-Cd, and Li-ion.</td>
<td>Carbon</td>
<td>Polymers, transition metal oxides</td>
<td>Carbon, Polymers, transition metal oxides</td>
<td>Carbon</td>
</tr>
<tr>
<td>Electrolyte Materials</td>
<td>Aqueous, SPE, GPE</td>
<td>Aqueous, Organic</td>
<td>Organic</td>
<td>Aqueous</td>
<td>Aqueous</td>
<td>Organic</td>
</tr>
<tr>
<td>Storage Mechanism</td>
<td>Electrostatic</td>
<td>Redox/Intercalation</td>
<td>Electrostatic</td>
<td>Redox</td>
<td>Electrostatic/Redox</td>
<td>Electrostatic/Intercalation</td>
</tr>
<tr>
<td>E (W h kg(^{-1}))</td>
<td>&lt; 0.1</td>
<td>~ 20 – 150</td>
<td>~ 6</td>
<td>~ 3</td>
<td>~ 8</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>P (kW kg(^{-1}))</td>
<td>&gt;&gt; 10</td>
<td>&lt; 1</td>
<td>~ 5</td>
<td>~ 10</td>
<td>~ 10</td>
<td>~ 5</td>
</tr>
<tr>
<td>Energy storage efficiency (%)(^a)</td>
<td>&gt; 99.9</td>
<td>75 – 85</td>
<td>&gt; 95</td>
<td>?</td>
<td>60 – 95</td>
<td>90</td>
</tr>
<tr>
<td>Time Constant</td>
<td>&lt; 1 ms</td>
<td>&gt; 60 s</td>
<td>0.1 – 2 s</td>
<td>&gt; 2 s</td>
<td>&gt; 2 s</td>
<td>&gt; 3 s</td>
</tr>
<tr>
<td>Cycle Life (cycles)</td>
<td>&gt; 10(^6)</td>
<td>~ 10(^3)</td>
<td>~ 10(^6)</td>
<td>~ 10(^4)</td>
<td>~ 10(^4)</td>
<td>~ 10(^5)</td>
</tr>
<tr>
<td>ESPW (V)</td>
<td>&gt;&gt; 10</td>
<td>2.25 – 4.2</td>
<td>~ 2.7</td>
<td>~ 1</td>
<td>1 – 2.2</td>
<td>~ 4</td>
</tr>
<tr>
<td>Self-Discharge</td>
<td>Moderate/ Fast</td>
<td>Slow</td>
<td>Moderate</td>
<td>?</td>
<td>Moderate</td>
<td>Slow</td>
</tr>
</tbody>
</table>

Values derived from [32, 10, 77, 21, 98, 99] and best represent commercially available devices.

\(^a\) This value depends significantly on the applied current rate. Higher currents result in lower energy efficiencies.

![Gravimetric energy and power capabilities of commercially available electrochemical and capacitor devices including specific EC configurations. Dashed lines indicate RC time constant; red and green areas indicate batteries. Adapted from ref [6].](image-url)
Shown in Figure 2.14 is a gravimetric Ragone plot, used to visually express the differences in device energy storage and power capability [5]. This includes the energy storage and power performance values of the specific EC configurations as listed in Table 2.1.

Device energy storage efficiency is extremely important as it represents how effective devices are at receiving and delivering energy. As can be seen from Table 2.1, devices which utilize covalent redox reactions exhibit lower energy storage efficiency than those which do not. Interestingly, hybrid LICs exhibit quite high energy storage efficiency; this can be explained by considering that no covalent chemical bonds are being formed. Whilst on the topic, it has been broadly found that as a device’s discharge rate is increased its energy storage efficiency decreases. This can be clearly visualised through the Ragone plot in Figure 2.14. The lines spread along this plot (i.e. red, green and blue) are created by testing the same device at increasing power rates, at low power rates the energy density is relatively constant but at high power rates energy density decreases dramatically. This decrease is not because there is less energy available but because more energy is being consumed in overcoming resistance, as per equation (2.4). The power and energy performance values of advanced EC devices shown in Figure 2.14 are thought to represent the point prior to energy density decreasing dramatically; it can be clearly seen that these devices present opportunities to fill the gap between traditional batteries and capacitors.

The time constant metric is based on an RC (resistor capacitor) model circuit which consists of a resistor and capacitor in series. In this model the voltage of an EC device, particularly of the EDLC variety, changes by 36.8% at time $t = \tau$, and by 98% at time $t = 4\tau$ where $\tau$ can be described by Equation (2.11).

$$\tau = \frac{R_{ESR}}{C}$$  \hspace{1cm} (2.11)

As such, to say that a device has a time constant of one second implies it can take as little as four seconds to fully discharge. This value can be a little misleading at times due to the many different ways in which a cell can be produced; a single continuous electrode in series may present higher $R_{ESR}$ values while a stack of electrodes, which cumulatively possess the same capacitance as of a single continuous electrode, may present lower $R_{ESR}$ values. Additionally, while an ideal battery does not exhibit capacitance, in reality there is a slight voltage decrease during discharge; this decrease which could be loosely associated with a capacitive value [100]. It may have been noticed by this point that Table 2.1 does not actually present capacitance
values directly; this is firstly because batteries and LICs do not exhibit a purely capacitive response and secondly because it is dependent upon more factors than could be expressed in this table. Specific EDLC capacitance values will be discussed in the following section, while pseudocapacitive related capacitance measures are presented in Appendix 2.

With respect to cycle life, the best performing EC configuration is that based exclusively on EDLC phenomena. This is almost certainly due to the lack of redox reaction as the value holds great similarity to that of capacitors, both of which function in an electrostatic manner. An LIC also appears to hold great potential for a long-lasting device. Taking consideration from the field of batteries, which also implement graphitic negative electrodes, it is believed that the value for LIC cycle life in Table 2.1 is optimistic. Extensive studies have shown that graphitic negative electrodes, if not implemented correctly, are susceptible to pulverisation and lithium plating which can greatly reduce cycle life [101, 102].

The ESPW values of different electrolytes have been discussed in-depth in the previous section. Of all EC devices, EDLCs which use ionic liquids and LICs which use organic electrolytes attain the highest values. This is reflected by their relatively high energy density values which are squarely proportional to the ESPW. In addition, a low ESPW makes application in consumer devices difficult; many applications require a minimum voltage for operation and as such multiple low voltage devices in series would be required in order to achieve this minimum state. This is considered the reason that purely pseudocapacitive devices have not seen widespread commercial adoption.

The final aspect of the electrochemical energy storage devices presented in Table 2.1 is that of self-discharge. This term essentially expresses the ability for a device to retain a charged state over a length of time; a device which is said to have a slow self-discharge may retain energy for months while a device with a fast self-discharge may retain energy for only seconds or minutes. It was found that EC devices associated with an EDLC electrode exhibited moderate self-discharge with a 20% loss in voltage over a period of one month while in LICs this loss in voltage is around 5% over three months [32].

2.3.3 Summary and Conclusions

The three core EC configurations have been identified as EDLCs, pseudocapacitors and hybrid capacitors; EDLCs and pseudocapacitors operate in a symmetric charge storage manner while hybrids are asymmetric. Hybrid capacitors are of interest due to their broad ESPWs and
relatively high energy storage capabilities compared to other ECs. LICs in particular are appealing devices due to their reasonable power capability, long cycles life and slow self-discharge rate; due to these enticing properties, it has been deemed suitable to develop these devices further.

Despite this, it has been found that EDLCs represent the majority of EC devices commercially available, as LICs are relatively new devices. With respect to energy storage they possess modest capabilities but those which utilise aqueous electrolytes offer high specific power; unfortunately, aqueous electrolytes are generally limited to ~1 V. As such, the most common electrolyte implemented is TEA⁺BF₄⁻ in ACN, which achieves an ESPW of up to 2.7 V and specific power of ~2 kW kg⁻¹. As the fundamental operation of these devices is well understood, it has been deemed appropriate to pursue advanced understanding, particularly in the area of organic electrolytes, which may lead to better insight as to how EDLCs can be fully optimised.

Pseudocapacitors, particularly those hybridised with EDLCs, are interesting devices which offer good energy storage and power capabilities. Despite this, they appear lacking in energy storage efficiency and their ESPWs are very narrow which discourages their application; these devices will not be further considered in this work. In conclusion, a general understanding of EC device configurations and related performance has been presented. Areas of interest have been identified and will be pursued in depth for the remainder of this review.

2.4 Organic Electrolyte based EDLCs: Materials and Considerations

It has been identified that improvements in EDLCs can only be achieved by gaining comprehensive understanding of what factors influence and contribute to their performance. The initial focus of this section will be to review carbon based EDLC electrode materials, properties and their associated capacitive values when using TEA⁺BF₄⁻ and ACN electrolyte. In depth considerations will be taken of their internal and external structures, along with other aspects such as toxicity and applicability.

Moving on from this, there will be a focus on the relationship between specific surface area (SSA), pore size distribution (PSD) and capacitance. This will start by discussing how SSA and PSD are calculated and what considerations should be made when assessing such metrics in EC research. From this, an investigation as to the effects SSA and PSD have on capacitance will be conducted, it will be of interest to find if there are any notable effects which may boost
performance. The final topic of investigation in the field of EDLCs is cell ageing and its minimization through electrode-mass-balancing. Additional consideration will be taken to see if there are any methods by which the ESPW of TEA⁺BF₄⁻ and ACN may be increased.

### 2.4.1 Electrode Materials and Associated Capacitance

#### Activated Carbon

EDLCs commonly utilise AC (activated carbon) as the active material. AC is an allotrope of carbon which has undergone activation, a process resulting in a highly porous internal structure, thus exhibiting high SSA (i.e. the total surface area of a material per unit mass). It is used for many reasons: carbon has a relatively low electronic resistance [10, 70] which lends itself well to achieving high power devices; its high surface area can provide high capacitance, as per equation (2.6); and due to carbon’s electrochemical stability all types of electrolyte can be used [34].

There are two methods for producing AC from precursor materials, physical activation and chemical activation. Physical activation involves two reaction steps: precursor carbonisation (slow pyrolysis) followed by gasification. Chemical activation of a precursor involves reaction with a chemical agent such as KOH and NaOH at elevated temperatures. The precursor material can be either natural or synthetic and greatly affects the SSA and capacitance capability; an extensive discussion of this can be found in [103].

Physical and chemical activation processes develop an extremely porous structure and consequently, a high SSA value. Extreme examples of AC with above 3,000 m² g⁻¹ have been reported in literature [104, 105, 106] but these values are inappropriately derived from Brunauer-Emmett-Teller (BET) analysis which has long been known to not be fully applicable in the case of porous structures with narrow nanometric pores [107], this matter is discussed further in Section 3.4.1.
Figure 2.15 (A) Schematic of microporous graphitic planes, present as a substantial component in AC, representing relative pore size and ion size. (B) Schematic of AC with a hierarchical pore structure.

As such, the precise internal structure of AC is of great interest. Commonly it is believed to be amorphous, i.e. without long-range crystalline order, but observations through high resolution transmission electron microscopy (HRTEM) suggest they may possess fullerene related structures [108]. It has also been shown possible to use techniques, such as nitrogen adsorption analysis, to model the internal structure [109]. Such a technique has the benefit of producing SSA, and specific porous volume (SPV) values alongside an associated PSD.

It has been found that AC has an internal structure mostly consisting of nanopores [70]. This nanoporosity can be subdivided into 3 size categories, macropores are greater than > 50 nm, mesopores are between 2 – 50 nm and micropores are less than < 2 nm [110]. Micropores, illustrated in Figure 2.15 (A), are the main contributor to high SSA values, and thus capacitance; they are of significant interest in EC applications because they approach the size of common electrolyte ions [10, 34, 111, 69]. Macropores are considered to have insufficient surface area to significantly contribute to energy storage but along with mesopores they do facilitate rapid ion transport to and from deep microporous regions [112]. A representation of AC with a hierarchical structure of all three pore sizes is presented in Figure 2.15 (B).

While the internal nanoporous structure of AC is where the majority of energy storage occurs [113] power capabilities are significantly influenced by the external structure, of which there are three primary classes: powdered activated carbon (PAC); activated carbon monolith (ACM); and activated carbon cloth (ACC). Using a scanning electron microscope (SEM) it is possible to examine the external structure at macro and possibly meso-pore level [114, 115].
Figure 2.16 SEM images of (A) powdered activated carbon [114] reproduced under CC BY-NC 3.0 licence; (B) activated carbon monolith [115]; and (C) activated carbon fibres [116] reproduced under CC BY 3.0 licence.

PAC, Figure 2.16 (A), is classified as AC powder in which 90% of particles have a size of 500 µm or less [117] and is produced by milling large particles down to size. It is recommended that the median particle size (D50) be limited between 4 to 8 µm for optimal implementation as an electrode material [32], with the belief that it will minimise ion diffusion and maximise particle-particle conductivity. To be used as an electrode material it is commonly mixed with a binder such as PVDF and thinly deposited onto a conductive substrate; this approach allows for good control over electrode shape and thickness. However, while the manufacturing process is simplified, the use of nonconductive binding materials and inter particle conduction paths can introduce strong electronic resistances, thus limiting power capability [32]. It is possible to partially overcome these limitations through the use of post-fabrication electrode densification [118] and adding small quantities (∼5%) of highly conductive materials such as acetylene black [119] or graphite itself. PAC is the most common form of AC used in research and industry.

ACMs, Figure 2.16 (B), are binderless, semi-continuous structures which can be formed directly from monolithic precursors or through the compaction of PAC. The primary benefits of using ACMs in EDLC electrodes are the elimination of both nonconductive binders and high resistance particle-to-particle point contacts. Additionally, if the pore volume is relatively small then a volumetric capacitance improvement over PAC can result. Despite these benefits there are issues with electrode production, and tightly packed particles can limit ion diffusion throughout the electrode [103].

ACC, Figure 2.16 (C), can be described as a flexible textile consisting of individual or bundled activated carbon fibres (ACF). Only a small selection of precursors can be used to produce ACCs, with regenerated cellulose (rayon), polyacrylonitrile (PAN), and phenolic resins being the most common. From these it has been noted that SSA values for rayon- and PAN-derived ACC are limited to 1450 and 870 m² g⁻¹, respectively, while phenol-derived ACC can achieve up to 2000 m² g⁻¹ [120]. Conductivity along a fibre’s axis is excellent [121] but there is
an issue with volumetric capacitance as circular fibres do not pack efficiently when forming ACC, thus reducing overall material density [122].

EDLCs using AC electrodes and organic electrolytes, such as TEA⁺BF₄⁻ in ACN, present electrode mass specific capacitance values between 50 to 150 F g⁻¹ [10, 103]. This range of values is thought to be primarily due to differing levels of AC activation and consequential SSA. Considering this range of half-cell specific capacitance values and that organic electrolytes generally operate at a maximum of 2.7 V [10], it is possible to estimate their effective full-cell energy storage capability by implementing equation (2.11) followed by equation (2.8). Thus, considering only the mass of two electrodes, the specific energy of a full cell for discharge to ½ \( V_{\text{max}} \) has been estimated to be between 9.5 W h kg⁻¹ and 28.5 W h kg⁻¹. It may be noticed that this range is significantly higher than the general performance values stated in Section 2.3.2; this is due to the general performance values being per mass of a fully-contained device including the mass of electrolyte, current collectors, separators and containers. Such a stark difference warrants investigation into how cells are designed and manufactured, as benefits might be achieved through further optimisation.

**Carbon Nanotubes**

Carbon nanotubes (CNTs) are an allotrope of carbon with a cylindrical nanostructure; they are formed by the rolling of graphene sheets at specific angles through the catalytic decomposition of hydrocarbons. The number of rolls determines whether a CNT is a single-wall carbon nanotube (SWCNT, see Figure 2.17) or a multi-walled carbon nanotube (MWCNT) [70, 123]. The diameter of CNTs can range from 0.4 to 50 nm; MWCNTs are greater than 10 nm in diameter while SWCNT diameters are smaller [124]. The length of CNTs can vary substantially depending on production method, ranging from 0.5 \( \mu \)m [125] to over 10 cm in length [126]; as such, CNTs can exhibit extremely high aspect ratios. They are considered to have excellent electric conductivity along their length [70, 127, 128] which has been found to make them ideal additives for improving electrode conductivity for AC-CNT composites [129, 130, 131].
Chapter 2: Literature review

Figure 2.17 Example of SWCNT with an open-tip structure. By Begemotv2718, reproduced under CC BY 3.0 licence.

Much thought should be taken when considering CNTs for EC devices as not all types are appropriate. Raw and untreated CNTs commonly exhibit low SSA values (~100 m² g⁻¹), particularly when of the MWCNT variety [132, 133], they can also have heavy metal contamination, which leads to significant self-discharge of the device [134, 135, 136, 137]. Improvements in SSA have been achieved through their activation in a similar manner to ACs [132], producing values of ~400 m² g⁻¹, or by opening closed-tip CNTs [133]. In addition, an acid treatment stage can be used to remove contamination and to improve wettability of hydrophobic CNTs [123]. When combined with TEA⁺BF₄⁻ in ACN they present electrode mass specific EC capacitance values between 20 to 80 F g⁻¹ [10].

Due to the nanometric size of CNTs there are associated potential health issues. It is common knowledge that long-term exposure to particulate matter (PM) less than 2.5 µm in size can have a detrimental effect on cardiovascular health [138, 139]. CNTs may exhibit a wide variety of physiochemical properties, due to this it has been difficult to fully quantify their health impact. Despite this, it is widely agreed that excessive interaction with SWCNTs is significantly more harmful than MWCNTs [140, 141]. In addition, long term exposure to CNTs in general has been proven undesirable [142]. Related research has recently been presented showing that CNTs are a substantial component of PM produced by vehicle exhaust, with CNTs being found in the airways of Parisian children [143].

The general form of MWCNTs is agglomerated bundles and obtaining good dispersion of these agglomerations is key to their successful application in composite materials [144]. It is widely recognised that ultrasonic treatment of these agglomerations is a viable method for producing dispersed solution [145], but it has been found that this may only be a temporary
effect with subsequent re-agglomeration 5 minutes after ultrasonic treatment [146]. If more persistent dispersion periods are desired, then a surfactant may be added [146]. The maximum concentration of MWCNTs that can be homogeneously dispersed in aqueous solution is about 1.4 m% (percent of total mass) [147].

**Graphene**

A graphene sheet is a two-dimensional single layer allotrope of carbon; it is considered to be the parent of all graphitic forms [148]. Current synthesis methods include exfoliation from graphite, epitaxial growth on an insulator surface and chemical vapour deposition (CVD) on the surfaces of single crystals of metal [148]. While graphene in its most basic form is considered single sheet, the production methods above often produce what is known as few layer graphene (FLG); graphene which contains 3-10 layers of two dimensional sheets. Chemically modified graphene with a surface area of 705 m² g⁻¹ was tested with TEA⁺BF₄⁻ solvated in ACN and presented an electrode mass specific EC capacitance of 100 F g⁻¹ [149].

Electrical properties have been found to vary depending upon arrangement and number of graphene layers [148]. An excellent review of graphene has been conducted by Rao el al. [150] considering different synthesis methods and discussing in depth electrical, electrochemical, magnetic, optical and surface properties. One of their primary conclusions was that synthesis of graphene with a desired number of layers is difficult at large scale.

**Carbide Derived Carbon and Templated Carbon**

Both carbide derived carbon (CDC) and templated carbon (TC) can achieve internal nanoporous structures with highly specific PSDs. These have been used to investigate the effect of particular PSDs on EC performance, specifically of the EDLC variety.

CDCs are produced by the extraction of metals from carbides using chlorination at temperatures ranging from 600 – 1000 °C [113]. Through this method, a wide range of PSDs, and subsequently SSA values, have been reported, with the precise structures depending strongly on production temperature [64, 49, 151]. The production process is in fact so tuneable that it is said to be possible to control the growth of carbon on the atomic level with better than an angstrom (0.1 nm) accuracy [152]. Unfortunately, the production process exhibits a low mass yield and, as such, CDCs are quite expensive [32]. It has been stated that CDCs commonly achieve SSA values between 1000 and 1600 m² g⁻¹ [10] but this runs contrary to their ability to form a wide variety of structures. CDCs prepared between 500 and 1000 °C were tested with
TEA-\(\text{BF}_3\) in ACN and presented an electrode mass specific capacitance of between 100 and 140 F g\(^{-1}\) [64]. Interestingly, it was found that capacitance decreased as SSA was increased contrary to naïve expectation. This matter will be further discussed in the next section.

TCs are usually prepared in three steps: a carbon precursor is infiltrated into the pores of a template (such as silica); this is followed by carbonisation (i.e. removal of unwanted precursor elements); ultimately, the template is removed leaving behind a highly-ordered carbon structure [113]. Traditional templates have been found effective at producing narrow PSDs with better than ångstrom accuracy [152], an issue with this is that capacitance and fast ion transport require micropores and mesopores, respectively. In order to achieve a PSD which accommodates a range of pore sizes it is has been necessary to implement colloidal crystals [153] or non-silica oxides [154], which have been found to provide a good compromise in terms of high capacitance and fast ion transportation. TC tested with TEA-\(\text{BF}_3\) in ACN presented an electrode mass specific EC capacitance of between 120 and 145 F g\(^{-1}\) [10, 155]. The production of TC is still primarily at the research phase and as such the true cost and viability of mass production is not yet known.

### 2.4.2 Relationship between SSA, PSD and Capacitance

Initial investigations into the relationship between SSA, PSD, and EDLC capacitance were undertaken in the mid 1990’s and suggested that higher SSA improves capacitance [77]; this finding has been controversial with some later investigations confirming the link [156, 157], while others do not [32, 64]. Despite this, there is clear evidence that most AC materials do present a positive SSA-capacitance correlation [20, 32]. A weakness in the publications which support this correlation is that they implement the BET analysis method upon calculating their SSA values from \(\text{N}_2\) isotherms, which, as stated before, is not entirely appropriate for microporous materials.

Advancing beyond SSA-capacitance relations, modern investigations have suggested instead that a stronger relationship occurs between area specific capacitance, calculated by dividing material capacitance by material surface area, and use of carbons with PSDs of a strongly microporous nature [158, 159], as depicted in Figure 2.18.
Figure 2.18 (A) Experimental data of CDCs and template carbons in ACN electrolyte versus specific capacitance normalised by BET SSA. ● TEA-BF₃ 1.5 M [64], ■ TEA-BF₃ 1 M and 1.4 M [157] and ▲ TEAMS 1.7 M [163]. (B to D) Schematics of solvated ions residing in pores with distance d between adjacent pore walls (B) greater than 2 nm, (C) between 1 and 2 nm, and (D) less than 1 nm. Adapted from [64].

Considering the ion size and pore size interaction, recall that bare TEA⁺ and BF₄⁻ ion diameters will be stated as 0.67 and 0.46 nm, respectively, and ACN solvated TEA⁺ and BF₄⁻ ion diameters will be stated as 1.58 and 1.2 nm, respectively. Traditional thinking suggested that this solvation shell was difficult to remove [77] and thus prohibited ions from accessing pores smaller than their solvated diameter. Contrary to this, modern investigations utilising CDCs and TCs suggest that it may be possible for ions to partially desolvate [158, 159, 160, 161], as shown in Figure 2.18 (B to D), thus decreasing the charge separation distance across the EDL and consequently increasing the capacitive response, as per equation (2.6). Theoretical insights into this relationship using computational density functional theory present strong agreement with the experimental results found in Figure 2.18 [49, 162]. The capacitance increase in sub-nanometer pores was attributed to constructive interference of the EDL structures between opposing pore walls [162].

Further, it has been found that the mass specific capacitance of the positive electrode, which primarily associates with BF₄⁻ ions upon charging, increases dramatically as the electrode pore size approaches that of a bare ion. This is also true in the case of TEA⁺ ions at the negative electrode but the effect on capacitance is much less pronounced. To quantify this, a porous structure with pore sizes of 0.8 nm width (assuming slit like shape) could produce a mass specific capacitance of 120 and 125 F g⁻¹ for BF₄⁻ and TEA⁺, respectively. If the pore sizes are decreased
to 0.74 nm the mass specific capacitance increases to 155 and 128 F g⁻¹ for BF₄⁻ and TEA⁺, respectively. A further decrease in pore size to 0.7 nm yields mass specific capacitance increases for BF₄⁻ (170 F g⁻¹) but not for TEA⁺ (118 F g⁻¹); this is thought to be due to the pore size approaching the bare TEA⁺ ion size but not that of a bare BF₄⁻ ion [160]. From this, it is plausible to state that a capacitance optimal EDLC cell, using AC and TEA⁺BF₄⁻ in ACN electrolyte, should use materials with different PSDs at each electrode.

2.4.3 Cell Ageing and Mass Balancing

An important issue to be assessed is cell ageing. Typically, cell ageing is quantified in terms of cycle lifespan, the number of full charge-discharge cycles (i.e. from minimum voltage to maximum voltage) a cell can sustain until it no longer possesses adequate capability. Another method of assessing ageing is to hold a cell at constant voltage (potentiostatic) for a quantity of time, this is again conducted at a voltage at, or approaching to, a cells maximum voltage; this is done until a device no longer possesses adequate capability thus defining a cells ‘high voltage potentiostatic lifespan’ [164]. Both cycle life and ‘high voltage potentiostatic lifespan’ are approaches to quantifying cell ageing.

The term ‘adequate capability’ can be subjective as adequacy may vary, general consideration leads the author to believe that it is either the point at which the cells resistance has increased to the point of causing an excessive drop in voltage during operation, or the capacitance (charge storage capability) has become insufficient for an operation to be completed successfully. Manufacturers of EDLC devices state that end of life is when capacitance has fallen to between 70% and 80% of its initial (beginning of life) value and resistance has increased to ~2 times its initial value [97, 165].

It has been found that degradation of organic electrolytes can occur for three reasons: (1) applying high cell voltage, at or beyond the electrolytes ESPW, resulting in adverse electrode reduction/oxidation; (2) permanent electrolyte ion intercalation or electrochemical reaction of organic electrolytes, and (3) harsh working conditions, such as high temperatures [34]. Reasons (1) and (2) are of most interest because they essentially present a trade-off between high energy density, through high voltage, and cycle life. Reason (3) is more of an extrinsic issue related to application and environment (e.g. location).

In TEA⁺BF₄⁻ solvated in ACN two ageing mechanisms have been identified through electrochemical ageing and post-mortem analysis of symmetrical AC cells by Ruch et. al. [166].
The first is the gaseous decomposition of the electrolyte, which is presumed to be due to the reaction of the electrodes with trace water. The second is the loss of an electrode’s available surface area, significantly affecting capacitance as per Equation (2.6); this loss was attributed to either solid electrode-electrolyte degradation products or the functionalisation of electrode surface. This degradation was most prevalent at the positive electrode, suggesting it was operating outside of the device’s ESPW [167]. In-fact, subsequent work by the same team found that the ESPW versus a carbon quasi-reference electrode of TEA⁺BF₄⁻ in ACN is \( \approx 1 \) V for the positive electrode (which attracts BF₄⁻) and \( \approx 2 \) V for the negative electrode (which attracts TEA⁺) [166]. As such, the maximum ESPW for an EDLC based on AC utilising TEA⁺BF₄⁻ solvated in ACN can be stated as 3 V, but of course this value depends on both electrode and electrolyte purity (especially considering water contamination).

![Diagram showing Oxidative and Reductive Decomposition](image)

**Figure 2.19**  Schematic of CCCD charge–discharge processes for one EDLC device with symmetric cell capacitance and one with asymmetric cell capacitance, up to a peak voltage of 2.7 V. Oxidative and reductive boundaries represent ESPW for TEA⁺BF₄⁻ solvated in ACN [164].

The voltage response of an electrode experiencing a change in charge will be dependent upon the mass specific capacitance of each electrode. Upon charge transfer between electrodes of equal mass and capacitance the voltage change on both electrodes will be equal, a schematic of this symmetric cell capacitance is presented in Figure 2.19. This may increase the cell ageing process as according to the previous findings, the negative electrode can achieve a stable voltage twice that of the positive electrode. This was realised and research was conducted, using 1M TEA⁺BF in ACN and the same AC (YP17 Kuraray Chemical Japan) material for both electrodes, whereby the mass ratio between positive and negative electrodes was varied in order to ascertain the maximum ESPW and by proxy, reduced cell ageing. It was found that the mass
ratio, taken as positive electrode mass divided by the total electrode mass, of 0.65 is optimal for achieving the least ageing effect [168]; a schematic of this asymmetric cell capacitance is presented in Figure 2.19. A similar effect has been reported in EDLCs using aqueous electrolytes [169] and hybrid ECs based on EDLC/pseudocapacitance [170].

In other words, when using 1 M TEA⁺-BF₆ in ACN and the same AC material for both electrodes, for every gram of positive electrode mass there should be ~0.54 grams negative electrode mass. Interestingly, the actual focus in this matter appears to be balancing the capacitance; doing so by varying the electrode mass ratio is simply a means to an end. It would be of interest to assess if ‘capacitance balancing’ could instead be achieved through a material asymmetric EDLC, i.e. an AC material with high mass specific capacitance for the positive electrode and an AC material with a low mass specific capacitance for the negative electrode.

2.4.4 Summary and Conclusions

A review of possible carbonaceous electrode materials for EDLCs has been conducted. It has been found that while many varieties of “carbon” exist, it is AC which presents the highest electrode mass specific capacitance capability of 150 F g⁻¹ when used with TEA⁺BF₆ in ACN. Also, it was of interest to find that there are many external structures upon which AC can be formed. PAC is the most common in literature and industry, which is probably due to the level of control over electrode shape and thickness which can be achieved. The use of ACC in EC related research appears to be relatively uncommon despite achieving excellent SSA values, they appear to present an interesting opportunity to simplify EC production as they do not require a binder which can reduce conductivity and capacity. ACMs present issues during electrode production; they can be extremely brittle and tightly packed particles can limit ion diffusion throughout the electrode, thus reducing power.

MWCNTs produce a capacitance up to 80 F g⁻¹ when used with TEA⁺BF₆ solvated in ACN; instead of being the primary energy storage material it seems they are better suited as additives for improving electrode conductivity. Caution should be taken as to when and how these are implemented due to toxicological concerns, particularly with the SWCNT variety. A further issue is the dispersion of MWCNTs, especially when they compose a large percentage of an electrode coating. This has been identified as a potential point of focus for this research project.
Capacitive Energy Storage: Filling the gap

Graphene presents interesting properties alongside a reasonable capacitance of 100 F g\textsuperscript{-1}, when used with TEA\textsuperscript{+}BF\textsubscript{6}\textsuperscript{-} solvated in ACN, but production and characterisation proves challenging. It might be better suited for use in extremely small EC devices where the electrode possesses sub-micron thickness.

CDCs and TC have shown to be extremely useful in understanding the influence of microporosity on capacitance but until issues with high cost and low production yields have been overcome they will not be considered viable methods of improving EC performance.

Interesting insight has been attained as to the relation between PSD and capacitance. It has been found that as a pore size approaches that of a bare ion there can be an increase in capacitance. This is believed to be due to partial ion desolvation which enables a closer charge association across the EDL. As this effect is unique for ions of different sizes, and in common electrolytes the ions present are of different sizes, it is probable that the optimal EDLC configuration uses materials with different PSDs at each electrode.

Ageing has been found to be an issue with EDLC cells. The dominant causes have been identified for EDLCs based on organic electrolytes and in-depth consideration has been taken for EDLCs with AC electrodes using TEA\textsuperscript{+}BF\textsubscript{6}\textsuperscript{-} in ACN. It has been found that the ESPW in such a case is 3 V; the negative electrode can achieve 1 V and the positive electrode can achieve 2 V, beyond which severe performance degradation occurs. In order to realise these unbalanced potentials, it is necessary to appropriately unbalance the capacitance of the two electrodes. This has been previously achieved by adjusting the mass of the electrode materials, but it may alternatively be possible to achieve by varying the materials at each electrode. In this alternative approach, appropriately unbalancing the capacitance of the two electrodes may be achieved while maintaining a balanced mass ratio, this is a topic of interest [166, 167, 168, 169, 170].

2.5 Investigations of Lithium Ion Capacitors

Several sources point to hybrid EC devices, particularly LICs (lithium ion capacitors), as a promising technology for increasing EC specific energy density for a fully packaged device beyond 10 W h kg\textsuperscript{-1} while maintaining a specific power density of 5 kW kg\textsuperscript{-1} [10, 38, 86]. The use of an intercalative negative electrode brings two key benefits, namely a wider ESPW and high energy density. This can be clearly envisioned by comparing the representative constant current charge/discharge (CCCD) plots of an EDLC, Figure 2.19, and an LIC, Figure 2.20.
Firstly, consideration is given to a wider ESPW. Recall that intercalation is a process in which a guest atomic or molecular species is inserted into a host lattice structure; in the case of an LIC this guest atomic species is commonly lithium (Li⁺) and the host lattice structure is GC (graphitic carbon). This intercalation system enables reaction at little over 0V versus Li/Li⁺ [86]. As implied by Figure 2.20, this extremely low reaction potential lies well within the electrode/electrolyte reductive decomposition region and a solid electrolyte interphase (SEI) is produced; the SEI layer is highly unreactive and presents a barrier to further solvent reaction but still allows for Li⁺ transport [171]. The fact that Li⁺ intercalates-deintercalates at an almost constant voltage is due to GCs homogeneous structure consisting purely of graphitic planes, this presents the singular fully lithiated state of LiC₆, i.e. one Li⁺ ion per six carbon atoms [84]. If other lithiation states were present, such as in CNTs, voltage would be non-constant; this is due to tubes of different diameters possessing different intercalation voltages [172].

![Figure 2.20 Schematic of charge-discharge processes in an LIC from an initiation voltage (i.e. nonzero base voltage) of ~2.95 V up to a peak voltage of 4.3 V, as derived from [86]. Oxidative and reductive boundaries represent ESPWs found in common used organic electrolytes [34].](image)

Before discussing the energy density of LICs it is necessary to understand how capacitance and voltage values for an EDLC electrode can be related to an amp hour (A h) value; this is necessary because the intercalation electrode does not exhibit significant capacitance and as such it is most appropriate to work in A h. Consider equation (2.5) in which capacitance is related to charge and voltage. If the capacitance of an EDLC electrode is known, it stands that the quantity of charge transferred in order to achieve a specific voltage change is also known. This quantity of charge can be related to A h through the knowledge that the quantity of charge transferred by a current of 1 A over 1 h is equal to 3,600 C. If capacitance is presented mass
specifically, this specificity can be carried through to find the mass specific capacity (A h g⁻¹). An example of this should be appreciated: take a capacitive AC electrode with a gravimetric capacitance of 100 F g⁻¹, increase the potential by 2.7 V, and the specific quantity of charge transferred will then be equal to 270 C g⁻¹ or 75 mA h g⁻¹.

Let us discuss energy density in LICs. It can be theoretically shown that charge capacity for a GC electrode should be 372 mA h g⁻¹ (Appendix 3). As can be implied by Figure 2.20, GC remains close to 2.95 V relative to its initiation potential [86, 173, 174]. Due to the quasi-stable voltage, it is suitable to apply equation (2.3) to calculate the theoretical gravimetric energy density as 1,116 W h kg⁻¹ for a single GC electrode. This is a large value, and reinforces why LIBs and LICs possess such high gravimetric energy density. But while impressive, the whole picture has not yet been ascertained.

For the GC electrode to be charged, the AC electrode must also be charged; this is where care must be taken. As implied by Figure 2.20, if the AC electrode is pushed beyond ~1.3 V it will experience oxidative decomposition; an example of this is presented in [91]. Consider again a capacitive AC electrode with a gravimetric capacitance of 100 F g⁻¹; if this were to experience a voltage change of 1.3 V it would consequently experience an increase in charge of 36 mA h g⁻¹. This is significantly lower than the charge transferred to the GC electrode. What this implies is that if an equal mass of material is used at each electrode then upon fully charging the EDLC electrode, the intercalation electrode will be underutilised. Conversely, if the intercalation is fully charged then the EDLC electrode will be pushed far into the oxidative decomposition region, thus significantly degrading EDLC cell performance.

The electrode capacitance must be properly balanced at an appropriate mass ratio; this mass ratio is commonly derived by ensuring that both electrodes have matching charge capacity [92, 91]. In the case presented above the positive EDLC electrode would require approximately ten times more mass than the negative intercalation electrode (i.e. a ratio of 10⁻¹:1) to present balanced gravimetric charge storage capacities.

Recall that the energy stored in an EDLC cannot be calculated by equation (2.3) as voltage is not constant; instead, and noting that all the energy is now accessible due to the nonzero base voltage, equation (2.7) should be used. Thus, it is possible to hypothesise that an LIC device based on balanced charge capacity, using the previously stated material specifications, which is charged from 3 to 4.3 V, will present a gravimetric energy density of 119 W h kg⁻¹ per total electrode mass (Appendix 4). This is not far off the experimental result of 104 W h kg⁻¹ per total
electrode mass for an LIC presenting similar conditions and considerations as those above [91]; the difference in value may be accounted for by considering added electrode mass, such as binders, and the effect of different charge–discharge currents.

In recent times silicon (Si) has been considered as an alternative intercalation material for LIB negative electrodes, this is due to its extremely high theoretical capacity of 4,200 mA h g⁻¹ in the lithiation state Li₂Si₃ (Appendix 5). Upon further investigation into the matter it was found that Li intercalation in an Si negative electrode undergoes reaction at ~ 0.4 V versus Li/Li⁺ [175] and that Si experiences significant volumetric expansion (~ 410%) when transitioning from an uncharged to a fully charged state [173]. Using similar principles as above i.e. a negative AC electrode with 100 F g⁻¹ but charged from 2.6 to 3.9 V; a theoretical LIC device utilising a Si negative electrode would require an electrode mass ratio of 116⁺:1⁻ to maximally utilise both electrodes. At such a ratio one could expect to achieve a gravimetric energy density of 117 W h kg⁻¹ per total electrode mass (Appendix 6), a theoretical decrease over traditional GC based LICs; the decrease is primarily due to the lower intercalation potential of Si.

The maximum power capability of GC-based LICs has been reported in literature as 10 kW kg⁻¹ while being capable of delivering ~100 W h kg⁻¹, both values are per total electrode mass [91]. Interestingly, it was found that as the mass ratio was decreased (i.e. less GC was utilised) the power capability increased at the cost of energy storage. This was attributed to the lower GC utilisation, which is known to have less power capability than AC due to slow Li⁺ diffusion throughout its lattice structure [36].

Further consideration to this has been taken and the theoretical gravimetric energy density of LICs, based around both GC and Si, utilising different percentages of their negative electrodes theoretical maximum charge capacity has been calculated (Appendix 7):
Figure 2.21  Theoretical gravimetric energy density (per total electrode mass) of LICs, based on both GC and Si, utilising different percentages of their negative electrodes theoretical maximum charge capacity.

The result is interesting to say the least. Despite Si performing relatively similar to GC at high negative electrode capacity utilisation they differ greatly at lower negative electrode capacity utilisation. This is of interest for two reasons: firstly, it may be that implementing a highly-underutilised silicon electrode presents high power capabilities as found in GC underutilisation [91]; secondly, this may reduce the negative impacts associated with volumetric expansion.

In the particular case of LICs a salt containing lithium, such as lithium hexafluorophosphate Li⁺PF₆⁻; must be used. The PF₆⁻ ion is preferred over a more traditional BF₄⁻ due to the resulting higher conductivity and improved stability when interfacing a graphite electrode [176]. It is common in battery research for this salt to be solvated by a 1:1 ratio of ethylene carbonate and diethyl carbonate with a molar concentration of 1M [177].

Further, it has been noted that pre-lithiation of the negative electrode is necessary for optimal LIC performance [86]. It is believed this is primarily to overcome the initial high charge-transfer resistance present in low lithiation states [178]. Commonly this is achieved through: (i) short circuiting the Li and GC electrodes externally, (ii) short circuiting through an appropriate resistor, or (iii) by galvanostatic charging at low charge rate [93]. While all three approaches worked, their setup was elaborate and required the use of pure lithium, a hazardous material to handle. Another approach has been found in which lithiation occurred by extracting lithium from the electrolyte using formation cycles [91]. During such cycles, the cell is repeatedly charge to a high voltage i.e. a high lithiation state, followed by long periods of self-discharge. In
principle, this should shift the potential of GC to lower potentials i.e. a lithiated state, and in practice appears successful.

2.6 Design and Fabrication of EC Devices

Thus far, the review has primarily focused on fundamental cell material considerations such as electrode and electrolyte properties. It is now appropriate to take high level considerations as to how ECs are designed and fabricated; this will be beneficial from the point of conducting research to a high standard and possibly lead to the production of large scale devices.

The first consideration will be towards the general components, such as current collectors, electrode binders and separators, that are required to produce an EC cell. This will aim to find the optimal components currently available for EC fabrication; the primary factor will be impacts on specific electrochemical performance but other considerations such as corrosion resistance and cost will also be considered.

Subsequently, it will be suitable to study the effect electrode thickness has upon EC device performance. From this, methods of electrode fabrication can be reviewed and discussed to develop appropriate methods which respect the findings related to electrode thickness. A broad range of methods will be considered and judged on their coating performance (i.e. uniformity, continuity and practicality). The primary aim is to find a method which enables laboratory scale research to be conducted in a consistent manner and the secondary aim is to investigate methods which may provide benefits at a larger scale of production.

The final consideration will be towards cell containment. This aspect is important as it has been previously noted organic electrolytes are highly susceptible to water contamination which can significantly impact performance. Different types of packaging and cell design, such as coin cells and pouch cells, will be discussed along with any possible modifications which may prove useful in EC research.

2.6.1 General Components

Current Collectors

The most popular method for achieving low resistance, and thus high power, is to use a current collector (CC). A CC is in direct contact with the electrode and behaves as the electronic link between electrode active material and an external circuit. It should be highly conductive
(significantly more so than the active material), be of low mass to aid gravimetric performance, resistant to corrosion, be of low cost, and provide appropriate mechanical stability [32].

In the case of ECs which use organic solvents and ionic liquids, aluminium has been found the most applicable CC material. This is due to its low price and density while maintaining good conductivity and corrosion resistance [32]. One issue with aluminium is surface oxidation [179], a thin nonconductive coating in an electric circuit (e.g. an oxide layer) can greatly increase interface resistance thus reducing power capability. A simple method for overcoming this issue has been to electrochemically etch the CC, as is the case with traditional electrostatic capacitor electrodes [32]; more advanced methods have been to attach carbon particles to an etched Al surface, either with a polymer binder [180] or as AlC3 whiskers [181, 182]. It is not possible to use an aluminium CC with common aqueous electrolytes such as HCl, H2SO4 and KOH [183, 184, 185]. Instead, other metals, such as nickel and stainless steel, must be used but they are known to be heavier and more costly than aluminium CCs.

Special considerations must be made when using an electrolyte containing a lithium based salt, such as in a lithium ion capacitor. If an aluminium CC is used as the negative electrode the lithium will react with the aluminium at a voltage lower than that required for intercalation to occur. Copper is used instead because it is electrochemically stable up to higher voltages, but it has the drawbacks of being heavier and more expensive [186].

**Electrode Binders**

An electrode binder is often required to enable adhesion between active materials and the CC. Despite its necessity, the binder content in an electrode must be low (e.g. less than 10% of the total weight) for the following reasons [32]:

1. A maximum of particle-particle contacts and particle-current collector contacts must be ensured.
2. The electrolyte must impregnate the particles: intergranular volumes must not be clogged by the binder.
3. Most binders are insulating polymers: a high binder content in the electrode could increase resistance of the component.
4. Binders are usually non-electrochemically active materials and can decrease volumetric and gravimetric energy performance.
A key consideration when selecting a binder is the desired dispersion liquid. Some binders, such as polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) are soluble only in organic solvents such as n-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF), etc. These solvents are known to be quite toxic and require measures for environmental control. Others, such as polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) are soluble or dispersed in water and as such are considered environmentally friendly and minimize the requirement for environmental control.

The desire to use greener and cheaper production methods has led to the preferred use of aqueous based binders, but there are drawbacks. CMC and PVA have been found to lose thermal stability at around 120 °C when dried under vacuum [187], potentially increasing production time; CMC may degrade when applied in the positive electrode of EDLCs using organic electrolytes, particularly when it passes +1.3 V versus a standard hydrogen reference electrode [188]. In addition to this, SBR is known for poor adhesion strength [32]. To overcome these issues, it has been proved desirable to mix CMC and SBR together using CMC as a thickening/setting agent and SBR as the primary electrode binder [189].

**Separators**

Electrodes in an EC cell are prevented from electronically short circuiting (i.e. direct electronic contact) by an electronically insulating separator. Note the use of the term electronically rather than the more encompassing electrically; this separator should still facilitate ion transportation between electrodes, commonly by being semi-permeable.

The separator thickness and porosity is believed to be a highly influential property. Consider EDLCs; in this type of EC, charge of a single polarity is extracted from the bulk electrolyte to produce a sufficient EDL counter-charge at each electrode. This sudden ion extraction of a single polarity leaves the bulk electrolyte local to each electrode in an imbalanced state. Since this occurs in an opposing fashion at each electrode, the bulk electrolyte on each side of the separator is opposingly charged. As such, to achieve a balanced state of charge, also known as electroneutrality, ions diffuse across the separator.

As can be appreciated, different EC devices with thicker separators, and otherwise constant properties, will have longer diffusion times and thus a higher resistance [190, 191]. In addition, a thicker separator will require more electrolyte to be fully wetted, thus adding additional inactive weight. Despite this, a separator must not be so thin as to allow punctures to occur [32].
Separator porosity is often found in the order of 45-90% but should not be to the point where free carbon particles can create electronic contact between electrodes [32].

Numerous separator materials exist but the most commonly used in EC devices are cellulose and polypropylene (PP) derived [32]. Cellulose is considered a cheap and environmentally friendly option while PP is more expensive and petroleum derived. Capacitance and power capability has been found to be higher in cellulose separators than in those based on PP of similar thickness but cellulose separators also show relatively high self-discharge rates [192].

A separator of high electrochemical stability is desired to maximise operating voltage and prohibit adverse side reactions. It has been found in cellulose-based separators that the maximum operating voltage in EDLCs is 3V; beyond this, oxidative deterioration occurs in electrolytes containing organic solvents, resulting in a considerable decrease in mechanical strength [193]. For this reason, manufacturers tend to choose the more expensive PP alternative. Interestingly, this limitation is not exhibited when using cellulose separators with batteries [194], this indicates that the organic EDLC electrolyte is at fault for cellulose separator degradation. Finally, when using high voltage non-aqueous electrolytes, it is strongly advised that separators are well dried to avoid water contamination [32].

2.6.2 Effect of Electrode Thickness

The electrode thickness is an important consideration when fabricating ECs because it is directly related to volumetric capacity while impacting energy density and power capabilities. Different perspectives can be taken on this matter; it has been suggested that if the focus is to build an energy intensive device then it is better to produce electrodes with thicknesses greater than 150 µm but if a powerful device is desired then electrode thickness should be ~100 µm or less [195]. This is broadly true when considering a fully packaged device as there would be a higher proportion of electrode material to component and containment material; despite this, it has also been found that mass specific energy storage mildly decreases in thicker electrodes above 200 µm [196]. As such, careful consideration should be taken to ensure the desired device properties are achieved.

Experimental electrode thickness should not, however, be extremely thin and/or contain very minute amounts of material. Such a case would produce an experimental setup with a very high signal to noise ratio and could lead to an overstatement of a material’s performance. To
achieve reliable measurements, it is thus recommended that capacitance should be at least 0.25 F and the mass of active material greater than 10 mg [197].

2.6.3 Methods for Active Electrode Material Deposition

Spin Coating

Spin coating is a procedure for uniform thin film deposition. As shown in Figure 2.22, a substrate material (e.g. a current collector) is fixed onto the spin coating device and a solvent solution or active material slurry is deposited at the substrates centre. The substrate is subsequently rotated at high speed by the spin coater to spread the fluid by centrifugal force [198]. The substrate is then left to dry and the process may be repeated to prepare a multilayer structure.

![Spin Coating Schematic](image)

Figure 2.22  Schematic of spin-coating process. Taken from ref [198] under CC-BY 3.0 licence.

This process is extremely effective at producing films from a few nanometers to a few microns in thickness; it is also relatively simple and easy to use, known for producing highly consistent depositions. Its main drawbacks lie in manufacturing significant quantities of material, as a batch process its production rate is reduced; it is also estimated that 90% of the material is flung off to the side and wasted during operation [199]. As such, its primary role has been found in academic and limited production processes.

The use of spin coating in producing EC electrodes and cells is limited to certain specialist areas. It is often not desirable to deposit extremely thin coatings; they provide diminishing performance returns as active material weight and volume may be dwarfed by other cell components. One interesting area of application is the fabrication of thin graphene films [200, 201] for use as electrodes in flexible, and possibly transparent [202], ECs and batteries.

Dip Coating

Dip coating is a deposition method where the substrate (e.g. a current collector) to be coated is immersed in a solvent solution or active material slurry; it is then withdrawn with a
well-defined withdrawal speed under controlled temperature and atmospheric conditions [203]. A schematic of this process is shown in Figure 2.23; before withdrawing there is a limited dwell time which enables total substrate wetting. As a batch process, it is difficult to achieve a high production rate but it is considered to be low cost [204].

![Diagram](image)

**Figure 2.23 Schematic of dip-coating process.**

The primary benefit of such a method is its simplicity; the coating thickness is controlled by the solvent solutions viscosity and the drawing rate. In addition to this it is also easy to build dipping tanks to accommodate substrates of all sizes. The main drawbacks are primarily control issues; if the drawing rate is too quick the final film thickness may vary from top to bottom, as demonstrated in Figure 2.23; and the solution must be well dispersed to prevent sedimentation. If control over the process is firmly established, consistent thin films from 20 nm up to 50 μm in thickness can be produced [203].

**Tape Casting**

Tape casting is a method of depositing a consistent coating onto a narrow substrate. Essentially, slurry is fed onto a substrate via a small gap of desired thickness followed by drying and post processing such as calendaring; feeding can be conducted by either moving the deposition tool or the substrate [205]. A common deposition tool used is a doctor blade in which the blade height is adjustable; other sides behave as container walls. An example process using a doctor blade is shown in Figure 2.24. There are many ways in which drying can be conducted, for small scale product it may be suitable to cut samples and place into ovens but for large scale production it is desirable to use heated air which flows over the substrate [205]. Although the gap height will set the initial wet slurry thickness, upon solvent evaporation the thickness is likely to change.
Figure 2.24  Schematic of tape casting process using a doctor blade.

Tape casting is a very adaptable process which is suitable for producing many types of coatings; it works well with highly viscous slurries and in principle should have excellent material efficiency. In addition, it can be thought that a wide variety of substrate materials can be used. It has been found that coatings from 25 μm to 1 mm can be achieved using relatively simple deposition tools, such as a doctor blade [206], but it is important to ensure that the slurry does not contain particles larger than the gap thickness, as this can otherwise lead to coating smear or substrate tear [205].

Tape casting has been used to deposit EC type electrodes of all varieties (EDLC, pseudocapacitor and intercalation). Flexible pseudocapacitors containing carbon nanofibres have been made using tape casting and found to offer high mass specific capacitance values of 812 F g⁻¹ when scanned by cyclic voltammetry at 5 mV s⁻¹ [207]. In another case, flexible graphene-based paper electrodes with mass specific capacitance values of up to 195 F g⁻¹ were fabricated by tape casting [208]. In both of the above cases, it is believed aqueous type electrolytes were used.

**Spray Coating**

Spray coating is a deposition method in which a slurry is atomised (i.e. converted into fine droplets) and sprayed onto a substrate material. This approach is considered beneficial because it does not involve direct contact with the substrate and electrode coatings can be applied to uneven surfaces and irregular shapes [207]. In theory, coatings with multiple layers are simple to produce, possibly allowing for interesting electrode properties [208].

Atomisation can occur by one of three methods: rotary disk atomisation; pneumatic atomisation and pressure nozzle atomisation. Rotary disk atomisation involves acceleration by centrifugal forces which produces a fine mist of small droplets. In this approach the slurry feed rate is independent from the atomisation process, allowing fine control over coating thickness, but the slurry must have a low (water like) viscosity. Pneumatic atomisation comprises slurry
dispersion by a high velocity gas phase; a central inner nozzle is surrounded by high velocity gas flow which forces slurry dispersion through shear stresses at the inner nozzle tip and an outer nozzle is often used to focus the spray. This method can spray highly viscous solutions but requires fine control (i.e. of gas flow rate and slurry flow rate) for a quality coating to be achieved. In addition, the high velocity gas phase may cause premature drying at either nozzle, resulting in blockage. Pressure nozzle atomisation is the simplest method of spray coating; slurry is ejected at high pressure through a small nozzle causing atomisation as liquid pressure is converted into kinetic and surface energy. While simple, a particular nozzle can only operate at particular flow rates; if one wishes to dramatically increase flow rates it would be more appropriate to add nozzles than increase pressure. This approach works best with low (water like) viscosity liquids [207]. Subsequent drying and post processing may be conducted after each of the above methods.

As previously stated, the maximum concentration of MWCNTs that can be homogeneously dispersed in aqueous solution is about 1.4 m% [147]. It has been found that electrode coatings based purely on MWCNT’s and fabricated by spray deposition tend to exhibit low thicknesses (150 nm to 5 µm) [209] and areal densities less than 1 mg cm⁻² [210]. The cause of this is believed to be low concentration limit (1.4 m%) of MWCNTs that can be homogeneously dispersed in aqueous solution [147].

Spray deposition of supercapacitor electrodes has been previously attempted in literature. In one case, functionalised single-walled and multi-walled carbon nanotube films were deposited, they were found to present mass specific capacitances of up to 177 F g⁻¹ when combined with 0.1 M H₂SO₄ electrolyte [213].

The author hypothesizes that incorporating conductive material at specific locations within the electrode may be possible; this is due to the possibility of depositing additional coatings upon previous coatings. Such an approach has not been found in the literature and as such is of great interest.

2.6.4 Cell Containment

Cell containment is an important consideration at both research and industrial scales but it can be difficult to achieve to a satisfactory standard. An interesting observation has been made by Zhong et. al. [34]; around 83% of the published literature related to EC research employed aqueous electrolytes and one of the suggested reasons, among others, was that it is easier to
experiment with in the laboratory; considering the previous finding that organic electrolytes, such as TEA\textsuperscript{+}BF\textsubscript{4} in ACN, are highly susceptible to water contamination, it can be understood why this is so.

As previously mentioned, EC cells containing organic electrolytes can be tested in three electrode (half-cell) or two electrodes (full-cell) configurations. To implement a three-electrode setup, it is necessary to place a reference electrode near the working electrode; this is not particularly difficult to achieve [211, 212] but its primary purpose is for testing single electrodes. To accurately represent applicable devices, it is necessary to use a two-electrode configuration.

There are many methods and approaches to containing a two-electrode device but some key considerations are seal quality and mechanical stability. Aspects such as the containment pressure applied to the cell and the chemical stability of the containment materials must also be taken into consideration. Typically, a commercial cell container is predesigned to meet the application constraints and requirements defined by the issues above, but in research there are custom options.

**Coin Cell**

A device commonly utilised in both research and industrial ECs is the coin cell (also known as “button” cells). They have the advantage of being simple, inexpensive and come in a wide range of sizes [213] and configurations [214]. A disadvantage in the design is the lack of a gas release valve which would allow gas generated through electrolyte electrolysis or solvent evaporation to escape, thus reducing device safety if operating close to the cell’s voltage limit, where electrolysis is most likely to occur. As shown in Figure 2.25 (A), a coin cell utilises a cap and can with a sealing gasket to produce a fully contained environment. There are internal components which are specific to coin cells; a spring is used to maintain appropriate cell pressure while a spacer is used as a flat rigid surface upon which this pressure can be applied. Beyond these, standard cell components such as electrodes, electrolyte and separator also apply. Commercially available coin cells are predominantly of the non-rechargeable battery variety and have found application in portable electronics, toys and backup power [32].
Capacitive Energy Storage:
Filling the gap

Figure 2.25  Schematic of (A) traditional coin cell structure (B) a coin cell structure which incorporates a reference electrode.

It has been shown possible to modify a coin cell to implement a three-electrode analysis technique. Moshurchak et. al. presented the first known example of such a modification [215]; a quasi-reference electrode had been slipped between the cap and can and sandwiched between two sheets of separator to prevent electrode contact, an example of this is presented in Figure 2.25 (B). To prevent short circuiting between the cap and can the reference electrode was coated with PTFE with the tips exposed. It was considered a convenient and reliable three electrode cell. A more recent method utilised a custom cell design consisting of a coaxial reference electrode [216]; this appears to present benefits in accuracy but has complex production challenges.

Pouch Cell

A recent cell containment method which has also found common usage in both research and industrial ECs is the pouch cell. The pouch cell design differs from other containment methods in that it utilises a flexible laminated aluminium foil as the cell casing. The laminated aluminium foil commonly consists of nylon laminated on the outside and polypropylene laminated on the inside, the former aiding the cell’s structural integrity and the latter being chemically resilient [217]. The cell is enveloped in laminated foil and subsequently heat sealed around 3 of the edges. Through the 4th edge the electrolyte is inserted and then sealed under reduced pressure conditions; this introduces the external force of ambient pressure upon the cell. Figure 2.26 shows the schematic of a pouch cell design.
The primary advantages of this design lie in the absence of a thick casing, this helps to increase the relative mass of active material to component and containment material. Another advantage is its ease of fabrication, especially for small quantities. Simple electrode sheet stacking can be used in the formation of the cell and the pouch sealing process can be achieved with relatively compact and low cost apparatus.

One issue of concern is the lack of an obvious mechanism for pressure release in case of excessive gas evolution. Investigations to improve this situation have theorised that including multiple weaknesses at different locations on the pouch may allow for the material to yield and vent gas in the case of excessive gas evolution [220], but it is not known if this is commonly implemented in EC devices. Another concern to this design is that the soft pouch material can be pierced with significantly less force than is required for more rigid cell designs, this could result in electrolyte leakage and possibly fire [221].

A thought-provoking observation has been made while investigating EC devices and their containment methods, a comprehensive list of which can be found in [38]. From this it was found that on average, commercial EDLC capacitors of all packaging varieties possess 4.4 W h kg⁻¹. When considering purely laminated pouches this increases to 5.7 W h kg⁻¹ on average, a substantial improvement in energy storage capacity.

**Cylindrical and Prismatic Cells**

The cylindrical cell is one of the most widely standardised containment vessels. It has the advantage of good mechanical stability but can be difficult to fabricate as specialist winding equipment is required. The cylindrical shape provides uniform stress distribution along the axial plane thus allowing a high electrode stack pressure to be maintained, which has been shown to
improve cell performance up to a certain point [222]. The durability of cylindrical cells is good and they commonly possess a gas release vent located in the cylinder cap [32].

Prismatic cells utilise either metallic or plastic casings that are shaped in a cuboid form. This allows for the creation of thin shapes and sizes that can maintain a high pressure upon the electrode stack. They are space efficient with a packing density that is limited purely by the thickness of the canister casing and thermal considerations. Incorporation of a gas release vent is possible and the rigid can casing provides protection against piercing. Due to these advantages, they have found wide usage in small consumer electronics such as mobile phones and laptops [32].

2.6.5 Summary and Conclusions

The primary focus of this section was to report the design and fabrication of EC devices for research investigations. Initial consideration went to CCs, electrode binders and separators. With respect to CCs it was found that the use of pure aluminium is not recommended due to its thick oxide layer; instead, aluminium can be modified through etching and the subsequent addition of inert conductive materials. It was also found that aluminium cannot be used as the negative electrode in devices associated with a lithium based electrolyte, (such as LICs) due to adverse reaction with lithium at low potentials; instead, copper must be used as the negative electrode CC. Potential electrode binders were highlighted; traditional electrode binders such as PVDF and PTFE are only soluble in hazardous organic solvents. Other binders, such as SBR and CMC, are water soluble but there is concern over the potential at which CMC can operate without adverse chemical reactions, this may be overcome if combined with SBR. The desire to operate in an environmentally friendly manner makes this binder combination appealing.

Separator thickness and porosity are believed to be highly influential properties; such properties can indirectly limit power capability by restricting ion diffusion. Additionally, an excessive separator thickness will lead to reduced device specific properties; this occurs firstly because of the intrinsic separator mass/volume but also because the excess separator material requires electrolyte wetting. Two prospective materials have been identified, cellulose paper and PP sheets. With equal thickness and experimental setups, the cellulose separator presents better capacitance and power capabilities relative to PP, but also exhibits faster self-discharge. Thorough drying of the separator is essential.
Chapter 2: Literature review

The electrode thickness should ideally be between 100 and 200 μm for a device to present a reasonable balance between energy and power. It has been recommended that the capacitance of an electrode under investigation should be at least 0.25 F, and the mass of active material should be greater than 10 mg. Both spin coating and dip coating present thicknesses which are well below the recommendations above. Further, spin coating might not be able to achieve the recommended coating quantities stated above and dip coating may prove to have poor repeatability. The methods of interest for fabricating electrodes with the desired qualities are tape casting and spray coating. Tape casting presents the benefit of being a simple process but coating consistency may prove difficult to control due to solvent evaporation. Spray deposition appears to be a complex process but present benefits, such as multi-layer coating, which are of interest due to their possibility to incorporate conductive material at specific locations within the electrode.

The key requirements for cell containment are seal quality and mechanical stability. Seal quality is important for prohibiting contamination while mechanical stability is important for long term experimentation, such as device ageing. Coin (button) cells present an excellent compromise between batch scale, laboratory type cell production and industry scale, factory type cell production thus meeting secondary objective

2.7 Conclusion and Outlooks

The aim of this section was to identify possible avenues for improving the performance of ECs, this was achieved by conducting a review of prior literature related to this field. For certain topics within this field (such as LICs) this was taken a step further with advanced theoretical calculations being taken into consideration.

A variety of EC charge storage mechanisms have been studied, and their implementation in EC configurations has been assessed through the comparison of KPI (key performance indicators) such as energy density, power density, energy storage efficiency, cycle life, ESPW (voltage) and self-discharge. It has been found that EC devices which are based purely on the EDLC charge storage mechanism are on the route to becoming a mature technology i.e. highly developed; despite this, from the authors viewpoint there are still areas of uncertainty which, if better understood, may unveil beneficial advances to this technology.

One such area is capacitance balancing (see Section 2.4.3). This approach can be used to maximise a cells ESPW, thus improving energy storage and power capabilities, whilst
minimising degradation when operating at high voltages, thus improving cycle life. Currently, this approach appears to have only been assessed for cell configurations which use an identical material at both the positive and negative electrode which has been achieved through mass balancing. Instead of this, the author proposes that capacitance can be balanced through the use of non-identical materials at the positive and negative electrode, thus producing a material asymmetric EDLC. Another related matter of interest is the finding that microporous materials may offer a significant increase in capacitance for devices which utilise the industry standard TEA\text*{`}BF\text*{`} in ACN electrolyte. This is particularly true when the micropores of the associated material are predominantly 0.7 nm in width (assuming slit like shape) and this material is used as the positive electrode (see Section 2.4.2). Such information will be considered when selecting materials for producing a material asymmetric EDLC as it may lead to an increase to capacitance over more traditional EDLC designs, further improving energy storage capability.

Another possible avenue for the improvement of EDLC type EC devices is using spray deposition for depositing electrode active materials onto a CC (see Section 2.6.3). This deposition method is considered beneficial because it does not involve direct contact with the CC and coatings can be applied to uneven surfaces with irregular electrode shapes [207]. Whilst the benefits stated above may be useful from a manufacturing perspective, it is the prospect of producing multiple layer coatings which is most enticing. The author proposes that the introduction of highly conductive materials at specific locations in a layered coating i.e. the base layer or the top layer, may bring benefits to electrode power performance. In addition, little research appears to have been conducted on producing electrode coatings with high areal loading via spraying; the majority of research in this field focuses around the production of thin coatings which do not associate well with the coating thicknesses required to produce large EC devices.

While implementations of spray deposition may be pursued as a novelty, it has been deemed appropriate for most electrodes to be fabricated via tape casting. This is so because tape casting is a very adaptable process which is suitable for producing many types of coatings; it works well with highly viscous slurries and in the authors opinion should have excellent material efficiency. The exact coating thickness can be readily controlled, thus allowing flexibility during experimentation. On the topic of active material coatings, their thickness should ideally be between 100 and 200 μm for a device to present a reasonable balance between energy and power. It has been recommended that the capacitance of an electrode under investigation should be at least 0.25 F, and the mass of active material should be greater than 10 mg per electrode.
Chapter 2: Literature review

The LIC variety of EC device appears to offer substantial benefits over more classical EC devices, such as those based on purely EDLC charge storage (see Section 2.5). An LIC combines an EDLC positive electrode with a lithium intercalative negative electrode; this allows an LIC to operate between substantially higher voltages (3 to 4.5 V) than those found in more classical devices, thus improving energy storage. In addition, LICs have been found to retain good power capability, high energy storage efficiency, long cycle lives and slow self-discharge rates. As such, an LIC is an extremely desirable device for filling the gap between traditional batteries and capacitors.

At present, the state-of-the-art in an LIC type EC device is to use graphite as the intercalative negative electrode, a novel approach would be to instead use silicon for this purpose. It has been found that silicon possesses significantly improved charge capacity versus graphite (372 A h g\(^{-1}\) for graphite, 4,200 A h g\(^{-1}\) for silicon) but it also possesses an intercalation potential \(\sim0.35\) V lower than that of graphite, thus reducing the maximum EPSW. Together, these properties result in a silicon based LIC device which theoretically achieves a similar mass specific energy storage density as a graphite based LIC device when both electrodes are maximally charged i.e. fully utilised. Interestingly, it was found that if the negative electrode of a silicon based LIC device is not maximally charged during standard operation i.e. underutilised, then it still presents a mass specific energy storage density which is comparable to a fully utilised device. The author proposes that this dynamic could be exploited to achieve an improvement in power capability while maintaining high energy density.

It was identified that testing of electrodes can be conducted in either a half-cell or full-cell configurations; the benefit of a half cell (three electrode) configuration is that the potential of a single electrode can be inferred. It has been found that it is possible to produce a three-electrode system configuration whilst using coin (‘button’) cell containment. This is a highly desirable system as it brings the benefits of a three-electrode configuration into an industry standardised cell containment method, thus allowing the production of results which are relatable to commercially produced devices. Fabrication of such a system will be pursued.

The completion of this literature review meets PO 1 (see supplement A). It has led to the development of hypothesis to which the the scientific method can be applied, these have been clearly defined in Section 2.8 and thus PO 2 (see supplement A) has also been met.
2.8 Research Aims

The aims of the research pursued in this thesis are:

1. To develop and quantify an EDLC type EC device which possesses a stable high voltage ESPW through the use of capacitance balancing. Specifically, the aim is to achieve the proper capacitance balancing using material asymmetry at each electrode. Such a device should subsequently be assessed for improvements in capacitance if a material with high microporosity is used at the positive electrode.

2. To develop and quantify an LIC type EC device which possesses a novel silicon based negative electrode. Such a device should also be compared against current state-of-the-art LICs which utilise graphite based negative electrodes.

3. To utilise spray deposition in producing multi-layer electrode coatings. This should take the form of both coatings in which each layer is of the same material composition and coatings in which the material composition of each layer differs through the inclusion of conductive additives.

4. To produce or acquire electrodes suitable for use in EDLC and LIC type EC devices. The production of electrodes is to be attempted by both tape casting and spray deposition; both methods should be optimised and assessed with the aim of producing durable and consistent coatings.

5. Electrode coatings (in their final form) should possess thicknesses between 100 and 200 µm and the active material mass of a single electrode is to be greater than 10 mg.

6. To use materials and techniques (except those under investigation) which are closely related to current industrial standards. This aim has been included to maximise comparability under common research practices and with commercial devices.

7. To incorporate a QRE device into the coin cell containment method. This should provide the possibility for directly measuring (or inferring) the potential of both positive and negative electrodes while minimising possible interference with cell performance.
3 EXPERIMENTAL CONFIGURATIONS, MATERIALS AND CHARACTERISATION TECHNIQUES

3.1 Introduction

The previous chapter identified the core research aims of this thesis, the approaches used in achieving these aims will now be introduced. The first section of this chapter presents the experimental configurations implemented during experimentation; this section specifically introduces the cell configurations and cell containment method selected for use in experimentation. The subsequent section introduces the experimental materials selected for experimentation; this includes intended use, relevant material information and where possible the product code and manufacturer. The final section introduces the characterisation techniques used throughout experimentation, these include: nitrogen sorption measurement with isotherm analysis, scanning electron microscopy with elemental analysis, and electrochemical analysis.

3.2 Experimental Configurations

3.2.1 General Configurations

The fabrication of electrodes by spray deposition was one area of research, but as this area was still under development and not yet fully understood a more traditional approach to fabricating electrodes was conducted for other areas of research such as capacitance balancing of EDLCs and silicon based LICs. The approach selected for this was tape casting; this was known to offer a direct method of control over electrode thickness i.e. adjusting the doctor blade gap thickness. By controlling the electrode thickness it is possible to directly control the quantity of active material an electrode possesses, thus enabling specific electrodes to be fabricated which suit experimental requirements.

For cell containment, it was decided that coin cells should be used with a standard variety (such as CR2032) to be selected, thus helping meet the 6th research aim in Section 2.8. A silver
QRE (quasi-reference electrode) will be incorporated to directly measure (or infer) the potential of both positive and negative electrodes.

3.2.2 Electrode Material Asymmetric Capacitance Balancing

To meet the 1st aim described in Section 2.8 i.e. investigate electrode material asymmetric capacitance balancing of EDLC type EC devices, it was necessary to procure materials which possessed the appropriate capacitance values. As determined by Cericola et al. in [168], when using TEA⁺-BF₄ in ACN and the same AC material at both electrodes, for every gram of positive electrode mass there should be ~0.54 grams negative electrode mass. The author proposed that this could be translated to the following statement: ‘for every farad possessed by the positive electrode there should be ~0.54 farads possessed by the negative electrode when using TEA⁺-BF₄ in ACN with AC based electrodes.’ As such, active electrode materials with which produce an equal mass capacitance ratio of approximately 1:0.54 (part-to-part) should be procured.

Since the capacitance of a material is not often stated by the manufacturer it was proposed that materials should be procured based on SSA (specific surface area); there is clear evidence that most AC materials present a positive SSA-capacitance correlation [20, 32]. Additionally, the material selected for the positive electrode should possess a high proportion of micropores, ideally approaching 0.7 nm in size as per [160]. As such, AC materials with an SSA ratio of approximately 1:0.54 were to be sought after while also considering that AC material with highest SSA (that selected for the positive electrode) should possess significant microporous content. It was decided that the electrolyte for experimentation involving pure EDLC based EC devices should be TEA⁺-BF₄ in acetonitrile to maintain comparability with previous findings in this field.

The approach to this investigation includes validation of the prior work in this field i.e. varying mass ratio of material symmetric EDLC devices. This initial validation also confirms if a suitable experimental setup (detailed in Section 3.2.1) has been developed, alongside providing fundamental material assessment in which electrochemical properties (capacitance, resistance etc.) of each AC variety can be quantified.

3.2.3 Silicon Based Negative Electrode in Lithium Ion Capacitors

Fabrication of an LIC (lithium ion capacitor) which possesses a silicon based negative electrode was to be pursued (2nd research aim, Section 2.8), the author proposes that such an
electrode may offer energy densities greater than an LIC which possesses a graphite based electrode (state-of-the-art). This proposal is under the condition that the negative electrodes charge capacity is underutilised, a mechanism shown to improve the power capability of an LIC. As such, an external company was approached and a novel silicon based electrode material (in a pre-fabricated form) was provided. For the positive electrode, it was deemed desirable to use the AC materials associated with the experimentation described in Section 3.2.1 as this would provide better comparison between EC types. It was decided that the electrolyte for experimentation involving LIC type EC devices should be based on an industry standard electrolyte such as LiPF$_6$ ethylene carbonate/diethyl carbonate (EC/DEC).

Prior to experimentation with this novel electrode, it was deemed necessary to validate prior work in this field i.e. LICs with graphite based negative electrodes. This was to be achieved through the fabrication of graphite based electrodes using appropriate materials. In addition, for all LIC devices produced it was necessary to calculate the appropriate electrode mass of both positive and negative electrodes to ensure oxidative/reductive decomposition is minimised, thus maximising the ESPW.

All LIC devices require pre-lithiation to overcome the initial high charge-transfer resistance present in low lithiation states [178]; this will be achieved through the use of formation cycles [91]. The cell is repeatedly driven to high voltage followed by long periods of self-discharge. In principle, this should shift the intrinsic potential of GC to a lower potential i.e. a high lithiation state, than that with which it started with. One item of uncertainty in this matter is how lithiation will occur in the presence of a finite quantity of electrolyte and as such the quantity of electrolyte used in an LIC must be monitored.

3.2.4 Multilayer Spray Deposition

Using spray deposition for producing multi-layer electrode coatings (3rd research aim, Section 2.8) was to be pursued using an airbrush i.e. pneumatic atomisation; these electrode coatings were to be implemented in a purely EDLC type EC device. Contrary to other experiments conducted, the cell was to be material symmetric and the mass ratio between positive and negative electrodes was to be held constant at 1:1. Although this does not allow for the maximisation of ESPW, it does allow a simple and fair comparison between all materials deposited by spray deposition. Specifically, rather than having to combine electrodes from different spray sessions (to achieve different mass electrodes); the electrodes produced during the same spray session can be used together, thus allowing for clearer definition of cause and effect.
As a starting point, it was deemed desirable to use AC materials associated with the experimentation described in Section 3.2.1; this would provide better comparison between EDLC type EC devices which contain electrodes fabricated by wholly differing methods. Beyond this, MWCNTs (multi-walled carbon nanotubes) are to be combined with AC materials in varying quantities. This is to assess if the MWCNTs exhibited high-quality dispersion during spray deposition and if so, what effect this had upon an electrodes resistance.

Ultimately, multilayer composites are to be fabricated. The author proposes that introducing MWCNTs at specific locations within an otherwise standard AC based electrode (e.g. at the base layer or top layer) may in fact bring the benefits of lower electrode resistance without excessive use of MWCNTs, potentially lowering the cost and environmental impact of fabricating high power electrodes.

3.3 Experimental Materials

3.3.1 Electrolyte Salts and Solvents

**TEA⁺BF₄⁻ in Acetonitrile**

One of the underlying electrolytes selected for the work entailed is 1.5M TEA⁺BF₄⁻ in ACN. A plastic jar containing 250 g of TEA⁺BF₄⁻ salt was procured from Alfa Aesar (product code A10211). Specifically, it is of 99% purity and is noted as sensitive to moisture contamination. Additionally, a glass jar containing 100 ml of ACN was procured from Sigma Aldrich (product code 271004). This solvent is of 99.8% purity, has a volumetric density of 0.786 g mL⁻¹ and is stated as anhydrous (water content being <0.005%). The precise preparation procedure for this electrolyte solution can be found in Section 4.5.2.

**LiPF₆ in Ethylene Carbonate and Diethyl Carbonate**

For experimenting with LIC based EC devices, 1.0M Li⁺PF₆ in EC/DEC 50/50 (v/v) has been selected. It was found that this exact electrolyte is available premixed; thus, an aluminium bottle containing 100 ml was procured from Sigma Aldrich (product code is 746746); this electrolyte solvent mixture is said to contain impurities of <15 ppm water and <50 ppm hydrogen fluoride and has a density of 1.26 g mL⁻¹. It has also been noted that this product should not be used with glass equipment, the reasons for this are not entirely clear but it may be that the electrolyte degrades through interactions with light.
3.3.2 Active Electrode Materials

Activated Carbons

It was previously identified that two varieties of AC were required for this work. The SSA ratio between the two should be 1:0.54 (positive-to-negative) in order to assess capacitance balancing techniques while at least one should be in the form of PAC in order to assess spray deposition. For these requirements, Kynol ACC 507-15 (“Kynol ACC”) and Sigma Aldrich PAC C9157 (“Sigma PAC”) were procured from Kynol Europa and Sigma Aldrich, respectively.

Kynol ACC is in the form of a woven textile produced using a fibrous phenolic based precursor, and has been subjected to chemical activation. Individual fibres are believed to possess a diameter on the order of 10 μm. The specifications state it possesses areal mass of 120 g m^-2, a thickness of 500 μm and a SSA of 1,500 m^2 g^-1. Initially, it was believed this SSA value was calculated through nitrogen sorption with BET analysis as stated in the product specification [223]; clarification on this matter was requested from Kynol and it was subsequently discovered that SSA is instead calculated through advanced iodine adsorption tests [224]. Iodine adsorption measurement is similar in principle to nitrogen sorption measurement (section 3.4.1) but involves calculating the Iodine number which can subsequently be related to SSA as per ASTM D4607-94 [225].

Interestingly, in this communication [224] it was also stated that activation may not always be homogeneous and as such the SSA value is expected to vary by up to ± 10%. Further, it was stated that the internal microporous structure is believed to be completely amorphous i.e. without long range order. With respect to PSD, older (2001) work by Pelekani et al. found that the porous structure of phenolic-derived AC is unimodal [226]. This contrasts with the recent (2014) work of Boukhalfà et al. who found Kynol ACC 507-20, a similar variant to that used, presented a bimodal PSD [227].

Sigma PAC is an AC-derived from a peat bog precursor through physical activation. It has been acid-washed with hydrochloric acid; this is believed to be for stripping away trace metallic elements and results in a very pure internal structure. Generic product information was found which stated that this material possesses an SSA of 1,000 m^2 g^-1 (derived from BET analysis [228]); this permits two AC materials with an SSA ratio of 1:0.54. With respect to particle size, 10-15% is believed to be greater than 74 μm while 70-75% is greater than 10 μm. It is unclear as to whether the percentage greater than 10 μm includes the percentage greater than 74 μm.
**Carbon Black Additive**

It has been decided that a carbon black conductive additive will be required for LIC research. For this purpose, a laminated aluminium pouch containing 80g of TIMCAL Super P\textsuperscript{®}-Li carbon black was procured from MTI Corporation (product code EQ-Lib-SuperP). This material is specified as having a density of 160 kg m\textsuperscript{-3} and an SSA of 62 m\textsuperscript{2} g\textsuperscript{-1}.

**Multi-Walled Carbon Nanotube (MWCNT) Additive**

Part of the research into spray deposition will involve utilising MWCNTs as conductive additives. It has been reasoned that for MWCNTs to bridge interparticle voids they must be longer than these voids. As such, nanotubes on the order of particle size are required. Thus, a glass jar containing 1g of Elicarb MWCNTs were procured from Thomas Swan (product code P940). According to the product data sheet \cite{229} they are “tens of microns” in length, possess an outer diameter of 10 to 12 nm and have a SSA of 250 to 300 m\textsuperscript{2} g\textsuperscript{-1}. Also provided in their specification sheet is an image acquired through transmission electron microscopy (TEM), that image confirms the outer diameter and displays the inner diameter as \textasciitilde8 nm.

**Silicon Based Electrode**

For research into silicon based LICs, a novel silicon electrode was provided by an external company which specialises in silicon electrode development; it has been designated NXA-513. This electrode came prefabricated with active material having been deposited onto copper foil followed by compaction under a pressure of 483 kPa. The binder used is stated as PVDF but the precise quantity is not defined. The areal density of deposited material is stated as 3.55 mg cm\textsuperscript{-2}; 2.45 mg cm\textsuperscript{-2} is stated as silicon and thus 1.10 mg cm\textsuperscript{-2} accounts binder and additives.

**Graphite**

For research into LICs it was reasoned necessary to assess the current usage of graphitic electrodes. For this purpose, a plastic jar containing 28g of synthetic graphitic powder was procured from Alfa Aesar (product code is 40798) This material has been passed through a standard 325 sieve mesh, which implies all particles will have major dimensions below 44 \textmu m. This material was selected primarily because of its high purity which is stated as 99.9995\%, with the remaining traces being metal based.
3.3.3 General Components

**Current Collectors**

Two CC materials were required for the research. The primary CC material for EDLC electrodes was Toyal Carbo®; this is an aluminium-based material which has been coated on both sides with carbon particles, the thickness of this coating is 1 μm. The foil is then kept at high temperature in a hydrocarbon atmosphere which induces the growth of Al2C3 nanowhiskers, which in effect firmly bind the carbon particles to the surface [181]. A large spool of 30 μm thick and 12 cm wide Toyal Carbo® was procured from Toyo Aluminium K.K.

The secondary CC material was copper foil; this was used as a CC for the negative electrode material in LIC research. It possesses a thickness of 20 μm, a width of 12 cm, and an areal density of 9 mg cm⁻². Unfortunately, this material (battery grade) was provided from a prior research partner who did not state where it was procured.

**Electrode Binder**

A single electrode binding material, which would be suitable for all experimentation and minimise handling hazardous solvents, was desired for research. As such, a plastic bottle containing 1L of modified styrene-butadine copolymer hydrophilic binder was procured from Targray Technology International Inc. (product code PSBR-100). This material uses SBR as the primary binder and CMC as a thickening/setting agent. As this material is hydrophilic it is suitable for using water as the slurry solvent; it comes in a pre-diluted form of which 15% ± 0.5% is binding material and the remainder is water. This material is stated as suitable for use in the fabrication of both positive and negative electrodes [230].

**Electrode Separator**

It has been deemed suitable for a single electrode separation material to be used in all experimentation. Thus, a large spool of 60 μm thick cellulose separator was procured from Nippon Kodoshi Corporation (NKK) (product code TF40-60).

**Quasi-Reference Electrode**

Silver was required for producing QREs (Section 3.4.3). As such, a plastic box containing a 50 mm by 50 mm piece of 100 μm thick annealed silver foil was acquired from Alfa Aesar (product code 42317). Material purity is stated as being 99.998% with trace elements being metal based.
**Coin Cell Containment (“Button” Cells)**

It was decided that cell containment would be achieved through the use of coin cells. For this purpose, the CR2032 standard was selected. This casing type is specified as having an outer diameter of 20 mm and a height of 3.2 mm when fully sealed. This variety of casing is suitable for circular electrodes which are no larger than 15 mm in diameter. Note, if the aim of assessing electrodes with an active material mass greater than 10 mg is to be met, the areal density of active material must be greater than 5.6 mg cm\(^2\). A full cell typically consists of four components: a spring for maintaining internal pressure, a spacer (thickness 0.5 mm) to provide a level supporting surface for the electrode, a negative cap with an inbuilt O-ring and a positive base; an image of these components can be found in Figure 3.1.

![Coin Cell Containment Components](image)

**Figure 3.1** Image of coin cell components with labels above.

Commonly these components are made from stainless steel (SS) AISI 316, but it was found out during the process of procuring coin cell cases that at voltages > 4 V an SS positive base may react with the electrolyte, particularly in the case of those which contain LiPF\(_6\) salt [231]. As such, a second variety of coin cell was found in which the SS positive base has been coated in a thin layer of aluminium; this variety can tolerate voltages up to 5.5 V. Thus, a set of 200 SS cases and a set of 100 SS coated with aluminium cases were procured from Gelon LIB Co (China). Each set contains one of each component listed above. The spacers were 1 mm thick while the spring was of the Belleville variety.

### 3.4 Characterisation Techniques

The research programme involves investigating a wide variety of EC materials, electrodes, and devices; this section will present the experimental techniques and configurations used in their characterisation.
3.4.1 Nitrogen Sorption Measurement and Isotherm Analysis

As recognised in Section 2.4.1, an important aspect of an electrode material is its porous structure; this has been determined to have a significant influence over how an electrode will perform when utilised in electrochemical devices. Nitrogen sorption is a technique for characterising the porous structure of materials; it can provide SSA (specific surface area), SPV (specific porous volume), and PSD (pore size distribution) quantification.

**Principles of Sorption Analysis**

One of the most popular methods available for calculating the SSA, SPV, and PSD of a material is gas sorption analysis. The basic concept of adsorption/desorption (sorption) analysis is to investigate the relationships between the quantity of gas molecules physically adsorbed onto a solid surface and the resulting gas pressure change. Specifically, gas sorption in this work employs the manometric, often appropriately termed volumetric [232, 233], experimental technique and is described as follows: a sorbent sample is placed in a vessel with constant volume and temperature; this vessel is evacuated to vacuum; a known quantity of sorptive gas is dosed into the vessel and adsorbed onto both internal and external sample surfaces due to weak van der Waals interactions. Any sorptive gas (sorbate) that cannot be adsorbed will remain in a gaseous phase and result in an increase in pressure, measured using a pressure gauge [234]. The relationship between the quantity of sorptive gas dosed and pressure is known as an isotherm, of which there are six primary classifications [235], shown in Figure 3.2. These classifications have been labelled with commonly associated pore structures, i.e. microporous (0-2 nm), mesoporous (50 nm) and macroporous (>50 nm).

![Figure 3.2 IUPAC classifications of physisorption isotherms, arrows indicating increasing relative pressure indicate adsorption while arrows indicating decreasing relative pressure indicate desorption. Each is labelled above with commonly associated pore structures [236].](image)

Richard Fields - February 2018
In the case of microporous materials, the dominant isotherm response is type I; purely by visual assessment it is possible to see that this isotherm indicated strong adsorption at low relative pressure $P/P_0$. The isotherm is an experimental response which is, in essence, the only ‘true’ part of sorption analysis.

Sample preparation is an important step towards achieving a trustworthy result in SSA, SPV and PSD analysis; it is primarily focused around the removal of moisture which could otherwise block pores. The process involves heating samples at high temperature in the presence of nitrogen for extensive periods of time to aid removal of impurities; this process is known as degassing.

**Equipment and Configuration**

Prior to measurement, a sample must be weighed and degassed. Weighing was conducted with two varieties of analytical balance; a Denver Instrument Sl 234, with a resolution of 0.1 mg, was used for samples weighing over 100 mg whilst an Ohaus Discovery, with a resolution of 0.01 mg, was used for samples weighing under 100 mg. Degassing was achieved with a BELPREP Flow II under a stream of nitrogen.

Finding appropriate equipment for conducting nitrogen sorption measurements can be a challenge. Three instruments were available onsite: a Coulter SA3100, a Micromeritics Gemini 2380 and a BELSORP (BS) Mini II; all three devices use pressure gauges which can produce an accurate isotherm between $P/P_0$ values of 0.001 and 0.997 [237, 238, 239]. This range is inadequate for properly assessing micropores $\sim$1 nm in size but suitable for assessing mesoporous materials [232].

As such, the BS Mini II was selected for mesoporous material analysis due to its advanced software capabilities and ability to test three samples simultaneously; in addition, its Dewar can maintain a suitable quantity of liquid nitrogen for at least 30 hrs. In this case the isothermal temperature is 77 K, the boiling point of liquid nitrogen.

Help in assessing microporous materials was kindly provided by Giuliano Laudone at the University of Plymouth who offered to analyse two samples on a BS Max, an instrument capable of producing accurate isotherms between $P/P_0$ values of $1 \times 10^{-8}$ and 0.997 [240]. An example of the difference between the BS Mini II and Max is presented in Figure 3.3 in which isotherms of an identical material, prepared and analysed in a similar manner, present differing experimental responses at $P/P_0$ values below $10^{-3}$. The inset of Figure 3.3 shows the full range of these two
instruments, the slight difference in maximum gravimetric absorption quantity is attributed to human error in sample weighing.

![Graph](image)

**Figure 3.3** Nitrogen adsorption isotherms, with a logarithmic $P/P_0$ scale, comparing Belsorp Max and Mini instruments. Inset: full isotherm profiles with linear scale.

**Configuration**

Sample weight is an important aspect of nitrogen sorption measurements; a large quantity of material takes longer to analyse than a small quantity. It has been stated that the quantity of material used for analysis should be that which will present between 2 to 40 m$^2$ of surface area for nitrogen interaction [233] (i.e. if a material possesses a SSA of 1000 m$^2$ g$^{-1}$ then between 2 and 40 mg should be used for experimentation). This necessity is not driven by considerations for accuracy, although accuracy does improve with larger quantities; instead, it is driven by the length of time which the Dewar can maintain a minimum quantity of liquid nitrogen. All AC materials were tested with a sample weight of ~50 mg while materials where a lower surface area was expected were tested with sample mass $>$100 mg.

Degassing for all samples was conducted at 305 °C for 3 hours under a light flow of nitrogen; care was taken to ensure no sample material was lost due to excessive flow rates which can cause material to be blown out of the sample tube.

Nitrogen sorption measurements are conducted in dosing steps for which there are two primary control parameters. The first is dosing amount; in general, a smaller dosing amount leads to greater accuracy but longer experiments. A material with a low SSA value absorbs less gas and as such, a low dosing amount should be used. This was the case for NXA 513 and AA
graphitic powder where a dosing amount of 0.01 cm$^3$ g$^{-1}$ was used. For high surface area materials, a dosing amount of between 2 and 10 cm$^3$ g$^{-1}$ were selected, low dosing amounts were used when the isotherm was relatively constant while high dosing amounts were used when the isotherm was rapidly changing, finding the appropriate values at each isotherm position (or region) was a matter of evaluation over multiple experiments.

The second control parameter is the $P/P_0$ values at which recordings are taken; a large number of recordings is desired in order to capture minute variations but can lead to excessive analysis times. Thus, instead of making arbitrarily periodic recordings it was better to focus around $P/P_0$ values of interest e.g. in Type I isotherms focus was placed on the initial adsorption response at low $P/P_0$ values.

**Isotherm Analysis**

Theoretical interpretation of an isotherm is required to acquire SSA, SPV values and its derived PSD. The first theoretical approach was developed by Brunauer, Emmett and Teller (BET) in 1938 [241] and can determine SSA and SPV. The BET method can be readily applied to Type II-VI isotherms but, as previously mentioned, it has long been known not be suitable for accurate determination of the SSA in microporous (Type I) materials [107]. This has recently been reiterated in an IUPAC report [235]:

“The BET-area derived from a Type I isotherm must not be treated as a realistic probe to accessible surface area. It represents an apparent surface area, which may be regarded as a useful adsorbent “fingerprint””.

As such, this method is still widely used but the SSA values it presents must not be taken at face value as materials with different true SSA values may present the same BET derived SSA value.

Advanced theoretical analysis methods, such as non-local density functional theory (NLDFT) and Grand Canonical Monte Carlo (GCMC) simulations, have been developed in recent years. These can interpret an isotherm with molecular considerations and are considered to provide superior SSA and SPV values alongside improved PSD accuracy. These methods have gained substantial popularity [235] but it must be considered that they too involve simplifications and may not be ‘true’ to reality.
One key assumption in this process is pore shape: in BET analysis pores are assumed to be open (i.e. flat) surfaces; in NLDFT and GCMC analysis the user can assume either slit, cylindrical or cage shaped pores [233]. For AC materials, the shape is widely assumed to be slit-like [242, 243], while in carbon nanotube materials the commonly assumed pore shape is cylindrical, as might be expected.

An introduction to BET analysis can be found in [233]. Advanced consideration has been taken as to the operation of NLDFT and GCMC analysis as these are deemed state-of-the-art techniques. In general, these methods assess a theoretical PSD by producing a theoretical adsorption isotherm for such PSD. The error between this theoretical adsorption isotherm and the experimental adsorption isotherm is minimised iteratively until a conclusion can be drawn as to what PSD best fits the experimental isotherm result [233].

Specifically, in NLDFT the intrinsic free energy functional of an individual pore is minimised (e.g. by solving the Euler-Lagrange equations) at a multitude of relative pressures; this allows a ‘local’ theoretical adsorption isotherm to be created for that pore. This process is repeated at various pore diameters and by assessing individual pore contribution to a ‘global’ or ‘non-local’ isotherm (through varying associated pore volume); it is possible to compute the PSD which best matches the experimental adsorption isotherm [233, 244]. This approach assumes adsorptive molecules are spherical in shape and does not consider individual molecular interactions. Due to these simplifications, this method is computationally inexpensive [233], but it remains scientifically naive.

In GCMC a different approach is taken; this method essentially models an adsorption experiment on a virtual porous carbon to create an adsorption isotherm. This is achieved through repeatedly generating/annihilating virtual adsorptive molecules in the space of the virtual pore; simulating their movement; and relocating them in order to stabilise the systems energy. This process is conducted for many pore diameters, volumes and gas pressures in order to simulate a ‘global’ adsorption isotherm which most appropriately matches the experimental isotherm, thus providing the appropriately matching PSD [233, 244]. GCMC is beneficial because molecular interactions can be modelled while the individual molecules are assumed to have structures which closely represent reality [233]. Also, in-depth investigation has revealed that GCMC is preferred over NLDFT for modelling systems with pore sizes that approach the adsorption molecule size, i.e. > 1 nm; this has been attributed to the loss of applicability for the weighted density approximation (WDA) used in NLDFT at these sizes. The main drawback of
GCMC method is computational expense, but this has been reasonably overcome with modern computing capabilities [233].

Based upon this knowledge it was decided to implement BET and GCMC analysis methods upon experimentally derived isotherms; for this, BElMaster version 2.3.1 was used. SSA values derived from BET analysis were calculated at a \( P/P_0 \) of 0.3 for non-microporous materials and according to ISO9277 [245] for microporous materials, total SPV (specific pore volume) was always calculated at a \( P/P_0 \) of 0.990. GCMC analysis in this software was intrinsically able to produce PSDs, but SSA and SPV values had to be inferred from the PSD as per [243]; that process is detailed in Appendix 8.

**SPV Interpretation**

SPV does not appear intrinsically useful as it is not directly related to capacitance (2.6); instead, it requires interpretation for useful information to be ascertained. Knowing that graphitic carbon has a density of \( \sim 2.2 \text{ g cm}^{-3} \) [246] it is apparent that its specific volume is 0.45 cm\(^3\) g\(^{-1}\), summing graphite’s specific volume with the SPV value and taking the reciprocal of the result will approximate the porous particle density (PPD) for graphitic materials. This knowledge may be useful when evaluating an electrode’s volumetric capacitance. It could also be useful in modelling the internal porous structure of materials, such as estimating the number of graphitic planes in pore walls, but this will not be conducted in the work entailed.

**3.4.2 Scanning Electron Microscopy and Elemental Analysis**

One of the simplest, yet most effective, methods of characterising an object is to observe it; information such as surface topology, elemental composition and particle size distribution may possibly be associated with nitrogen sorption or electrochemical phenomena. For this purpose, scanning electron microscopy, a technique capable of resolving microscopic and nanoscopic structures, and energy–dispersive X-ray analysis (EDX), a technique capable of elemental analysis, were used.

**Principles of SEM and EDX**

A microscope is an extremely important observational tool which is used to magnify objects too small to observe with the naked eye. Traditional light microscopes use visible light and lenses to enlarge an object for the viewer but are only suitable for viewing objects on the microscopic \( (10^{-6} \text{ m}) \) scale due to the wavelengths of visible light [247].
Chapter 3: Experimental configurations, materials and characterisation techniques

To overcome this limitation and observe objects on the nanoscopic ($10^{-9}$ m) scale it is necessary to use a scanning electron microscope (SEM), one in which an electron beam, rather than visible light, is shone onto a sample. An electron gun is used to produce a primary beam of electrons which are subsequently condensed and electromagnetically steered to a single point on the object surface; these impacting electrons energise the surface causing it to emit secondary electrons which are subsequently detected and interpreted as a brightness value for that particular surface point. The beam is raster scanned across the object surface to produce a full image. The extremely small nature of electrons allows images of excellent detail to be produced, in some cases sub-nanosopic spatial resolution is achievable.

It is often desirable to know the elemental makeup of a surface, particularly if it is comprised of differing materials. For this purpose, it is possible to use an analysis technique called EDX spectrometry. X-rays can be produced when an electron beam causes electrons in low nuclear shells to be emitted, thus allowing high energy electrons from outer shells to take their place. In order for these high-energy electrons to drop to lower shells they must first emit energy in the form of electromagnetic radiation (X-rays), the wavelength of photons produced is ideally unique to each element and thus EDX analysis of the energy spectrum can identify relative quantities of elements present at a surface.

**Equipment and Configuration**

For both SEM and EDX analysis a JEOL JSM-7100F fitted with a Thermo Scientific triple analysis system including an UltraDry EDX detector was used. All samples were tested under high vacuum using the standard operating setup of 15 kV acceleration voltage. Sample preparation varied depending on material; powder based materials are not directly put into the instrument because they may damage the detector and vacuum pump; instead they are lightly adhered to a suitable conductive substrate. If they are in a final electrode form, then the electrode base is adhered to the conductive mount.

Samples were cut with a scalpel into approximately half centimetre squares except for fabric like materials in which individual threads were selected. To maximise equipment run time, samples were prepared in advance to allow the silver paste adhesive to fully cure and degas. Depending on whether planar or cross-sectional views were required a horizontal or vertical sample mount could be used.
3.4.3 Electrochemical Analysis Techniques

For characterising an individual electrochemical electrode or cell it is necessary to implement electrochemical analysis techniques. Such analysis techniques can provide high level insight, such as charge storage, energy storage and power capabilities, for EC devices. If effectively applied, they can also prove extremely insightful as to the underlying phenomenon involved. While a myriad of techniques exist, there are three techniques which are particularly useful in this field of research [248]. While their most common implementation in this work will be in two electrode configurations, effort has been taken to produce a quasi-reference electrode which allows these techniques to be applied in a three-electrode configuration. The third electrode will be discussed in this section and its precise implementation will be discussed in Section 4.5.3.

**Constant Current Charge-Discharge**

One of the most popular analysis methods available is constant current charge-discharge (CCCD), also known as galvanostatic cycling. It involves charging and discharging at a constant current level, often repetitively, to characterise an EC device or working electrode. To achieve a balanced evaluation between devices, the current is often stated relative to a single electrode mass or volume i.e. (A g⁻¹) or (A m⁻³); in a two electrode cell specific current should be detailed specific to each individual electrode. The output of CCCD analysis is a plot of cell or electrode voltage against time. An example of a two electrode EDLC cell CCCD cycle is presented in Figure 3.4; from such a plot it is possible to calculate almost all major parameters concerning an EC device.

![CCCD plot](image)

*Figure 3.4  CCCD response of an EDLC showing voltage variation versus time. The key to variables is given in the text.*
Chapter 3: Experimental configurations, materials and characterisation techniques

Equivalent series resistance (ESR) $R_{ESR}$ is essentially the electric resistance of a cell or device; it is exhibited in CCCD as a drop in voltage $\Delta V_1$ down to $V_{drop}$ at the start of discharge. If at peak voltage $V_{max}$ the cell is instantaneously switched from charge to discharge, then the change in current $\Delta I$ is actually twice that of the constant current value. This is important to note because it is also possible to conduct a CCCD experiment in which the cell is left to dwell at peak voltage before discharge is initiated, in this case the change in current is the same as the constant current value. As such, $R_{ESR}$ for the example in Figure 3.4 can be calculated as:

$$R_{ESR} = \frac{\Delta V_1}{2 \cdot \Delta I} \quad (3.1)$$

An interesting but uncommon method for assessing $R_{ESR}$ has been found in [249] and is based upon IEC 62576, a standard for basic electrical characterisation of EDLC devices [250]. It states that a cell can be analysed using CCCD at multiple current densities; what should arise is a linear response between $\Delta I$ and $\Delta V$, as shown in Figure 3.5, of which the gradient is $R_{ESR}$ as per Ohm’s law.

![Figure 3.5 Schematic of resistance analysis method based upon multiple CCCD test currents, identified as points [249].](image)

Capacitance should be calculated from the discharge phase of CCDC between points in which the voltage-current relationship is linear e.g. 80% and 40% that of the $V_{drop}$ [251]; these points are shown in Figure 3.4. This is done as to avoid the possible nonlinear capacitance region near $V_{drop}$, also shown in Figure 3.4; this nonlinear capacitance region is generally associated with restricted ion movement and does not best represent true material capacitance [248]. For the calculation of $C$, equation (2.1) is combined with equation (2.5) to produce equation (3.2)
where the change in time $\Delta t$ and voltage $\Delta V_2$ is that which occurs between 80\% and 40\% of $V_{\text{drop}}$.

$$C = \frac{I \Delta t}{\Delta V_2} \quad (3.2)$$

The magnitude of the electrochemical stable voltage window $V_{\text{ESPW}}$ of a cell can be assessed by steadily increasing the $V_{\text{max}}$ during sequential CCCD cycling until a nonlinear capacitance response forms as the voltage approaches $V_{\text{max}}$ during the charge phase. The values of $R_{\text{ESR}}$, $C$ and $V_{\text{ESPW}}$ are the fundamental values required in order to calculate energy storage and power capabilities.

The energy storage capability of an EC device can be calculated directly through the integration of energy transferred at each CCCD time step, or indirectly through the application equation (2.7). A common method [38] for comparing the power capability of different devices is to assume an external load is applied with resistance equal to $R_{\text{ESR}}$, this situation is termed matched load specific power and is given by:

$$P_{\text{max}} = \frac{V_{\text{max}}^2}{4 \times R_{\text{ESR}}} \quad (3.3)$$

The use of equation (3.3) has limitations as the load resistor in a practical application rarely matches $R_{\text{ESR}}$. Other methods are stated in DOE-FreedomCar, IEC 62576 and the pulse energy storage efficiency [95] but appear to be uncommon in laboratory scale research. Thus; matched load specific power is used to maintain comparability with other work in this field.

In addition to these fundamental parameters; CCCD, and variations of; can be used to find the time constant, leakage current, peak current, charge storage efficiency, energy storage efficiency and cycle life [38]. The time constant metric is based on an RC model circuit which consists of a resistor and capacitor in series and has been described by Equation 2.12 in Section 2.3.2.

Due to the thermodynamic instability of EC electrodes (again particularly of the EDLC type) an EC tends to self-discharge over time [252]. This can be assessed in either of two ways. The first method is to hold an electrode or cell at constant voltage, also known as potentiostatic
state, whilst allowing the cell to draw current as required to maintain said voltage. Under appropriate testing configurations the current drawn will decrease until constant, thus defining the current which is leaked at that voltage. The second method is to again achieve a constant voltage across a cell and then disconnect the external electronics, thus leaving an open circuit. With no electronic charge transfer the voltage will drop until it reaches zero due to non-equilibrium thermodynamics; the rate and manner in which this occurs can also define self-discharge.

The charge and energy efficiencies relate to charge or energy input (on charge) versus their output on subsequent discharge; it is ideal to have high efficiencies for both but energy storage efficiency is commonly less than charge storage efficiency. Charge storage efficiency is mostly influenced by irreversible chemical reactions in which charge is permanently consumed. Energy storage efficiency is dependent on charge storage efficiency but more so on energy loss in overcoming resistance, particularly at high currents, as described by equation (2.4).

CCCD lends itself well to cycle life analysis because it can accurately represent most real-world usage scenarios. As such, the ability of CCCD, and its variations, to define many parameters make it an invaluable tool in assessing EC performance. Further, this method can be implemented from laboratory up to industrial scales, facilitating validation of scalability and thus making it widely used.

**Cyclic Voltammetry**

Cyclic voltammetry (CV) is an electrochemical analysis technique in which a linear voltage saw tooth, known as the scan or sweep rate \( v_s \) (V s\(^{-1}\)), is applied to an electrode or cell between two voltage limits whilst the resulting current is measured. Presented in Figure 3.6 is an example of CV analysis, at a scan rate of 10 mV s\(^{-1}\) between 0 and 2.5 V, on a real world two electrode EDLC device containing a variety of ACC and TEA\(^{+}\)BF\(_6\) in ACN.
Figure 3.6 Example cyclic voltammetry plot for a two electrode EDLC device at a scan rate of 10 mV s\(^{-1}\) between 0 and 2.5 V. Note that both current density and capacitance may also be represented specifically.

Capacitance is the matter of primary interest in CV analysis of ECs; it can be calculated at each experimental step through equation (3.4). As demonstrated by Figure 3.6, the stepwise capacitance is not always constant during a CV cycle. This phenomenon is common in EDLC devices and has been attributed to either the reduction or compression of the solvation layer at the electrode/electrolyte interface due to increasing coulometric forces [253].

\[
C = \frac{1}{v_f} \tag{3.4}
\]

Another approach in calculating capacitance would be to calculate the total charge transferred during either the upward or downward sweep along with the voltage limit range and implement Equation (2.5). This result could be used in monitoring changes in capacitance over multiple CV cycles (i.e. cycle life) but application of CV in this manner is rare as CCCD better represents real world cycling scenarios.

CV analysis has roles aside from assessing capacitance. Evaluating kinetic response (i.e. power capability), albeit in a rather qualitative manner; this can be achieved by implementing CV analysis at wide range of scan rates and evaluating how the plots differ. Essentially, at low scan rates a CV presents a ‘rectangle’ like response while at high scan rates this ‘rectangle’ will become skewed into a ‘rhombus’ shape with rounded corners; such a shape is presented in
Figure 3.6. This transformation occurs due to $R_{ESR}$ slowing the change in current, it is analogous to the voltage drop experienced in CCCD but is significantly harder to quantify.

Another role is to scan for the occurrence of Faradaic reactions; these typically present themselves in a CV plot as voltages at which excessive current is measured, also known as redox peaks. These redox peaks may arise for two reasons: the first is through detrimental irreversible reactions, these signify the $V_{ESP}$ of a device, and the second is through reversible, pseudocapacitive reactions. Interestingly, in a two electrode (full-cell) setup the $V_{ESP}$ is presented as a single absolute value but in a three-electrode (half-cell) setup the $V_{ESP}$ is presented relative to a reference potential, thus having two voltage values between which a device can operate in a stable manner.

**Electrochemical Impedance Spectroscopy**

Electrochemical impedance spectroscopy (EIS) is a complex electrochemical analysis technique which requires advanced understanding to be implemented effectively. It commonly involves applying a low amplitude oscillating voltage signal and measuring the corresponding alternating electrical current (a.c.) response. This should be conducted at a stationary voltage in order for the linearisation of current-voltage characteristics to occur. From this linearisation it is possible to infer electrochemical properties, such as capacitance, energy and power, at that stationary voltage value. EIS could also involve controlling the current and measuring voltage but this is uncommon. The input oscillation is applied at many different frequencies $f$ (Hz), typically high to low; this in principle allows electrochemical processes, such as charge transfer, mass transport and charge storage mechanisms, to be distinguished (resolved) based on their time constants.

EIS is an important tool capable of enriching our understanding as to what phenomena occur in EC devices. Despite this, it is widely regarded by many as a daunting topic which is difficult to fully comprehend. In depth understanding can be developed from [254] while analogies can be drawn from explanations on the matter received at a forum for electronic engineers [255].

EIS is a technique which uses a.c., this implies that the current and/or voltage is trying to change. The results of such a system are three forms of impedance: electronic resistance, capacitive reactance and inductive reactance. Electronic resistance has been previously discussed in section 2.2.1. Reactance is the a.c. “resistance” equivalent for a capacitor.
or inductor; this will be now discussed. Consider again how a capacitor operates and recall that as an electric field gathers in strength, so does its opposition to changes in charge transfer, i.e. current; this opposition is the a.c. “resistance” described above. It is likewise applicable to an inductor in which interacting magnetic fields “resist” changes in current. As the formation of strongly interacting magnetic fields is not common in EC devices the focus will now be on electronic resistance and capacitive reactance.

The response of these two forms of impedance $Z \, (\Omega)$ are linked in a complex manner. Electronic resistance $Z_{Re}$ (or $Z'$) is the real ($\Re$) aspect and is associated with work such as resistive heating. In contrast, capacitive reactance $X_C$ is the imaginary aspect and is associated with work done through the formation of electric fields. A more mechanically related method of understanding this is to say that $Z_{Re}$ is like friction against the motion of electrons whilst $X_C$ is like inertia against the motion of electrons. Through the implementation of a vector equation it is possible to equate capacitive reactance to imaginary impedance $Z_{Im}$ (or $Z''$) resulting in $X_C = -Z_{Im}$; a detailed discussion of this can be found in [256].

$$\Phi = \arctan \left( \frac{Z_{Im}}{Z_{Re}} \right)$$  \hspace{1cm} (3.5)

The overall impedance effect can be deduced by considering the phase angle $\Phi \, (^\circ)$, calculated using equation (3.5), between applied voltage oscillations and responding current oscillations. If the oscillations are synchronised, such that $\Phi = 0^\circ$ then the system exhibits purely electronic resistance. If on the other hand, the responding current oscillation precedes the voltage, such that $0^\circ > \Phi > -90^\circ$ then the system exhibits both electronic resistance and capacitive reactance. Finally, if $\Phi = -90^\circ$, then the system exhibits purely capacitive reactance. The fact that current oscillations precede the input voltage oscillations may seem counterintuitive; consider that for a capacitor there can be no change in voltage without prior current flow. Most EC devices do not exhibit purely capacitive reactance; this reflects the presence of non-ideal behaviour possibly caused by electrode surface roughness, variation of local capacitance inside a porous electrode and faradaic charge transfer reactions [257].

EIS analysis is typically conducted through the analysis of $Z_{Re}$ and $-Z_{Im}$ at a multitude of voltage oscillation frequencies and is most often expressed as a Nyquist plot. While electronic models describing Nyquist plots of EC devices do exist, such as a Randles equivalent electrical
circuit, it has been found they provide little benefit when experimentally assessing device performance. Instead, a more intuitive understanding of a Nyquist plot will be developed with the intention of aiding device comparison throughout this thesis.

A classic example of a Nyquist plot is provided in Figure 3.7 and shows the response of a commercially available EDLC. This type of plot compares $Z_{Re}$ and $Z_{Im}$ responses at varying frequency; far left points are at high frequency and proceed rightwards as frequency decreases.

![Nyquist plot for EDLC based EC](image)

**Figure 3.7** Example Nyquist plot for EDLC based EC. Each marker represents a unique frequency, decreasing left to right; and $R_{ESR}$ determination methods are marked in red. Adapted from [95].

The left-most point at which the plot intercepts $Z_{im}$ is known as the solution resistance and is determined by ionic concentration, type of ion, temperature and area of cell. Beyond this there are three areas of importance: the polarisation “loop” located after $Z_{im}$ becomes positive, enlarged in top right inset; the middle “Warburg” region, and the right side capacitive region which exhibits a sharp upwards slope.

The charge transfer “loop” is present at high frequencies due to polarisation resistance between the electrodes and electrolyte. It has been found from literature that this loop may develop for three reasons: the first reason could be the occurrence of chemical reactions at the electrode [258, 259]; the second reason could be semi-infinite electrolyte diffusion limitation caused by constricted porous networks, a visualization of this is presented in Figure 3.8 and further understanding can be attained from [260]; the third reason could be contact impedance between the CC and electrode material e.g. due to an oxide layer [180]. Further consideration has been given to the third reason; at high frequency, charge would wish to rapidly transfer to/from the electrode but the nonconductive coating hinders transfer; due to this, excessive charge forms on both sides of the interface and thus, a capacitive “loop” response is exhibited.
until the frequency decreases to the point where charge transfer is no longer significantly impeded at this location.

![Figure 3.8](image)

Figure 3.8 Calculated impedance for various shapes of a single pore assuming a capacitive interface. From ref [260].

The Warburg region, also known as diffusion impedance, occurs after the charge transfer “loop” but before the capacitive region. It is taken as an indicator of the ability for electrolyte to diffuse to/from charge storage sites. In a physical sense, it can be considered the time after electronic charge arriving at the electrode surface but before ionic counter charge arriving at the interface. This region can provide insight as to electrode structure and ionic conductivity; it has been extensively studied by de Levie [248] and can be visualized through Figure 3.8.

In the final capacitive region charge transfer rate is slow enough, due to the low input frequency, that an EDLC is formed at the electrode–electrolyte interface. Due to its dominantly capacitive response, this region should have $\Phi$ approaching 90°. If this value is not reached, it may imply charge is being consumed by Faradaic reactions and as such may be taken as an indicator of charge storage efficiency.

There are two methods of assessing cell resistance $R_{ESR}$ from EIS. The first method is to take the real resistance at which the diagonal line of the Warburg region intersects the $Z_{Im}$ axis, as denoted by the red dashed lines in Figure 3.7. The second method is to take the real resistance at the knee frequency which is commonly 1 kHz in EDLC devices (see inset of Figure 3.7). It has also been found in the literature that the value of $R_{ESR}$ from EIS analysis is typically lower than the $R_{ESR}$ from CCCD analysis [248]. Upon knowledge of $R_{ESR}$ it is possible to calculate the theoretical power capability using equation (3.3)
\[ C_{Re} = \frac{-1}{2\pi f Z_{lm}} \] (3.6)

A common method of assessing the capacitance from EIS is through the implementation of equation (3.6). In this equation, the frequency and its corresponding imaginary impedance are input and the real capacitance is output. As long as this value is determined from a point in the capacitive region, and has \( \Phi \) close to 90°, then the capacitance value provided will reflect that of the electrode or cell being tested. This approach can be built upon by calculating the real capacitance at all frequencies and presenting the results in a Bode plot (a plot showing the frequency response of a system). In such a plot the capacitance value for an EDLC device should plateau upon entering the capacitive region with \( \Phi \) being close to -90°. Upon knowing capacitance, it is possible to calculate the theoretical energy density at varying voltages, as per Equation (2.7). If there is uncertainty about the exact knee frequency it can be determined from a Bode phase angle plot as the point at which a capacitive response is initiated (i.e. \( \Phi < 0 \)).

**Quasi-Reference Electrode**

For parts of the research it was decided to utilise a quasi-reference electrode (QRE) to conduct three electrode experimentation on a coin cell device in situ. First, the purpose of a true reference electrode (RE) must be discussed. An RE allows control over the working electrode potential relative to that RE. Knowledge of the RE potential is desired in order to build a well-established reference point; in order to do this, an RE exists in a state of thermodynamic equilibrium which arises from being in an independent redox system. Thus, the RE system and the electrode/electrolyte system under investigation are adjacent and interact through a ‘frit’ of extremely low permeability. Furthermore, REs are commonly ideally nonpolarisable (carries no current) implying their potential will not shift during experimentation [261].

A QRE is a device which “almost” behaves like an RE with the primary difference between them being the lack of thermodynamic equilibrium in a QRE. This arises due to a QRE being located within the electrode/electrolyte system of interest and thus does not possess its own static redox system; as such, a QRE must be calibrated prior to usage. This calibration process can be achieved by either referencing a QRE against an RE or by measuring a QRE potential against an internal reference material and its reaction, such as ferrocene, in the same electrolyte used in experimentation. The benefit of a QRE is its simplicity; as they are immersed
directly into the experimental system the impedance effect is small and cross contamination of electrolyte systems is eliminated. Unfortunately, as they do not possess their own electrochemically stable system, there can be a shift of their potential during measurement; this depends on the current density being applied [261]. In this work a silver QRE has been implemented, its characterisation and implementation is described in Section 4.5.3.

**Equipment and Configuration**

For CCCD and CV analysis a Solartron 1480 potentiostat/galvanostat was used, this instrument is capable of testing eight independent devices with a maximum applied voltage range of -3 V and 10 V combined with currents not exceeding 4 A. The voltage measurement range is selected automatically to be either 10 V, 1V or 100 mV at an accuracy of ± 0.1% the measurement range. The current measurement range is selected automatically to be 500 mA, 50 mA, 5 mA, 500 μA or 50 μA at an accuracy of ±0.1% the measurement range. Cells were connected to the analysis instrument by crocodile clips (i.e. clips with teeth).

Coupled with the device above was a Solartron 1255B frequency response analyser (FRA) for EIS analysis; this device is capable of producing sinusoidal waves between 10 μHz and 1 Mhz at a minimum resolution of 5mV with an associated error of 1%. One issue with this device is that measurements can only be conducted on one device at a time; if multiple devices are to be tested they must be queued; devices that are queued can either be done so at constant voltage of user selection or left in an open circuit state. On the surface this may seem to be merely a matter of longer experimentation time but in fact it causes problems, particularly when testing at high voltages. If experimentation is to be conducted at a potential at or just beyond \( V_{EWP} \) then devices must be queued at that potential but by the nature of a queue, some devices will spend longer at this potential than others before being tested, possibly influencing the results. The alternative is to allow cells to be in an open circuit state, which can cause their potential to decrease due to self-discharge. Upon initiating EIS analysis the cell must achieve the desired test voltage but in doing so may require stabilisation time which occurs while the experiment is running, this too can significantly influence results. As such, a compromise has been decided in which cells will be queued at a constant voltage which matches the testing voltage when testing below \( \frac{1}{2} V_{EWP} \) while above this they will be queued at \( \frac{1}{2} V_{EWP} \).

Another issue was found in which the current would not always respond in a smooth manner during CV analysis, as exemplified in Figure 3.9. This issue is believed to be caused by interference between concurrent experimentation on multiple channels, particularly if one
channel is running EIS analysis; this is believed because upon repeating tests with a single operational channel the phenomenon could not be reproduced. As such, experimentation was conducted in a manner which minimised concurrent EIS and CV analysis, but this situation could not always be avoided.

![Cyclic voltammogram exemplifying current response issue. Note that the top and bottom current plateaus are not smooth.](image)

Incorporating a QRE into coin cell experimentation using these instruments was challenging. The optimal solution was to set one channel to drive device experimentation while a second channel was used to sense the voltage between the QRE and either the positive or negative electrode, it is important to note that the second channel did not transfer any current during experimentation. By knowing the overall device voltage and the relative voltage of one electrode it is possible to calculate the relative voltage of the other electrode, this is possible because the voltage across both electrodes must sum to match the overall device voltage.

3.5 Conclusion

The purpose of this chapter was to introduce the reader to the approaches used in achieving the research aims described in Section 2.8; this included experimental configurations, experimental materials and characterisation techniques. The completion of this partially meets PO3 and certainly all of PO4 (see supplement A). The remaining aspects of PO4, such as development and implementation of experimental procedures, will be tackled in Section 4.

Viable experimental configurations were devised (Section 3.2) in which cell containment is achieved through the use of coin cells and, when possible, utilise a QRE (quasi-reference electrode) device to provide additional understanding of the processes under investigation. The
majority of electrodes are to be fabricated by tape casting, except in experiments which explicitly study the effect of spray deposited electrodes.

Experimental materials were selected in order to meet the research aims detailed in Section 2.8. Two varieties of electrolyte were utilised, TEA⁺BF₄⁻ in ACN for EDLC type EC devices and Li⁺PF₆⁻ in EC/DEC for LIC type EC devices; these are both research and industry standard electrolytes thus aiding result comparability. Two varieties of AC were selected: Kynol ACC 507-15 (“Kynol ACC”) and Sigma Aldrich PAC C9157 (“Sigma PAC”). These were found to have mass specific surface areas which may provide the optimal capacitance ratio required for material asymmetric mass balancing. In addition, both materials are suitable for use in LIC type EC devices and Sigma PAC can be used in spray deposition (due to its particulate nature). Other materials selected were TIMCAL Super P®-Li carbon black for use in fabricating graphite electrodes, Elicarb P940 MWCNTs for use in spray deposited electrodes, Silicon Based NXA-513 electrode for use as a novel LIC negative electrode and Alfa Aesar synthetic graphite (product code 40798) for use in a traditional LIC negative electrode.

General components were also defined. For the current collectors, Toyal Carbo (30 μm thickness) and battery grade copper foil were selected; copper foil was used exclusively for the negative electrode in LIC type EC devices. The binder selected for all electrode compositions was Targray PSRB100; this material is stated as suitable for use in both the positive and negative electrodes. The NKK TF40-60 was selected as the separator material; this is believed to be an environmentally friendly alternative to other polymer type separating material. QRE devices are to be fabricated out of 100 μm thick annealed silver from Alfa Aesar (product code 42317); this is a low cost alternative to alternatives such as platinum foil. Coin cells of the CR2032 standard were selected for cell containment, two varieties were selected: standard stainless steel (316) for use in experiments operating below 4 V and aluminium clad positive caps for use in experiments operating above 4 V.

Characterisation required three primary methods, nitrogen sorption analysis, scanning electron microscopy (with EDX) and electrochemical testing. The principles of these methods have been described in detail and followed by in depth consideration of how they can be best applied to the experimental configurations at hand. Of note is the requirement for nitrogen sorption to be conducted at relative pressures (P/P₀) below 10⁻³, particularly for highly microporous materials.
4 PHYSICAL CHARACTERISATION AND FABRICATION TECHNIQUES

4.1 Introduction

Materials have been procured based upon the perceived experimental requirements. This Chapter starts by detailing what these experimental materials are, where they were procured from, and their significant properties. Following on from this, physical characterisation was conducted using SEM, EDX and nitrogen sorption analysis where appropriate. Subsequently the CC (current collector) material Toyal Carbo® was analysed by SEM and EDX analysis and the separator material NKK TF40-60 was analysed by SEM analysis.

Subsequently, a description of the tape casting deposition method is provided, this method was used for the experimentation described in Chapters 5 and 6. As spray deposition was unique to the experimentation described in Chapter 7, it is described in detail there. For both deposition methods, an analysis of the deposition was conducted with conclusions being drawn as to its effectiveness and consistency. The final aspect of this chapter is electrolyte preparation and cell configuration; this includes coin (button) cell fabrication methods and the approach towards incorporating a quasi-reference electrode into such a coin cell.

4.2 Active Material Physical Characterisation

Prior to cell fabrication and testing, material characterisation was conducted for all significant (over 5 wt% electrode mass) active electrode materials; this was done to define material characteristics which may be later associated with electrochemical phenomena. It also allowed for proper planning of the experimentation conducted in Chapters 5 and 6, particularly when considering material loadings for capacitance and capacity balancing.

4.2.1 Active Material Observations by SEM and EDX Analysis

Activated Carbons

Kynol ACC and Sigma PAC were examined using SEM at both low and high magnification. Presented in Figure 4.1 (a) is a single thread from a Kynol ACC yarn; it can be
Capacitive Energy Storage: 
Filling the gap

clearly seen that a single thread is approximately 500 μm, this is in agreement with the specifications. Each yarn comprises a multitude of individual ACF fibres, each about 20 μm in diameter; while in some areas this yarn appears tightly bundled, in others it is not; this may be due to the twisting processes in manufacturing or disruption when selecting individual fibres for analysis. In addition, due to the lack of tight bundling it is expected that upon the application of pressure the yarn thickness decreases.

![SEM image of Kynol ACC at (a) x100 and (b) x20,000 magnification.](image)

Figure 4.1  SEM image of Kynol ACC at (a) x100 and (b) x20,000 magnification.

Closer examination of the ACF surface is shown in Figure 4.1 (b); this image was produced with the hope that both the internal and external surfaces may become apparent. It is possible to see that the axial surface is predominantly smooth with slight surface pitting; there is no indication that this pitting is associated with internal voids. A full suite of SEM images for this material can be found in Appendix 9.

Presented in Figure 4.2 (a) is an SEM image of Sigma PAC; it clearly demonstrates the wide variation in particle size. This variation qualitatively matches (by observation) with the manufacturer’s specification wherein 70-75% of particles are greater than 10 μm in size.

![SEM image of Sigma PAC at (a) x200 and (b) x16,000 magnifications.](image)

Figure 4.2  SEM image of Sigma PAC at (a) x200 and (b) x16,000 magnifications.
Closer examination of an individual particle is provided in Figure 4.2 (b); from this image it is possible to tell that Sigma PAC possesses a rougher surface than individual Kynol ACC fibres at the magnification employed; this is probably due to the milling processes used to produce AC in a power form. Despite this, both materials exhibit similar pitting phenomena at the surface; the size of this pitting appears to be about 0.1 μm and as such might present itself in PSD analysis. A full suite of SEM images for this material can be found in Appendix 9.

**Thomas Swan Elicarb MWCNT**

![SEM image of TS Elicarb MWCNT at nanometric scales.](image)

In analysing TS Elicarb MWCNT there was the desire to clarify their outer and inner diameters along with individual tube length. From SEM, their outer diameter and length is theoretically identifiable; in practice it proved impossible to acquire an accurate estimate of either.

Attempts to clarify the outer diameter are presented in Figure 4.3 (a) and (b); this method of characterisation presents outer diameters greater than 16 nm which does not agree with the TEM images provided in the manufacturer’s specification [229]. Due to the obvious lack of image sharpness in Figure 4.3 (a) and (b) it is believed the supporting TEM evidence provides more reliable information i.e. the tubes have an outer diameter of 10-12 nm. Length clarification proved elusive due to MWCNT tangling, thus making it impossible to distinguish where one begins and another ends.

**NXA 513 Silicon Based Electrode**

As detailed previously, NXA 513 was provided as a prefabricated electrode; presented in Figure 4.4 (a) is an SEM image of this electrode’s surface. It is first noticeable that the particle size distribution appears to be very uniform with sizes being about 10 μm. Additionally, particles
appear to be ‘hairy’. Upon closer inspection, shown in Figure 4.4 (b), it was found that this ‘hairiness’ was attributed to a slit like structure protruding from the particle surface. This was not the only interesting aspect of the electrode material.

![SEM images of Silicon Electrode Nxa-513](image)

**Figure 4.4** SEM image of Silicon Electrode Nxa-513 at (a) x500 magnification and (b) x20,000 magnification.

![SEM image of Silicon Electrode Nxa-513](image)

**Figure 4.5** SEM image of Silicon Electrode Nxa-513 under EDX examination; POIs are elementally quantified in Table 4.1.

Upon further investigation, a site was located which possessed additive materials; this is presented in Figure 4.5, items were marked as points of interest (POI) for elemental quantification through EDX analysis. POIs 1, 2 and 5 appear to represent silicon particle surface while POIs 3 and 4 appear to be MWCNTs, believed to be due to their large diameter, and POI 6 is a spherical particle approximately 400 nm in diameter.
Chapter 4: Physical characterisation and fabrication techniques

<table>
<thead>
<tr>
<th>POI</th>
<th>Carbon %</th>
<th>Silicon %</th>
<th>Fluorine&lt;sup&gt;a&lt;/sup&gt; %</th>
<th>Oxygen %</th>
<th>Copper %</th>
<th>Silver %</th>
<th>Cadmium %</th>
<th>Aluminium %</th>
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<td>1</td>
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<td>58</td>
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<td>7</td>
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<td>71</td>
<td>3</td>
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<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
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<td>24</td>
<td>5</td>
<td>n/a</td>
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</tr>
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<td>2</td>
<td>4</td>
<td>48</td>
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</tr>
</tbody>
</table>

<sup>a</sup> Believed to have been originally confused with iron during experimental analysis.

The results of EDX analysis are presented in Table 4.1 and relate to POIs indicated in Figure 4.5; their corresponding spectra can be found in Appendix 10. First, the lack of fluocho and unexpected presence of iron must be discussed; it is believed that there has been an error in measurement between these two elements. Fluorine was expected because the binder material used in NXA 513 is known to be polyvinylidene fluoride (PVDF), of which due to its chemical nature is known to be one third fluorine [262].

As previously discussed, EDX operates through assessing the x-ray energy emitted as an electron drops to a lower electron shell; in the case of iron, it can be identified by x-ray energies of 0.705 and 6.398 keV [263] which associate with electron transmissions to L and K shells, respectively. Fluorine can be identified by x-rays with 0.677 keV of energy, which is associated with electron transmission to the K shell. It is believed that the close energy association, specifically between L shell transmission of iron and K shell transmission of fluorine, between these materials is the source of confusion when conducting instrumental analysis. This exact issue has been recognised by the instrument manufacturer [264].

In POIs 1, 2 and 5 significant quantities of carbon and silicon were found; part of this carbon can be associated with the PVDF binder, presumably the same quantity as fluorine since they present equal quantities in the polymer chain, but the remainder (~20%) must in some form be associated with the particles surface chemistry.

From observation, POIs 3 and 4 appear to have the forms of MWCNTs (Figure 4.5), this is supported by the high carbon content found through EDX analysis. Significant quantities of
silicon were also found at these points but they are believed to be due to the surface penetrating nature of EDX and thin carbon nanotube walls; it may be that silicon behind the MWCNTs is being detected. Notably, these points do not possess any oxygen; this indicates that oxygen is associated with the silicon particle surface chemistry. As such, the additional carbon and oxygen content may be associated with a thin surface coating of graphitic carbon, possibly functionalised with oxygen, or the presence of organosilicon compounds, but this matter is not certain.

The final additive found is located in POI 6; from EDX it appears that this is a silver nanoparticle. Trace elements of cadmium and aluminium were also found at POI 6. Further information was requested on this matter, it was found that silver was used in the Si preparation procedure and the particle found is in fact unintended residue. Despite this, the presence of silver residue along with MWCNTs may possibly provide improved electrical conductivity between particles. The quantity of PVDF binder in this electrode is believed to be 10%; this is based upon the average fluorine content of all points being about 3.3%.

**Alfa Aesar Graphite Powder**

Graphite powder was observed with the intent of obtaining a better idea as to its particle size distribution; these observations are presented in Figure 4.6 (a) and (b). The manufacturer specification states that particles should be less than 44 μm (~325 Mesh) [265]; qualitatively, the images appear to match this specification with particles apparently being about 20 μm along their major diameter. Some large particles were found which approached the upper limit, as shown in Figure 4.6 (b), but these were uncommon.

![SEM image of Alfa Aesar Graphite 325 Mesh](image)

*Figure 4.6  SEM image of Alfa Aesar Graphite 325 Mesh at (a) x500 magnification and (b) x950 magnification.*
4.2.2 Isothermal Response of Nitrogen Sorption

Kynol ACC and Sigma PAC, in their as acquired forms, underwent nitrogen sorption tests using a BELSORP Max; their respective isothermal response is shown in Figure 4.7. It can be seen that for both materials, adsorption starts at a $P/P_0$ value of $1 \times 10^{-6}$ with the rapid adsorption of about 5% total adsorbed quantity; between $P/P_0$ of $3 \times 10^{-6}$ and $1 \times 10^{-1}$ adsorption exponentially decreases. Shown in the inset of Figure 4.7 is the full range response on a linear scale, from this it can be seen that Kynol ACC possesses an almost ideal type I isotherm, indicating a strongly microporous material. Sigma PAC possesses aspects of both a type I and, partially, type II isotherms; this indicates a strongly microporous material with some mesoporosity.

TS Elicarb MWCNT, NXA 513 and AA graphite underwent nitrogen sorption tests using a BELSORP Mini; their respective isothermal response is shown in Figure 4.8. It can be seen that TS Elicarb MWCNT exhibits a type II isotherm, associated with mesoporous materials, while both NXA 513 and AA graphite exhibit almost negligible sorption responses (i.e. low surface areas). NXA 513 does present a sudden increase in adsorption rate as it approaches a $P/P_0$ of unity but this is not associated with any known isotherm type; this may be related to additive materials or surface properties and as such this matter will be reconsidered after further characterisation.

![Figure 4.7 Nitrogen adsorption (Ads) and desorption (Des) isotherms with a logarithmic $P/P_0$ scale. Inset: full isotherm profiles with linear scale. Isotherms were produced by a BELSORP Max.](image-url)
4.2.3 Specific Surface Area from Isotherm Analysis

It was known prior to purchase that Kynol ACC and Sigma PAC would present an SSA value of approximately 1500 m² g⁻¹ and 1000 m² g⁻¹, respectively; the former was calculated by iodine adsorption (by Kynol Europa GmbH) while the latter was calculated by BET analysis of a nitrogen sorption method. It can be seen from Table 4.2 that the GCMC value for Kynol ACC is in good agreement with the Iodine adsorption measurement while the BET value for Sigma PAC agrees very well with the manufacturer’s specification.

With regard to porous structure components, Kynol ACC possesses approximately twice the microporous SSA than that of Sigma PAC; this implies that Kynol ACC has undergone a stronger activation process than Sigma PAC. Additionally, if Equation (2.7) holds to be true, the capacitance of Kynol ACC should be approximately twice that of Sigma PAC. When considering mesoporous structure, the findings are reversed; Sigma PAC possesses approximately twice the SSA than Kynol ACC. This indicates that Sigma PAC may present improved ionic transportation kinetics with increased power capability as a consequence.
Table 4.2  Specific surface area (SSA) values acquired from nitrogen adsorption isotherm analysis by BET, BJH and GCMC methods. Values are presented as either total SSA values or pore related SSA values.

<table>
<thead>
<tr>
<th>Method</th>
<th>BET</th>
<th>GCMC</th>
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<td>SSA</td>
<td>SSA</td>
</tr>
<tr>
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<td>Total</td>
<td>Total</td>
<td>Micropore</td>
<td>Mesopore</td>
</tr>
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<td>1710</td>
<td>1560</td>
<td>1540</td>
<td>20</td>
</tr>
<tr>
<td>Sigma PAC C9157</td>
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<td>843</td>
<td>801</td>
<td>42</td>
</tr>
<tr>
<td>TS Elicarb MWCNT</td>
<td>196</td>
<td>198</td>
<td>0</td>
<td>198</td>
</tr>
<tr>
<td>NXA 513</td>
<td>6.41</td>
<td>4.55</td>
<td>0</td>
<td>4.55</td>
</tr>
<tr>
<td>AA Graphite Powder</td>
<td>4.34</td>
<td>2.32</td>
<td>0</td>
<td>2.32</td>
</tr>
</tbody>
</table>

a Isotherm from BELSORP Max
b Isotherm from BELSORP Mini
c GCMC analysis assumes cylindrical pore

TS Elicarb MWCNTs presented almost identical SSA values under BET and GCMC analysis, using the cylindrical pore assumption. The precise value was less than stated in the specification by between 50 to 100 m$^2$ g$^{-1}$. The entirety of the SSA in this case is mesoporous, partially validating that BET is a suitable SSA analysis method for mesoporous materials.

Both NXA 513 and AA graphite powder possess very small SSA values; BET analysis appears to yield a higher SSA than GCMC analysis but the difference is not significant compared to prior materials. GCMC analysis has been deemed appropriate for AA graphite due to its carbonaceous nature. NXA 513 has been shown to possess carbonaceous materials but is still predominantly a silicon-based material; as such, the appropriate analysis method is unclear. There is confusion as to whether the mesoporous surface area could purely represent the MWCNT additives or if the slit-like surface consists of mesoporous slits, upon analysing the results of PSD analysis this matter became clearer.

4.2.4 Specific pore volumes from Isotherm Analysis

Kynol ACC, Sigma PAC and TS Elicarb MWCNTs all possess significant SPV values; as previously stated, SPV is not directly related to capacitance and as such the exact influence of
SPV may be subtler. Again, there is a difference between BET and GCMC values; interestingly, this difference appears to be proportional to the quantity of mesoporous volume with materials which possess less mesoporous content achieving a closer match between BET and GCMC values.

Despite Sigma PAC having only ~2 times the mesoporous SSA of Kynol ACC it possesses a mesoporous volume ~8 times greater than Kynol ACC. A similar matter is also presented between NXA 513 and AA graphite powder; while NXA 513 possesses nearly double the mesoporous SSA of AA graphite their SPV values are different by a factor of 8. While this may suggest a cubed proportionality between micro- and mesoporous SPV values, it does not account for the precise size, or shape, of mesopores which will have a great influence on the mesoporous SPV exhibited.

Table 4.3  Specific pore volume (SPV) values acquired from nitrogen adsorption isotherm analysis by BET, BJH and GCMC methods. Values are presented as either total SPV values or pore related SPV values. Porous particle density (PPD) is interpreted taking the particle density of graphite to be 2.2 g cm$^{-3}$.

<table>
<thead>
<tr>
<th>Method</th>
<th>Analysis Type</th>
<th>Units cm$^3$ g$^{-1}$</th>
<th>Units cm$^3$ g$^{-1}$</th>
<th>Units cm$^3$ g$^{-1}$</th>
<th>Units cm$^3$ g$^{-1}$</th>
<th>Units cm$^3$ g$^{-1}$</th>
<th>Units g cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kynol ACC 507-15$^a$</td>
<td>BET</td>
<td>0.714</td>
<td>0.687</td>
<td>0.666</td>
<td>0.0210</td>
<td>0.876</td>
<td></td>
</tr>
<tr>
<td>Sigma PAC C9157$^a$</td>
<td>GC$^c$M$^c$C$^c$</td>
<td>0.537</td>
<td>0.498</td>
<td>0.340</td>
<td>0.158</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>TS Elitecarb MWCNT$^b$</td>
<td>SPV Total</td>
<td>0.989</td>
<td>0.847$^c$</td>
<td>0$^c$</td>
<td>0.847$^c$</td>
<td>0.768</td>
<td></td>
</tr>
<tr>
<td>NXA 513$^b$</td>
<td>SPV Micropore</td>
<td>0.0948</td>
<td>0.0680</td>
<td>0</td>
<td>0.0680</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>AA Graphite Powder$^b$</td>
<td>SPV Mesopore</td>
<td>0.0109</td>
<td>0.00854</td>
<td>0</td>
<td>0.00854</td>
<td>2.16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PPD Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Isotherm from Belsorp Max
$^b$ Isotherm from Belsorp Mini
$^c$ GCMC analysis assumes cylindrical pore

PPD (porous particle density) has been calculated for all materials except NXA 513, which is known to be predominantly silicon based. In the case of MWCNT is has been assumed that the multiple curved carbon layers which comprise their walls are comparable in density to that of planar graphitic carbon layers. As previously stated, these values can prove useful when interpreting the volumetric capacitance of electrode materials.
4.2.5 Pore Size Distribution from Isotherm Analysis

A PSD focused on the microporous region for both Kynol ACC and Sigma PAC is presented in Figure 4.9; included in this figure are the bare and ACN solvated TEA⁺ and BF₄⁻ ion diameters found in Section 2.2.3. Note that the incremental pore volume is the volume of free space associated with the marked pore width.

Firstly, both materials present PSD responses (calculated with GCMC analysis and pore-slit assumptions) which, while different in magnitude, appear to represent similar internal structures; this is despite possessing significant differences in the chemistry of their precursor materials, their manufacturing processes and external morphology. The bimodal PSD suggests the internal porous structure of AC has two primary dimensions, one ~0.7 nm in width and another ~1.35 nm in width; these values are in agreement with [227]. Unfortunately, it was not possible to assess whether these pore dimensions are associated, i.e. comprising the sides of a rectangular shaped pore, or independent; as it is generally considered that AC is amorphous, it is believed the latter is more likely. With respect to magnitude, at both peaks Kynol ACC possesses twice as much specific porous volume as Sigma PAC; this in agreement with the microporous SSA and SPV values they present.

![Figure 4.9](image_url)

Figure 4.9 Microporous PSD of Kynol ACC 507-15 and Sigma PAC C9157 from nitrogen adsorption isotherm on a BELSORP Max with GCMC analysis and slit assumptions. (a) Bare BF₄⁻ ion diameter, (b) bare TEA⁺ ion diameter, (c) ACN solvated BF₄⁻ ion diameter, (d) ACN solvated TEA⁺ ion diameter. (left) Differential pore volume, (right) Incremental pore volume.

It is helpful to plot (Figure 4.9) the bare and ACN solvated TEA⁺ and BF₄⁻ ion diameters; such a clear overlay was not found in any of the reviewed literature despite how the sizes of these common ions associate with the PSD of AC materials being of obvious interest. This has
been done in both differential and incremental formats as both forms are commonly used in literature.

Recall from Section 2.4.2 that the EDLC capacitance is related to pore size. Specifically, as the pore size decreases below the solvated ion diameter, mass specific capacitance increases while if the pore size decreases to approximately the bare ion diameter, mass specific capacitance will decrease. It can be clearly seen in Figure 4.9 that the bare BF₄⁻ ion diameter (a) lies below the pore width of both peaks; this implies that both peaks are accessible to BF₄⁻ ions thus, more surface area is accessible for an EDLC to form. As a consequence, both materials may present significant mass specific capacitance values when used as positive electrodes, as per Equation (2.7). It can also be seen that the bare TEA⁺ ion diameter (b) lies almost on top of the first peak at ~0.7 nm. This is the same value at which the mass specific capacitance of TEA⁺ was said to start decreasing in the work of Chmiola et al. [160]. As this matter is of great interest a preliminary experiment will be conducted in order to assess if Kynol ACC presents a higher capacitance than Sigma PAC.

![Figure 4.10 Mesoporous PSD of Kynol ACC 507-15 and Sigma PAC C9157 from nitrogen adsorption isotherm on a BELSORP Max with GCMC analysis.](image)

A PSD focused on the mesoporous region for both Kynol ACC and Sigma PAC is presented in Figure 4.10; note that the y-axis extends to only \(1/10\) of that in Figure 4.9. From this plot it is obvious that Kynol ACC does not possess a significant amount of mesoporosity, which is in agreement with mesoporous SSA and SPV values. Sigma PAC on the other hand does possess an amount of mesoporosity, the most significant quantity is 10 nm in width; aside
from this peak there appears to be a broad range of mesopores extending throughout the material. This will almost certainly aid Sigma PACs power capability as ions may be easily transported through mesopores to the high surface area micropores.

TS Elicarb MWCNT, NXA 513 and AA graphite all presented purely mesoporous structures, their corresponding PSDs are presented in Figure 4.11. TS Elicarb MWCNTs present a peak pore diameter of 7–10 nm; this fits well with the manufacturer specification that they possess an outer diameter of 10-12 nm. Assuming the distance between tube walls is the same as that between planar graphitic layers (0.335 nm [266]) implies that the tube wall is 6 to 9 layers thick.

![Mesoporous PSD of TS Elicarb MWCNT, NXA 513 and AA Graphite from nitrogen adsorption isotherm on a BELSORP Mini with GCMC analysis; the assumed porous structure is stated in the legend.](image)

NXA 513 appears to possess a mesoporous structure focused around a slit width of 30 nm; due to the presence of CNTs, analysis was also conducted using a cylindrical pore assumption but yielded no indication of their presence. As such, it is believed this slit like porous structure is associated with the slit like surface structure found in Figure 4.4 (b) and is probably carbonaceous in nature as per the findings of EDX analysis. This finding may have significant implications upon the electrochemical results of this potential LIC electrode material.

Finally, AA Graphite features a low amount of mesoporous structure with a well-defined slit width of ~8 nm. There is uncertainty as to where this mesoporosity arises; from SEM (Figure 4.6) it is possible to see the surface structure has overhanging ledges, the root of these ledges
could form a mesoporous structure prior to termination. Another possible source could be interparticulate contact planes which form a sort of pseudo-mesoporosity. It is also entirely reasonable that this mesoporosity arises as an internal structure and is associated with an unknown manufacturing process; this seems the most likely cause due to the well-defined pores structure.

4.3 Toyal Carbo® Observations by SEM and EDX Analysis

Toyal Carbo® was observed with the intent of understanding the Al₄C₃ nanowhisker binding mechanism used to adhere carbon particles to the sheet aluminium surface. Firstly, confirmation of the electrode thickness was desired; shown in Figure 4.12 (a) is a cross-sectional view of the Toyal Carbo® procured, it is clear to see that it does indeed possess a 30 μm thickness as stated in the manufacturer specification. Shown in Figure 2.12 (b) is a planar view observing the surface coating of Toyal Carbo®, it clearly shows the particulated surface but what is interesting is that these particles are not entirely disassociated, some apparently share common walls. This is not expected as a product report of Toyal Carbo® shows in a schematic form that the Al₄C₃ nanowhiskers do not protrude above the carbon surface [181] and it seems unlikely that carbon particles could be sintered (compacting and forming a solid mass of material by heat or pressure but without liquefaction) in this manner due to its extremely high melting point which far exceeds that of aluminium [267]. As such, Figure 2.12 (b) could indeed be showing the tips of Al₄C₃ nanowhiskers.

![Figure 4.12 Toyal Carbo® (a) cross-sectional SEM image at x1,500 magnification and (b) planar SEM image at x10,000 magnification.](image)

Upon closer inspection investigation, it was noticed that certain particles differ from others, they appear to possess a ‘rough’ surface texture. Such particles are presented in Figure 4.5 (a),
particles with apparently ‘rough’ surface texture are shown in POIs (points of interest) 1, 2 and 3 while standard ‘smooth’ particles are indicated by POIs 4, 5 and 6. A magnification of POI 1 is shown in Figure 4.5 (b), from this the apparently ‘rough’ surface texture is clearly visible. Shown in Table 4.4 are the results of EDX analysis which was conducted upon these POIs.

![Planar SEM image of Toyal Carbo® under EDX examination; POIs are elementally quantified in Table 4.4. (b) SEM image of possible Toyal Carbo® whisker tip at x80,000 magnification.](image)

**Figure 4.13** (a) Planar SEM image of Toyal Carbo® under EDX examination; POIs are elementally quantified in Table 4.4. (b) SEM image of possible Toyal Carbo® whisker tip at x80,000 magnification.

**Table 4.4** Normalised weight % of constituent elements found through EDX analysis of Toyal Carbo®, POIs as indicated in Figure 4.13.

<table>
<thead>
<tr>
<th>POI</th>
<th>Carbon</th>
<th>Oxygen</th>
<th>Aluminium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>1</td>
<td>33.8</td>
<td>2.4</td>
<td>63.8</td>
</tr>
<tr>
<td>2</td>
<td>30.6</td>
<td>2.2</td>
<td>67.2</td>
</tr>
<tr>
<td>3</td>
<td>49.5</td>
<td>1.5</td>
<td>49.0</td>
</tr>
<tr>
<td>4</td>
<td>52.0</td>
<td>1.1</td>
<td>46.9</td>
</tr>
<tr>
<td>5</td>
<td>43.6</td>
<td>0.9</td>
<td>55.4</td>
</tr>
<tr>
<td>6</td>
<td>53.7</td>
<td>0.8</td>
<td>45.5</td>
</tr>
</tbody>
</table>

The results of EDX analysis (Table 4.4) are interesting. They show that all POIs possess significant quantities of both carbon and aluminium alongside trace amounts of oxygen. This indicates that the outermost surface of Toyal Carbo® consists of Al₃C₃ nanowhiskers. POIs 1, 2 and 3 were selected for their apparently ‘rough’ surface textures; elemental analysis shows that POIs 1 and 2 do indeed possess differing quantities of elements (higher aluminium content, lower carbon content) than those shown in POIs 4, 5 and 6. Despite its apparently visual difference, POI 3 possesses an elemental configuration closer to that of POIs 4, 5 and 6; upon
closer inspection of POI 3 it was in fact noticed that a secondary particle resides on its surface which could have influenced the results. The oxygen content appears to loosely associate with the aluminium content and apparent surface roughness, this indicates that this is in fact an oxide layer which has formed on the AlC₃ nanowhiskers.

In conclusion, it has been deduced that the surface particles of Toyal Carbo® which possess apparently ‘rough’ surface textures are little more than manufacturing defects formed during the growth process. While this finding is not of particular interest to this work, the fact that the surface content of Toyal Carbo® possesses significant aluminium content may be.

4.4 Tape Casting and Disk Cutting of Electrode Coatings

Custom electrodes were built by tape casting which was followed by electrode disk cutting. The primary electrode coating composition used in the experiments was 95 mass percent (m%) Sigma PAC and 5 m% SBR/CMC binder. For this electrode material composition, a single large quantity (300 ml) of slurry was produced. Only a small number of graphite electrodes were required for research. As such, a small quantity (20 ml) of graphite based slurry was produced, described in section 4.4.2.

4.4.1 Equipment and Configuration

Weighing materials for small quantity slurries was conducted with a Denver Instrument SI 234 with a resolution of 0.1 mg; this device could not measure mass over 230 g and as such, for weighing large quantity slurries a Fisher Scientific Xe-7000, with a resolution of 10 mg, was used. Mixing of dry powders was conducted with a Stuart digital tube roller SRT9D while mixing of wet slurry was conducted for small quantity slurries with a Thermo Scientific VARIOMAG® Poly 15 magnetic stirrer; for large quantities of wet slurry a Heidolph RZR 2021 overhead mixer was used. Ultrasonic mixing was conducted with a Fisherbrand FB11002 ultrasonic heated bath and a Soniprep 150 with a 19 mm probe. Viscosity measurement was conducted with a Lamy Black One, unfortunately only a ASTM disk No. 4 was available and as such, this device could only operate with large (> 200 ml) slurry quantities.

Tape casting was conducted using a Sheen SH1133N automatic film applicator; this device features a vacuum bed for securing electrode substrates during the coating process and has film casting speeds ranging from 50 to 500 mm s⁻¹. In combination with this, a micrometer adjustable doctor blade was used (product code EQ-Se-KTQ-100 from MTI Corporation); it features a
100 mm casting width while the blade height, i.e. wet film thickness, can be set from 0 to 3,500 μm with an accuracy of 10 μm. A Heraeus Instruments Vactherm VT6025 oven was used for drying wet coatings.

4.4.2 Concentrated Slurry Preparation for Tape Casting

**Graphite Based Slurry**

A small quantity (~20 ml) of graphite based slurry was produced for LIC cells. This slurry solution was inspired by the recipe recommended by MTI corporation for producing water-based graphite slurry for use as the negative electrode in battery research [268]. The slurry consisted of 92.5 m% graphite, 5 m% SBR/CMC binder, 2.5 m% Super P<sup>®</sup>-Li conductive additive and the total mass of de-ionised water (DIW) added was ~150% that of the graphite mass. It should be noted the DIW content came from both the pre-diluted PSBR.100 binder solution (which contains 85 m% DIW) and DIW provided on site.

The slurry contained 7 g of graphite, 0.175 g of Super P<sup>®</sup>-Li, 2.34 g of PSBR.100 (consisting of 0.35 g SBR/CMC and 1.99 g of DIW) and 10 g of additional DIW. Firstly, graphite and Super P<sup>®</sup>-Li dry powders were added to a 100 ml plastic sample bottle with a screw cap. In order to produce a homogenous powder mixture this bottle was vigorously shaken by hand then placed on the tube roller, which ran at 10 rpm for 24 hours. Meanwhile, a binder solution of PSBR.100 and additional DIW was prepared. This solution was magnetically stirred for 30 minutes at 200 rpm followed by 30 minutes ultrasonic mixing (in an ultrasonic bath) at room temperature.

Upon completion of the above, the dry powder mixture was split into 4 equal batches while the binder solution was set on the magnetic stirrer at 300 rpm. Dry powder batches were added in steps using a weighing powder scoop. Each step was spaced 30 minutes apart, this allowed time for a homogenous slurry to form. One issue found was dry powder often settled on the surface of the solution and would not disperse, probably because of its low density. This surface powder could be mixed into the slurry with a glass stirring rod but due to the small quantity of slurry this was not desirable as it proved impossible to discern how much powder or solution was removed upon extracting the rod from the slurry. The optimal solution, which involved no material loss, was found to be rapidly fluctuations of the magnetic stirrer between 300 and 600 rpm about 15 minutes into each step; this appeared to distort the surface and allow surface powder to better disperse into the solution. Ultimately, the full slurry solution was
ultrasonically mixed (in an ultrasonic bath) for 30 minutes (and possessed a viscosity similar to runny honey), after which tape casting was conducted.

**PAC Based Slurry**

A large quantity (~300 ml) of Sigma PAC based slurry was produced. The slurry consisted of 95 m% Sigma PAC, 5 m% SBR/CMC binder and the total mass of DIW added was 160% that of the Sigma PAC mass.

The slurry contained 142.5 g of Sigma PAC, 50 g of PSBR.100 (consisting of 7.5 g SBR/CMC and 42.5 g of DIW) and 180 g of additional DIW. A binder solution of PSBR.100 and additional DIW was prepared, it should be noted that only 160 g of additional DIW was added at this point for reasons clarified later. This solution was magnetically stirred for 30 minutes at 200 rpm followed by 30 minutes ultrasonic mixing (in an ultrasonic bath) at room temperature. The dry powder to be added was a single component material and as such, tube rolling was not done.

Subsequently, the dry PAC powder was split into 4 equal batches while the binder solution was located underneath an overhead mixer. Dry powder batches were added in steps using a spatula. Each step was spaced 1 hour apart and included overhead mixing at 200 rpm for 40 minutes and ultrasonic mixing (by ultrasonic probe) at high intensity for 20 minutes. Due to the use of an overhead mixer the issue of powder forming on the slurry surface was mitigated while negligible quantities (in comparison to the cumulative quantity) of sample were lost during the transition between mixing devices.

Upon the addition of all material, it was necessary to test the viscosity; this was done using a viscometer with an ASTM disk No. 4 attachment. It has been suggested that a viscosity of ~50 poise (P) is ideal for tape casting [268]. The initial addition of 160 g DIW was due to the uncertainty as to the most appropriate viscosity value; it was deemed a simpler approach to require adding more DIW than to require adding more carbon/binder content. The initial viscosity measurement gave a value of 195 P, almost 4 times higher than the desired viscosity. Further DIW was added in increments of 5 g interspaced with further overhead mixing at 400 rpm for 10 minutes, this was done until 20 g of DIW had been added (bringing the total additional DIW content to 180 g) which provided a viscosity of 54 P, after which tape casting was conducted.
4.4.3 Tape Casting Deposition

Upon the completion of slurry preparation, tape casting was conducted. The desired foil CC (current collector) was cut to 20 cm in length and placed centrally on the automatic film applicator. To operate the vacuum bed effectively, suction ports outside of the CC area were covered with masking tape. The vacuum bed was activated and tissue paper was used to wipe down the CC surface and remove any trapped air pockets.

The doctor blade was adjusted to the desired operating height; this height directly influenced the wet film thickness. The doctor blade was located centrally on the CC and flush against the push bar of the automatic film applicator. The desired slurry material was extracted from mixing beakers using a 10 ml syringe; the amount extracted varied between 2 to 4 ml and influenced the length of coating upon CC. The material was then ejected from the syringe along the doctor blade base and the film applicator was rapidly activated with a coating speed of 100 mm s⁻¹.

Upon completion of the coating process, coated CC samples were carefully extracted from the automatic film applicator and placed into an oven at 80 °C for 30 minutes; care was taken to ensure the samples were kept level to minimise coating thickness variations. It should be noted that this drying process aimed to stabilise the electrode microstructure rather than to achieve total desiccation, a further drying process was conducted prior to cell containment for this purpose. Upon drying it was often found that some areas of the samples would be partially smeared (i.e. improperly coated); this could happen if excessively large particles blocked the coating gap, resulting in a build-up of material which was not properly deposited.

4.4.4 Electrode Disk Cutting

As the intended cell containment method was coin (button) cells, it was necessary to cut electrode and separator materials into circular disks. A compact precision disk cutter (product code MSK-T-07 from MTI Corporation), with a 15 mm diameter cutting die, was used for electrode cutting for coin cells. The thickness of electrode cuttings was measured using a Mitutoyo IP65 with a resolution of 1 μm. Cuttings were taken from close to the point at which coating was initiated while areas which showed smearing were avoided.

Once cut, individual electrodes were weighed to a resolution of 0.1 mg while their thickness was taken as the average of three points of measurement. Using knowledge of the CC
material it was thus possible to calculate the active material thickness (total thickness minus CC thickness) and the active material areal density (total areal density minus CC areal density).

4.4.5 Tape Casting Method Analysis

The analysis of electrodes produced by tape casting is presented in this section. A comparison between doctor blade gap thickness and average coating thickness for electrodes made from 95 m% Sigma PAC and 5 m% SBR/CMC binder is shown in Figure 4.14. It should be noted that these values do not exhaustively represent all samples produced, unfortunately a data file was corrupted during analysis and as such additional sample information was lost. It can be clearly seen that samples produced with the same doctor blade gap thickness can show variability in final average coating thickness; this could be due to variations in sample cutting location (i.e. samples taken from the coated edges or in areas of non-obvious smearing) or due to human error in recording the set doctor blade gap thickness. The numerical range of thickness measurements (three for each sample) was calculated for each sample; the maximum range was found to be 34 μm (at high areal density), the minimum range was 1 μm (at low areal density) and the average range was 9 μm. These values represent variations in coating thickness measurement across a 1.767 cm² sample of approximately ±5% and as such, coating thickness measurement is not deemed the source of variation.

![Figure 4.14 Scatter plot comparing the doctor blade gap thickness and average coating thickness of electrodes fabricated by tape casting and dried at 80 °C. The active material consists of Sigma PAC (95 m%) and SBR/CMC binder (5 m%) while the current collector is Toyal Carbo®.](image-url)
The correlation between areal density and average coating thickness for electrodes made from 95 m% Sigma PAC and 5 m% SBR/CMC binder is shown in Figure 4.15; the values presented associate with the sample values presented in Figure 4.14. A linear fit has been identified, it possesses good agreement (R² error = 0.921) and shows an x-axis intercept (i.e. maximum particle size) of ~90 μm; this agrees well with the known particle size distribution, of which 10-15% is stated to be greater than 74 μm [228]. At areal density values below 2.5 mg cm⁻² it appears the average coating thickness begins to decrease; this is believed to be due to the inability of particles at the upper end of the particle size distribution to pass beneath the doctor blade gap, resulting in only particles below the gap size being deposited.

The cutting and measurement process described above was also conducted for graphite based coatings but the quantity of coatings was limited and as such no discernible information about coating processes (i.e. a relationship between coating thickness and areal density) could be inferred.

Shown in Figure 4.16 are SEM images of electrode (95 m% Sigma PAC and 5 m% SBR/CMC binder) coating surface at different electrode thicknesses: Figure 4.16 (a), (b) and (c) refer to thicknesses of 150 μm, 250 μm and 310 μm, respectively. It should be noted that the electrodes featured in Figure 4.16 (a) and (b) were fabricated with almost matching doctor blade
gap thicknesses i.e. 150 μm gap thickness produced a 150 μm electrode coating and 220 μm gap thickness produced a 200 μm electrode coating. Figure 4.16 (c) did not exhibit a close match between doctor blade gap thickness, it was set at 400 μm but produced a 310 μm coating. Coating thicknesses of 150 μm and 250 μm possess a mostly uniform surface, but there are noticeable small scale cracks. In contrast, the surface of a 310 μm thick electrode coating possesses small scale cracks and large scale voids which are approximately circular in shape.

![Figure 4.16 SEM images of electrodes fabricated by tape casting and dried at 80 °C with thicknesses of (a) 150 μm, (b) 250 μm and (c) 310 μm. Image (d) is a close up of the area identified in (c), it is a composite image produced by overlaying two separate SEM images captured with differing brightness and contrast settings. The active material consists of Sigma PAC (95 m%) and SBR/CMC binder (5 m%) while the current collector is Toyal Carbo®.](image)

A close-up inspection of a void found on the surface of a 310 μm thick electrode coating is presented in Figure 4.16 (d). It appears that the voids are in fact penetrating pores with diameters between 50 to 100 μm; judging by the particle sizes/quantities along the pore wall in
Figure 4.16 (d) the penetration depth appears to be at least 100 µm. The source of these voids has not been precisely determined but it is considered that these are vents for the release of excessive moisture during drying. This is indicated by the significant decrease of coating thickness from the set doctor blade gap thickness, indicating that the water content of the slurry deposited was higher than normal. Counter to this argument is that the viscosity of the deposited material would have been lower than normal, this phenomenon was not recalled but it was not necessarily obvious due to slurry being transferred by syringe to the doctor blade.

Further, the drying temperature of 80 °C may also have contributed to the production of vent-like voids; this temperature could have caused the rapid heating of water content near the CC base. In thinner electrodes, this may not be a problem as the moisture has a short distance to travel between CC and coating surface thus drying uniformly, but in thicker electrodes this distance is significantly increased, possibly resulting in the build-up of pressurised water vapour (steam). At a certain pressure this steam could erupt from deeper down in the electrode coating and thus produce the vent-like voids.

From Figure 4.14 and 4.13 it can be seen that tape casting is an adequate method for active material deposition. It can produce coatings with a reasonable consistency, particularly at thicknesses between 100 to 250 µm. While there is some degree of variability between samples of this thickness, this variability was accounted for in electrochemical experimentation by appropriately selecting compatible electrodes to fabricate EC cells with. Coatings with thicknesses approaching 310 µm appear to possess defects in the form of vents; as such, electrodes which were thought to exhibit this defect were not included in experimentation.

4.5 Electrolyte Preparation and Cell Containment

As discussed in section 2.6.4, a method of cell containment is required to ensure an appropriate environment exists for cell operation. For the research entailed it has been elected to utilise a two-electrode setup, thus allowing results to be related to commercially manufactured devices. This section details the electrolyte preparation procedure, coin (‘button’) cell containment method, and the incorporation of a novel quasi-reference electrode into such a containment method.
4.5.1 Equipment and Configuration

It has been previously noted that the electrolyte materials intended for use are highly sensitive to moisture. As such, electrolyte preparation and cell containment was conducted in an argon filled mBraun UNIlab glovebox with H₂O < 1 ppm and O₂ < 1 ppm, the main chamber was operated at an atmospheric pressure of ~1.2 bar. It should be noted that this pressure can vary due to the positioning and operation of the gloves; pressing in on the gloves increased the pressure while drawing the gloves out (which can occur when using materials stored near the front of the chamber) would decrease the pressure. Material transfer to and from this inert environment was conducted through an antechamber which was pumped down to a vacuum and re-pressurised with argon three times prior to material entering the main chamber.

Prior to material entering the glovebox it was necessary to thoroughly desiccate (dry) them, this is particularly true for materials which comprise core cell components such as electrode coatings and separation material. For this purpose, a vacuum oven was used (product code EQ-DZF-6050-UL from MTI Corporation). All drying was conducted at 100 °C under high vacuum for a minimum of 12 hours.

Inside the main chamber of the glove box was a Mettler College 150 analytical balance; it has an accuracy of 0.1 mg but is sensitive to changes in pressure. As such, care was taken to ensure zeroing (tare-ing) of the balance was conducted only upon imminent measurement and could be followed up by minor glove movement. Inside the main glovebox chamber was a hydraulic crimper fitted with a die for closing CR2032 coin cell cases (model MSK-110 from MTI Corporation). All cells were laid up in one of the two methods shown in Figure 4.17 and crimped at 70 kg cm⁻²; it should be noted this does not translate to a pressure of 70 kg cm⁻² being placed upon the electrode material as this pressure is also related to the thickness of the electrode material used (an empty case can still be sealed).

4.5.2 Electrolyte Preparation

All electrolyte materials were transferred into the glovebox upon arrival. The 100 ml of 1.0M LiPF₆ EC/DEC (ethylene carbonate/diethyl carbonate) came premixed from the supplier and as such no further preparation was required for this electrolyte.

To prepare a solution of 1.5 M TEA⁺BF₄⁻ in ACN it was first necessary to calculate the appropriate quantities of material required, this was done based upon the knowledge that TEA⁺BF₄⁻ has a molecular mass of 217.06 g mol⁻¹ and ACN has a density of 0.786 g ml⁻¹. It was
decided that production of this electrolyte would be done in 10 ml batches; as such, each batch contained 3.26 g of TEA⁺BF₄⁻ and 7.86 g (10 ml) ACN. These were measured out and added together into a 20 ml vial and vigorously shaken until all TEA⁺BF₄⁻ was dissolved.

4.5.3 Coin (‘Button’) Cell Fabrication

Fabrication Methods

Electrode disks and separation material were cut as per Section 4.4.4, it should be noted that the electrodes were cut to disks 15 mm in diameter while the separation material was cut to disks 19 mm. This slightly larger diameter for the separation material greatly reduced the chance of electrode disks directly contacting one another, thus preventing a short circuit from forming. All materials used in cell fabrication were dried in a vacuum oven between 100 and 120 °C under high vacuum for a minimum of 12 hours and transferred to the glovebox main chamber.

![Coin cell layup schematics showing (a) a coin cell layup using a single spacer and (b) a coin cell layup using two spacers.](image)

The CR2032 coin cell possesses four core components, a negative cap (with O-ring pre-attached), a positive base, a spring and a spacer. As detailed previously in section 3.3.3, there are two varieties of positive base, one which consists purely of SS (stainless steel) and another in which SS is coated with aluminium to maintain electrochemical inertness at voltages > 4 V. In total, 200 sets of pure SS casings and 100 sets of SS coated with aluminium were purchased, each set included one of each component listed above. One issue found during initial fabrication runs (using Sigma PAC coated CCs) was that the use of a single spacer (as per Figure 4.17 (a)) did not provide the necessary thickness to hold the electrodes in place; cells would not function and if shaken the internals could be heard to rattle. As such, two spacers were used per coin cell (as per Figure 4.17 (b)) which resulted in fully functioning cells.
Fabrication of a contained coin cell was conducted as follows: the negative cap (with O-ring pre-attached) was placed external side down on a flat work surface. The cone spring was loaded into the negative cap followed by two spacers on top. Subsequently, the negative electrode was placed (coating side up) centrally on the spacer followed by the separator, this was then doused with ~3 droplets (enough to provide sufficient wetting but not liquid pooling) of the desired electrolyte by a syringe. At this point it should be noted that careful attention was required; although mostly the negative electrode would remain central underneath the separator (which would become partially translucent upon wetting) it was also possible that the negative electrode would slip to one side. If this occurred it was necessary to slightly lift the separator and reposition the negative electrode to a central location, this had to be done rapidly to minimise evaporation of the electrolyte solvent. The next step was to place the positive electrode (coating side down) centrally on the separator, again care was taken to ensure the electrode remained central. The positive can was pressed down over the cell layup thus far; the complete but unsealed cell was then flipped to have the negative cap on top and placed into the die slot of the hydraulic crimping machine for sealing; all cells were subjected to a crimping pressure of 70 kg cm\(^2\).

Some key items to note about this process are that the quantity of electrolyte deposited was not directly measured. This could have been achieved with a fixed volume pipette but it was found that any excess electrolyte could be squeezed from the cell during crimping, thus causing a difference between the quantity deposited and the quantity contained. A solution to this was to cumulatively weigh cell materials prior to initiation of the fabrication process, upon completion of fabrication the cell could be wiped clean of excess liquid and reweighed thus telling the quantity of electrolyte which was contained within. Measurement of the electrolyte quantity was conducted for experimentation involving LIC (lithium ion capacitor) EC devices. The average coin cell mass (including all components such as electrode and electrolyte) was found to be 3.75 g, this was derived from a wide variety of cell types and configurations.

Small issues were found with this process. If a complete but unsealed cell was not placed exactly central on the crimping die the device could partially crush the positive can wall, thus making the cell un-sealable. Another issue in the process was related to human error whereby a small selection of fabricated cells did not contain two spacers. If these errors occurred samples were repeated if possible but in some cases this was not possible; samples which were produced incorrectly are indicated (if necessary) in the results section of the following experimental Chapters. Overall the fabrication of coin cells was deemed a success.
Incorporating a quasi-reference electrode

In this work a silver QRE (quasi-reference electrode) has been implemented. This device consisted of a flat silver strip approximately 0.5 mm wide which was polished with a stiff scouring pad. It was calibrated against 5 mM of ferrocene with 0.1M TEA$^+$BF$_4$ in ACN using two polished glassy carbon working electrodes; unfortunately, due to equipment limitations this calibration process could not be conducted inside an inert environment i.e. glovebox. To minimise possible contamination, the electrolyte was prepared inside a glovebox, sealed in a vial, transported to the electrochemical analysis equipment and only released once the experiment was fully prepared; the resulting CV cycle is presented in Figure 4.18. It is known that the ideal oxidation potential, the gap between reaction peaks, of ferrocene in pure acetonitrile is 57 mV [269]; the Ag QRE devised presents a value of ~71 mV. This difference is believed to be due either to interactions with the TEA$^+$BF$_4$ salt, possible moisture contamination, or impurities on the QRE.

![Cyclic voltammograms of 5 mM with 0.1 M TEABF4 in ACN against an Ag QRE at a scan rate of 50 mV/s for five cycles. Arrows indicate reduction potential.](image)

This calibrated silver QRE was incorporated into a coin cell thus producing a three-electrode device. First, the approach of incorporating a QRE into a coin cell as described by Moshurchak et. al. [215] was attempted. In this work, a quasi-reference electrode was slipped between the cap and can and sandwiched between two sheets of separator to prohibit electrode contact, an example of this is presented in Figure 4.19 (a). To prohibit short circuiting between the cap and can the reference electrode was coated with PTFE with the tips exposed. Attempts at reproducing this work were unsuccessful; a PTFE coating was produced by masking the tips and spraying the central section with PTFE (Ballistol 82188) but upon cell crimping this PTFE
coating would be shred away leaving the silver exposed. In addition, the crimping process would often cut the silver wire prohibiting connection to an external device.

![Diagram of coin cell layup schematic showing the components: Cap, Gasket, Cone Spring, Spacer, (-) Electrode, Separator, Reference Electrode, Separator, (+) Electrode, (-) Can.](image1)

![Image (b) shows a silver QRE device with kapton® shielding, it has been bent to fit onto the lip of a partially complete coin cell.](image2)

![Image (c) shows the same device in-situ; note that the device rests upon the lip of a negative (-) cap containing a cone spring and spacer.](image3)

**Figure 4.19** Image (a) shows a coin cell layup schematic showing a coin cell with an incorporated QRE. Image (b) shows a silver QRE device with kapton® shielding, it has been bent to fit onto the lip of a partially complete coin cell. Image (c) shows the same device in-situ; note that the device rests upon the lip of a negative (-) cap containing a cone spring and spacer.

As such, a slightly different approach was taken. Rather than coating the central section with PTFE it was decided to encompass it within kapton® tape. This was achieved by cutting kapton® tape (one side possessed an adhesive) into two strips about four times wider and about half the length of the silver QRE. The 1st strip of kapton® tape was laid (adhesive side up) on a flat surface, the silver QRE was placed centrally, and the 2nd strip of kapton tape was laid on top (adhesive side down); effort was made in this process to ensure no folds or air gaps were present. Ultimately the device was shaped as to fit over the lip of the negative cap as shown in Figure 4.19 (a) and (b); this was done as to aid correct placement during the cell fabrication stage. Note that this shaping should produce a QRE tip which only slightly protrudes into the central area occupied by the electrodes; it should be near the electrode circumference but not significantly protrude into the electrode area as this may cause additional ion transport resistance. Upon imminent cell crimping, the external QRE section was folded flush against the negative base as to avoid the QRE becoming crushed or distorted during the crimping process; upon completion of crimping it was unfolded.

It is important to note that this process requires the use of two separation sheets to prohibit electronic contact between the QRE and both electrodes, these were laid up as shown in Figure 4.19 (a). If experimentation required one or more cells to be fabricated with a QRE (thus two separation sheets) then all cells associated with this experiment also included two separation
Chapter 4: Physical characterisation and fabrication techniques

sheets, irrespective of whether they contained a QRE. This was done to minimize the possible number of variables between experimental results. Also, due to the use of two separators, the cell layup process required an additional drop of electrolyte (thus bringing the total to \( \sim 4 \) drops) to fully wet the additional separation material.

4.6 Conclusion

Physical characterisation has been conducted of the primary electrode materials to be involved in later experiments. This started with observation by SEM which included EDX analysis where required.

It was found that an individual Kynol ACC yarn is approximately 500 \( \mu \text{m} \) in diameter with individual ACF fibres being about 20 \( \mu \text{m} \) in diameter. The axial surface is predominantly smooth with slight surface pitting. Sigma PAC consists of particles which qualitatively match (by observation) with the manufacturer’s specification wherein 70-75\% of particles are greater than 10 \( \mu \text{m} \) in size; these particles also possess surface pitting, possibly from the milling process used in particle production. Assessment of MWCNT provided inconclusive results; as such, the manufacturers specifications [229] must instead be relied upon i.e. tubes have an outer diameter of 10-12 nm and lengths in the tens of microns.

The silicon based electrode material NXA 513 was found to consist predominantly of particles with ‘hairy’ surface structures but MWCNTs and silver nano-particles were also found. The MWCNT content was provided to aid material conductivity while the silver nano-particles are a by-product of the manufacturing process. It was also possible to deduce that the PVDF content of this electrode material was 10 \%. Alfa Aesar graphite powder was found to possess a particle size distribution in agreement with the manufacturer specification i.e. particles are smaller than 44 \( \mu \text{m} \).

The above materials were assessed using nitrogen sorption measurement; analysis was conducted using both BET and GCMC techniques using the slit assumption where appropriate. Sigma PAC and Kynol ACC possess SSA values in agreement with their manufacturer state specifications. By GCMC analysis Sigma PAC and Kynol ACC possess SSAs of 843 and 1560 \( \text{m}^2 \text{g}^{-1} \), respectively; this provides an SSA ratio of 1:0.54 between Kynol ACC and Sigma PAC. Sigma PAC was found to possess an SPV of 0.498 \( \text{cm}^3 \text{g}^{-1} \) while Kynol ACC has an SPV of 0.687 \( \text{cm}^3 \text{g}^{-1} \). Further analysis revealed Sigma PAC possesses mesoporous content 10 nm in width which accounts for 5 \% of its SSA but 32 \% of its SPV. Kynol ACC on the other hand
has negligible mesoporous content 3 nm in width which accounts for around 1 % of SSA and 3 % of SPV.

Microporous associated pore size distributions have been plotted for Sigma PAC and Kynol ACC, alongside bare (un-solvated) and solvated (by acetonitrile) ion sizes for TEA⁺ and BF₄⁻. Firstly, it was found that both types of AC material possess a bimodal pore structure with peaks at pore widths ~0.7 nm and ~1.35 nm. It was found that bare BF₄ ions are smaller than the smallest pore structure in both AC materials but bare TEA⁺ ions are exactly the same size as the smallest pore structure.

Elicarb MWCNTs were analysed by similar methods to the above except the use of a cylindrical structure assumption during analysis. They were found to possess a purely mesoporous structure with a tube diameters between 7-10 nm, an SSA of 198 m² g⁻¹ and an SPV of 0.847 cm³ g⁻¹. NXA 513 was analysed and found to have no microporous content and a relatively small amount of mesoporous content of 30 nm in width; the SSA and SPV associated with this were 4.55 m² g⁻¹ and 0.0680 cm³ g⁻¹, respectively. The final material assessed by this method was the graphitic powder; this was found to possess a minute amount of porous content around 8 nm in width with SSA and SPV value of 2.32 m² g⁻¹ and 0.00854 cm³ g⁻¹, respectively.

Due to its novel surface structure, Toyal Carbo® was also analysed by SEM and EDX analysis. It was found that the surface has an elemental structure consisting of almost equal amounts of carbon and aluminium content; it is quite possible this represents the Al₂C₃ nanowhiskers known to reside within its surface [181].

The equipment and configuration of tape casting, used for electrode material deposition, has been described in detail. Two types of slurry were prepared, one based on graphite (for use as the negative electrode in LIC type EC devices) and one based on Sigma PAC (for use as the positive EDLC type electrode). These were deposited by tape casting, the drying process has been described in detail. Subsequently, electrodes were cut to disks 15 mm in diameter; coating thickness and areal density were calculated through thickness and weight measurements of current collector with and without coatings. The resulting coatings were analysed for consistency; the relationship between coating thickness and areal density has been mathematically established with an R² error of 0.921. The thickest electrodes fabricated were 310 μm but exhibited surface defects in the form of vent like voids, these are believed to be due to the significant quantity of subsurface water. The thickest electrode with uniform coating quality was 250 μm.
Fabrication of the 1M TEA⁺BF₄⁻ in ACN electrolyte has been described in detail; this included the equipment used, its configuration and the procedures involved. Such a process was not required for the 1M Li⁺PF₆⁻ in EC/DEC electrolyte for use in LIC type EC devices as it was procured in a premixed form.

For cell containment CR2032 coin cells have been selected, their fabrication has been described in this chapter; this includes details on the pre-fabrication procedures such as electrode drying. Some items of note are the inclusion of two spacers (each 1 mm thick) and the inclusion of three droplets or more of electrolyte. It should be noted that accurate measurement of this electrolyte was not possible pre-fabrication due to the ejection of electrolyte upon sealing; as such, all cell components (including electrodes) were weighted pre- and post-sealing, the difference between these values indicates the quantity of electrolyte included. Such a process was only used for LIC type EC devices due to their intrinsic dependence upon the quantity of lithium available in the electrolyte.

The final section of this chapter described the incorporation of a QRE device into a coin cell. This involved altering the cell configuration by including two separators rather than just one; this allowed for the tip of the QRE device to sit between the separators and avoid electronic contact with the primary electrodes. The material used for a QRE was 100 μm silver foil, this was referenced against ferrocene to provide a static reference point for simple comparison between other research in this field.

As such, the material characterisation and experimental configurations detailed in this chapter completes PO3 and PO 5 (see supplement A). The approach to cell containment (i.e. coin cells) also meets SO1 i.e. to use techniques used at the industrial scale. In addition to this, the development of a silver QRE device also meets SO2 as it is considered an advanced research technique which may greatly assist research in this field.
5 THE IMPACT OF ELECTRODE CAPACITANCE RATIO ON ASYMMETRIC ACC/PAC EDLC ELECTROCHEMICAL CAPACITORS UTILISING ORGANIC ELECTROLYTE

5.1 Introduction

The primary aim of the experiments detailed in this section was to develop and characterise an EDLC (electrical double layer capacitor) type EC (electrochemical capacitor) device which possesses a stable high voltage (2.7 V) using capacitance balancing by material asymmetry (research aim 1, section 2.8); such an approach can extend the operational voltage window, thus maximising energy storage, alongside extending cell cycle life. Experimentation in this area focused around the use of TEA’BF₄ (tetra-ethylammonium tetrafluoroborate) in ACN (acetonitrile), an industry standard electrolyte; in addition to this, industry standard coin cell casings were utilised. Both approaches satisfied research aim 6 i.e. to use materials and techniques which are closely related to current industrial standards thus facilitating rapid deployment of any beneficial findings.

In essence, capacitance balancing is a method for adjusting the voltage operating window experienced by each electrode; this is desired to ensure neither electrode experiences performance-degrading chemical reactions which can maximize the total cell voltage (thus improving energy density) and decrease cell ageing (thus improving device lifespan) [168, 169, 170]. In the case of an EDLC type device using YP17 Kuraray AC (activated carbon) electrodes and TEA’BF₄ in ACN electrolytes, the ESPW (electrochemically stable potential window) has been found to be ~1 V in width for the positive electrode and ~−2 V for the negative electrode [166].

Previous work in the field of capacitance balancing has been reviewed. It was found that capacitance balancing is predominantly achieved by using the same material at both positive and
negative electrodes while altering the electrode mass ratio, sometimes taken as the positive electrode mass divided by the total electrode mass i.e. a part-to-whole ratio.

The unique aspect of the cell configurations proposed in this chapter is the attempt to achieve proper capacitance balancing through the use of material asymmetry at each electrode i.e. the material at each electrode may differ in mass specific capacitance but remain equal in their masses. Specifically, it has been identified (Section 2.4.3) that AC materials with an SSA (specific surface area) ratio of 1:0.54 (part-to-part) could be used; a high SSA material is used at the positive electrode while a low SSA material is used at the negative electrode. This SSA ratio should ideally translate to a material mass specific capacitance ratio of 1:0.54 for proper capacitance balancing to be achieved. Whilst on its own this approach may appear to be just another solution to an already solved problem, it in fact provides an interesting opportunity for maximising overall cell capacitance.

Such a device may also show improvements in capacitance if a material which possesses high microporosity content is used as the positive electrode. Modern investigations utilising CDCs (carbide derived carbons) and TCs (templated carbons) alongside TEA⁺BF₄⁻ in ACN electrolyte suggest that it may be possible for ions to partially desolvate [158, 159, 160, 161], thus decreasing the charge separation distance across the EDL and consequently increase the capacitive response, as per equation (2.6). This is particularly true when the microporous structure of the positive electrode (that which attracts smaller BF₄⁻ ions) is predominantly of pores 0.7 nm in width (assuming slit like shape); in such a situation capacitance was increased due to the partial desolvation of BF₄⁻ ions [160]. For the negative electrode, it was found that its microporous structure should have a majority of 0.74 nm pores to achieve maximal capacitance, this being due to the larger size of TEA⁺ ions [160] (see Section 2.4.2 for further details). Thus, material asymmetry may not only provide the same benefit of mass asymmetry (with respect to capacitance balancing), but it may also provide a beneficial increase in capacitance if the PSDs (pore size distributions) of the positive and negative electrodes are conducive to such a result.

Two types of AC material were selected for experimentation: Kynol ACC (activated carbon cloth) 507-15 and Sigma Aldrich PAC (powdered activated carbon) C9157. The manufacturer specifications for these materials can be found in Section 3.3.2; it should be noted that Kynol PAC and Sigma PAC have been derived from phenolic and peat-bog-based precursors, respectively, alongside their obvious morphological differences (i.e. fibrous cloth and
powder) which were clearly presented by SEM analysis in Section 4.2.1. Nitrogen sorption analysis was conducted on these materials prior to experimentation with SSA, SPV (specific porous volume), and PSD results being shown in Sections 4.2.3, 4.2.4 and 4.2.5, respectively. These results corroborated the manufacturer specifications and showed that the microporous SSA (by GCMC analysis) of Kynol ACC is 1540 m² g⁻¹ and for Sigma PAC is 801 m² g⁻¹ thus providing an SSA ratio of 1:0.52. This agrees extremely well with the desired SSA ratio of 1:0.54 for capacitance balancing [168] (see Section 2.4.3) but excludes the possible influences of their mesoporous structures. It should be noted that throughout the work entailed in this chapter there are two ratios at hand, a capacitance ratio and a mass ratio; as these could be confused in notation. All capacitance ratios (part-to-part) will be stated in the form of c(1:x) while mass ratios will be stated in the form of m(1:x), where x is value of the negative electrode relative to that of the positive electrode i.e. the ratios are part-to-part.

In addition to the above, the PSD values (section 4.2.5, Figure 4.9) showed that both Kynol ACC and Sigma PAC possessed pore width peaks at ~0.7 nm and ~1.35 nm. It is clearly visible that the incremental volume (‘quantity’) of pores at this width is proportional to the SSA value. In other words, the ‘quantity’ of micropores in Kynol ACC (0.666 cm³ g⁻¹) is almost double that of Sigma PAC (0.340 cm³ g⁻¹), while the SSA of Kynol ACC is also almost double that of Sigma PAC; this is corroborated by SPV values provided in section 4.2.4, Table 4.3.

It has been deemed appropriate to provide an overview of what may be required to assess the author’s hypothesis that capacitance balancing can be achieved through electrode material asymmetry:

1. Produce devices which can be used to assess the basic properties of cells with material and mass symmetry. This will establish mass specific capacitance values for the materials at hand; these values can provide confirmation as to whether the selected materials SSA ratio 1:0.52 does indeed provide a capacitance ratio approaching c(1:0.54) (as is required for capacitance balancing without mass balancing).

2. Validate previous work in this field [168], especially with regards to the electrode materials used in this study (which differ from those used in previous studies). This will require that cells are produced which are material symmetric but mass asymmetric with a capacitance ratio of c(1:0.54) (i.e. such that the positive electrode accounts for 65% of the total electrode mass [168]). Validation of this work will not
only provide sufficient basis to show that previous work in this field is well founded but will also validate the experimental techniques in use, alongside behaving as a control result for further experiments.

3. Test the hypothesis that appropriately matching different materials at each electrode (i.e. Kynol ACC as the positive electrode and Sigma PAC as the negative electrode) can adequately achieve capacitance balancing for cell lifespan extension. This should be achieved in fundamentally the same manner as the preceding validation experiments to maintain comparability. Upon completion of this there may be justification for further experiments to be conducted.

5.2 Methodology

5.2.1 Materials and Experimental Control

To produce high quality and trustworthy results it is necessary to establish control over experiment variables. In this work the core independent and control variables are:

- Positive/negative electrode – material(s), thickness, areal density, preparation method and deposition method, current collector, purity.
- Electrolyte – salt, solvent, molar concentration, fabrication method, quantity.
- Cell separation material.
- Cell containment materials and method.
- Temperature

The positive/negative electrode material(s) and thickness are the variables of interest in this work. Kynol ACC can behave as a single electrode material with no binder required while Sigma PAC based electrodes necessitated a binder, chosen as 5 m% SBR/CMC, and a CC (current collector), chosen as 30 μm Toyal Carbo®. The SBR/CMC binder was selected due to its solubility in water, thus reducing environmental impacts [230], and Toyal Carbo® was selected due to its reduced contact resistance [181]. All Sigma PAC based electrodes were fabricated using tape casting deposition as described in section 4.4; a wide variety of electrode thicknesses and corresponding areal densities (i.e. active material loadings) were fabricated and applied as required for experiments described in this chapter.
The electrolyte used for all experiments in this chapter was 1.5M TEA+BF₄⁻ in dry ACN; the salt, solvent and molar concentration were held constant and its preparation procedure is defined in Section 4.5.2. The only issue of concern was the quantity of electrolyte could not be directly measured. Even with a fixed volume pipette it was found that any excess electrolyte could be squeezed from the cell during crimping, thus causing a difference between the quantity deposited and the quantity contained. Regardless, it has been found from literature that providing significant electrolyte wetting (i.e. soaking) of electrode and separation materials will not impact cell performance (either positively or negatively) [148, 270]; it is only when insufficient electrolyte is added that a cell may behave sub-optimally.

Attempts were made to hold constant the variables related to cell separation material and cell containment method. Cell separation was achieved with 60 μm NKK TF40-60 cellulose separator and cell containment used industry standard CR2032 coin cell cases; the precise containment procedures followed are detailed in section 4.5.3. Note, a QRE (quasi-reference electrode) was not included during initial experiments related to establishing material capacitance values and validating previous work, this is due to the lack of refinement at these stages (attempts were still being made to implement the approach found in literature [215]). QRE refinement (by using kapton® tape) was not established until experiments relating to the hypothesis at hand were being conducted. The temperature was held constant at 25° C for all experimentation, using an environmental chamber.

5.2.2 Electrochemical Analysis and Key Performance Indicators

The electrochemical analysis techniques used in this chapter are CCCD (constant current charge discharge), CV (cyclic voltammetry) and EIS (electrochemical impedance spectroscopy); see section 3.4.3 for detailed descriptions of these techniques. In the case of CCCD the current density (A g⁻¹) can be stated with respect to the mass of positive electrode, mass of negative electrode or total electrode mass. In the case of the experiments at hand, as the mass of the positive and negative electrodes were sometimes varied, it was difficult to hold the current density constant with respect to individual electrodes. As such, the current density was held constant at 0.28 A g⁻¹ with respect to the total electrode mass (as per [164]). Three CCCD cycles were conducted between voltages of 0 and 2.5 V, three cycles ensured that device performance is stabilised; as the 1st cycle is often influenced by prior electrochemical analysis techniques.

CV analysis was conducted at a scan rate of 5 mV s⁻¹ between voltages of 0 and 2.5 V. This technique allowed for definition of adverse chemical reactions at higher voltages while also
providing a qualitative view of cell performance. It should be noted that CV analysis was not used for deriving any quantitative properties, as they are difficult to derive and there is a lack of substantial definition: a min/average/max capacitance derived from CV bears little meaning in comparison to the definite capacitance values, which can be derived from CCCD and EIS. Again, three cycles were conducted with the third being used for analysis. The EIS analysis technique was conducted at a stationary voltage of 0 V with a superimposed low amplitude oscillating voltage signal of 5 mV between frequencies of 100,000 to 0.01 Hz.

The quantitative properties of interest (and their method of derivation) in the following experiments are:

- Mass Specific Capacitance (from CCCD and EIS)
- Areal Resistance (from CCCD and EIS)
- Charge Storage Efficiency (from CCCD)
- Energy Storage Efficiency (from CCCD)
- Mass Specific Energy Density (from CCCD)
- Mass Specific Power Density (from CCCD)

Using these properties, it was possible to definitively identify trends in the gathered results. It should be noted that resistance is presented specific to electrode area; while all electrodes in this work do possess an equal area it aids in comparing results to those found in literature. Note: the capacitance is derived per total active material mass of both electrodes within the cell.

Additionally, it is worth noting that most literature reports mass specific capacitance specific to the mass of a single electrode through the assumption that the capacitance is equal at both electrodes (see Section 2.3.1); throughout the work detailed in Chapter 5 the capacitance is consistently and deliberately unbalanced and as such the conversion from full cell capacitance to single electrode capacitance is not justified. This is particularly true considering that the material of the positive/negative electrode will not always be the same thus using single electrode capacitance would not represent the capacitance of either electrode.

5.2.3 Cell Ageing

As previously mentioned in Section 2.4.3, cell ageing can be quantified in terms of cycle life (achieved through long term cycling) or high voltage potentiostatic lifespan (achieved through high voltage potentiostatic ageing). Both methods of quantification represent differing
cell use cases; cycle life best represents the ageing of a cell which experiences constant use (e.g. voltage stabilization), while high voltage potentiostatic lifespan best represents the ageing of a cell which experiences limited use but must be ready for use any moment e.g. for emergency power.

In cyclic ageing a cell is repeatedly charged and discharged from minimum to maximum voltage; recall that cell ageing generally occurs at (or close to) the maximum voltage and as such a cell is truly being aged for only a fraction of its cycle life. This thought does not consider that a cell is also ageing when ions are in motion i.e. during charge/discharge. It has been understood that for ageing to occur there must be a significant (approaching maximal) voltage. In contrast, high voltage potentiostatic ageing is a constant process in which ageing occurs at all times; this brings the benefit of representing the worst-case usage scenario while also condensing the ageing process into manageable timeframes (e.g. hundreds of hours compared to cyclic testing which may take thousands of hours [164]).

The cells under examination in this work experienced high voltage potentiostatic ageing. This was achieved in a similar process as to that described in [164]:

1. Prior to the ageing process a set of CCCD and CV cycles, alongside EIS, were used to deduce the initial electrochemical performance of a cell.

2. Ageing was conducted by holding a cell at 2.7 V for 10 hours.

3. CCCD and CV cycles were used to assess the impact of cell ageing after each 10 hour period of ageing.

4. Steps 2 and 3 were repeated until either cell failure or 100 hours total ageing has been completed.

An example of this process has been visualised in Figure 5.1, note that CCCD and CV analysis were conducted 3 times consecutively to establish a constant representative value by the 3rd cycle.
Figure 5.1 The potentiostatic cell ageing process. Initial cell properties are deduced close to 0 hrs using 3 CCCC cycles and 3 CV cycles. The impacts of ageing are deduced by CCCD and CV after each 10 hour ageing period.

5.3 Electrochemical Analysis of AC Materials in both a Material and Mass Symmetric Cell Configuration

5.3.1 Cell Configurations - Material and Mass Symmetric Cells

The focus of this section was to produce EDLC devices which can be used to assess the basic properties of cells with material and mass symmetry and subsequently assess whether the selected materials SSA ratio 1:0.52 provided a capacitance ratio approaching 1:0.54. In the case of both materials, four sample cells were created to ascertain mean values and relative standard deviation (RSD%) of their electrochemical properties.

Shown in Table 5.1 are the cell configurations for material and mass symmetric samples containing Sigma PAC. The areal density and mass values refer to the active material alone i.e. not including other cell components such as current collector. To confirm that capacitance is indeed an intrinsic property (i.e. mass specific) of the electrode material it was decided to create two sets of samples with different combined total active electrode material mass, samples A and B possess a total of ~21.5 mg while samples C and D possess a total of ~17.5 mg. It can be clearly seen that the mass ratio tends towards m(1:1) but is not ideal; this was due to difficulty in producing electrodes with absolutely identical mass. In addition to this, all samples meet the
desired thickness range set in research aim 5 i.e. electrode coatings should possess thicknesses between 100 and 200 μm. Samples C and D do not meet the desired single electrode mass i.e. being greater than 10 mg, it was of interest to see if this caused the results of electrochemical analysis to differ significantly.

Table 5.1 Cell configurations for material and mass symmetric samples containing Sigma PAC. Note that areal density and mass values refer to the active material alone.

<table>
<thead>
<tr>
<th>‘PAC:PAC’ Areal Density (+/-)</th>
<th>Single Electrode Mass (+/-)</th>
<th>Mass Ratio m(+ : -)</th>
<th>Combined Electrode Mass</th>
<th>Average Electrode Thickness (+/-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg cm²</td>
<td>mg</td>
<td>mg</td>
<td>μm</td>
<td></td>
</tr>
<tr>
<td>Sample A</td>
<td>6.24 / 6.17</td>
<td>11.02 / 10.90</td>
<td>1 : 0.97</td>
<td>21.93</td>
</tr>
<tr>
<td>Sample B</td>
<td>6.03 / 6.07</td>
<td>10.66 / 10.72</td>
<td>1 : 1.01</td>
<td>21.39</td>
</tr>
<tr>
<td>Sample C</td>
<td>4.99 / 4.94</td>
<td>8.81 / 8.72</td>
<td>1 : 0.99</td>
<td>17.54</td>
</tr>
<tr>
<td>Sample D</td>
<td>4.90 / 5.05</td>
<td>8.65 / 8.92</td>
<td>1 : 1.03</td>
<td>17.58</td>
</tr>
</tbody>
</table>

Table 5.2 Cell configurations for material and mass symmetric samples containing Kynol ACC. Note that areal density and mass values refer to the active material alone.

<table>
<thead>
<tr>
<th>‘ACC:ACC’ (1:1) Areal Density (+/-)</th>
<th>Single Electrode Mass (+/-)</th>
<th>Mass Ratio m(+ : -)</th>
<th>Combined Electrode Mass</th>
<th>Average Electrode Thickness a</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg cm²</td>
<td>mg</td>
<td>mg</td>
<td>μm</td>
<td></td>
</tr>
<tr>
<td>Sample A</td>
<td>12.79 / 12.64</td>
<td>22.60 / 22.33</td>
<td>1 : 0.99</td>
<td>44.93</td>
</tr>
<tr>
<td>Sample B</td>
<td>12.51 / 12.55</td>
<td>22.10 / 22.17</td>
<td>1 : 1</td>
<td>44.27</td>
</tr>
<tr>
<td>Sample C</td>
<td>13.06 / 12.94</td>
<td>23.08 / 22.86</td>
<td>1 : 0.99</td>
<td>45.94</td>
</tr>
<tr>
<td>Sample D</td>
<td>12.73 / 13.05</td>
<td>22.50 / 23.06</td>
<td>1 : 1.02</td>
<td>45.56</td>
</tr>
</tbody>
</table>

Table 5.2 shows the cell configurations for material and mass symmetric samples containing Kynol ACC. The areal density and mass values refer to the active material alone i.e. not including other cell components such as current collector. As this material came prefabricated it was not possible to vary the quantity of material at each electrode without shrinking the electrode diameter, which could have possibly compromised experimental control; it was decided all cells should ideally be of equal combined mass. The mass of individual electrodes
was found to be not entirely constant as one might expect from a bulk cloth material and is believed to associate with the SSA variations mentioned by the manufacturer [224]. Regardless, it was possible to find electrodes with approximately equivalent masses thus allowing the production of samples with mass ratios tending towards m(1:1). One final note on this material is with regards to thickness; while the manufacturer specification stated that Kynol ACC has a thickness of 500 μm it was subsequently found that under compression (as would be the case in a coin cell) the average electrode thickness reduced to 350 μm. This fact was not fully appreciated until later experimentation in this chapter and as such throughout Section 5.3.2 only a single coin cell spacer was used in cells containing Kynol ACC.

5.3.2 Results and Analysis - Material and Mass Symmetric Cells

**CCCD Testing**

The results of CCCD testing at 0.28 A g⁻¹ for material and mass symmetric cells containing Sigma PAC and Kynol ACC are shown in Figure 5.2 (a) and (b), respectively. It can be clearly seen that Sigma PAC (Figure 5.2 (a)) demonstrates generally consistent performance; the top right inset shows initiation of the discharge phase while the bottom right inset shows the end of the discharge phase. One item of note with respect to Sigma PAC is that sample A features a slight curve (i.e. nonlinear capacitance) at the beginning of discharge, while samples B, C and D do not. Such a phenomenon has been previously discussed in section 3.4.3 and is generally associated with restricted ion movement [248]. The corresponding KPIs (key performance indicators) derived from samples presented in Figure 5.2 (a) are shown at the end of this section in Table 5.3.

![Graph](image)

Figure 5.2 Results of CCCD testing at 0.28 A g⁻¹ (3rd run) for material and mass symmetric cells containing (a) Sigma PAC and (b) Kynol ACC.
Kynol ACC (Figure 5.2 (b)) does not appear to demonstrate the same level of consistency as that of Sigma PAC; samples A, B and D are loosely bunched together while sample C is set apart. Qualitatively it does appear that the capacitance values of each cell are approximately equal, as demonstrated by the parallel charge/discharge plots; the aspect which truly differentiates them is the voltage drop upon the initiation of the discharge phase (indicated in the top right inset); this voltage drop, which is sharp in nature, is strongly associated with electronic resistance [248]. It is also noticeable that the charge/discharge plots are not entirely linear, there is a very slight element of bowing in both charge and discharge, particularly at high voltage, which indicates the occurrence of chemical reactions. The corresponding quantitative KPIs derived from samples presented in Figure 5.2 (b) are shown at the end of this section in Table 5.4.

CV Testing

The relationships between mass specific cell capacitance and voltage for material and mass symmetric cells containing Sigma PAC and Kynol ACC are shown in Figure 5.3 (a) and (b), respectively. All samples of Sigma PAC appear to be reasonably consistent with one another but again, sample A differentiates itself as being more resistive (see right inset). The mass specific capacitance varies between 12.5 F g⁻¹ at 0 V up to 21 F g⁻¹ at 2.5 V; it is also noticeable that the mass specific capacitance increases rapidly after 2.25 V indicating a chemical reaction is occurring above this voltage.

![Graphs showing capacitance-voltage plots for Sigma PAC and Kynol ACC](figure5_3.png)

Figure 5.3 Mass specific cell capacitance-voltage plots derived from CV testing at 5 mV s⁻¹ (3rd cycle) for material and mass symmetric cells containing (a) Sigma PAC and (b) Kynol ACC.

Samples of Kynol ACC (Figure 5.3 (b)) present a skewed ‘rhombus’ shape with rounded corners; this also indicates high resistivity (as with Sample A of Sigma PAC) [271]. The mass
specific cell capacitance varies between 20 F g\(^{-1}\) at low voltages up to \(\sim 37.5\) F g\(^{-1}\) at 2.5 V. For samples A, B and D it is again noticeable that the mass specific capacitance increases rapidly after 2.25 V, this indicates that a chemical reaction is occurring above this voltage. Sample C does not present this rapid increase but it does still present a significant resistance.

Consider the possible presentation of resistivity in CV analysis techniques. Recall that this CV analysis is being conducted at 5 mV s\(^{-1}\), charging a cell between 0 and 2.5 V will thus take 500 seconds alongside a further 500 seconds for discharging, 1000 seconds in total. Thus, in comparison to CCCD analysis which took between 250 and 450 seconds in total the cells in CV analysis are experiencing a lower charge transfer rate as indicated by the longer charge/discharge time. This lower charge transfer rate (i.e. current) diminishes the impact of electronic resistance as per Equation (2.4). As such, the resistance exhibited by the skewed ‘rhombus’ shaped CV plots presented in Figure 5.3 (a) and (b) could be predominantly associated with ionic resistance but if electronic resistance is significant (and qualitative assessment of CCCD analysis suggests it is) then this may also be a cause.

**EIS Testing**

EIS testing was conducted at 0 V for material and mass symmetric cells containing Sigma PAC and Kynol ACC. Data has been presented graphically in the form of Nyquist plots (Figure 5.4). Bode mass specific capacitance (BMSC) plots (Figure 5.5) and Bode phase angle (BPA) plots (Figure 5.6) where graphs (a) and (b) associate with Sigma PAC and Kynol ACC respectively. The fundamentals of EIS analysis techniques can be found in Section 3.4.3.

Shown in Figure 5.4 (a) are Nyquist plots of Sigma PAC samples. The point at which these plots cross 0\(\rightarrow\)Z\(_{in}\) is known as the solution resistance (i.e. electrolyte resistance); while all samples present < 4 Ω solution resistance there is a large degree of variability. The frequency at which these plots cross 0\(\rightarrow\)Z\(_{in}\) is 2\times10\(^3\) Hz; at this frequency, the BMSC plot (Figure 5.5 (a)) shows there is a minor capacitive excitation in all samples and the BPA plot (Figure 5.6 (a)) shows that all samples cross the boundary between inductive and capacitive behaviour. The polarization resistance, is negligible for these samples (see Figure 5.4 (a) right inset); this is believed to be partially due to the use of Toyota Carbo\(^\circledast\) as the CC, which has been shown to significantly reduce polarization resistance [182, 248] and is also an indication that ionic migration to/from charge storage sites is not significantly restricted. This is certainly related to the fact that the porous structure of AC contains mesopores which aid ion transfer to and from micropores.
The Warburg region, an indicator of the ability for electrolyte to diffuse to/from charge storage sites, is well defined for samples B, C and D of Sigma PAC and is visible in the right inset of their respective Nyquist plots; this region occurs between frequencies of 1 and 10 Hz, thus indicating ion diffusion is rapid. These same samples subsequently approach ideal capacitive behaviour at frequencies below 1 Hz, as indicated by the capacitance ‘plateau’ in BMSC plots (Figure 5.5 (a)). The corresponding BPA plots indicate a starting knee frequency of 1 kHz and good energy storage efficiency as Φ approaches -90°. Also, note how the peak value (10 mHz) of the Nyquist plot for sample B is lower than that of samples C and D; this is due to the larger quantity of active material possessed by sample B presenting a higher extrinsic capacitance value; this corresponds to lower imaginary impedance as defined by Equation (3.6). When this capacitance value is considered in mass specific manner, as in the corresponding BMSC plots, the intrinsic material capacitances agree with one another.

Figure 5.4  Nyquist plot from EIS testing at 0 V for material and mass symmetric cells containing (a) Sigma PAC and (b) Kynol ACC.

Figure 5.5  Bode mass specific cell capacitance (BMSC) plot from EIS testing at 0 V for material and mass symmetric cells containing (a) Sigma PAC and (b) Kynol ACC.
Chapter 5: The impact of electrode capacitance ratio on asymmetric ACC/PAC EDLC electrochemical capacitors utilising organic electrolyte

Figure 5.6 Bode phase angle (BPA) plot from EIS testing at 0 V for material and mass symmetric cells containing (a) Sigma PAC and (b) Kynol ACC.

Sample A of Sigma PAC does not present the same overall trend as samples B, C and D; From its Nyquist plot in Figure 5.4 (a) this differentiation is clearly shown. Per the BMSC plot in Figure 5.5 (a), sample A’s capacitance is generally reduced, albeit that it does eventually fit with other samples at a frequency of 10 mHz, but without a plateau-like approach. This corresponds with the BPA plot in (Figure 5.6 (a)) which shows Sample A reaches a maximum $\Phi$ of $\sim75^\circ$ i.e. non-ideal capacitive behaviour. According to information provided in [248], this indicates the cell is either experiencing restricted ionic diffusion or a chemical reaction is occurring. Consider again that all samples are being tested at 0 V with sinusoidal voltage oscillation of 5 mV; as such, it is extremely unlikely that any chemical reactions are occurring and therefore is most likely associated with restricted ion diffusion.

In contrast to Sigma PAC samples, all Kynol ACC samples present strong polarization resistance as indicated by the formation of a full polarization ‘loop’ in Figure 5.4 (b); such a loop is attributed to either significantly restricted ionic diffusion or contact resistance. It is known that Kynol ACC possesses a predominantly microporous structure and as such ion diffusion may be limited. Large contact resistance may have arisen due to the external morphology of Kynol ACC; as individual fibres are circular in nature they are likely to possess small contact areas with other fibres and surfaces, thus increasing contact resistance. In addition to this, the lack of control over how these fibres pack together could have produced the significant variability in loop size between samples. A further cause of contact resistance may be due to a lack of electrode stacking pressure due to the use of a single spacer, but it is believed that the impact of this would have presented itself in a more consistent manner. Polarization resistance varies dramatically between samples, with A producing the lowest at $\sim18$ $\Omega$ and C producing the largest at $\sim40$ $\Omega$. 

Richard Fields - February 2018

143
At this point it should be noted that sample C presents abnormal behaviour at a frequency of 200 mHz; the causes of this are either instrumentation error or sample movement during analysis. No abnormal instrument behaviour was noticed and the second cause was initially considered unlikely as cells were contained within a controlled environment for the duration of testing, but upon closer inspection of the environmental chamber it was noticed that a fan was being used to circulate air which could have caused a poorly positioned cell to move during testing.

The Warburg region for all samples is discernible in BMSC Figure 5.4 (b) and corresponds to frequencies between 100 mHz and 10 Hz on the BMSC and BPA plots. This region is effectively an indicator of the ability for electrolyte ions to diffuse to/from charge storage sites; if a cell under EIS analysis is within the Warburg region at low frequencies (i.e. 100 mHz) then this indicates significant diffusion restriction is occurring, which is consistent with the PSD (pore size distribution) of Kynol being predominantly microporous. These samples subsequently approach ideal capacitive behaviour at frequencies below 100 mHz, as indicated by the capacitance ‘plateau’ in BMSC plots (Figure 5.5 (a)). The corresponding BPA plots present a starting knee frequency of 1 Hz and also show that a low phase angle is achieved by all samples at 10 mHz (i.e. after oscillations 100 seconds long), this indicates Kynol ACC may have poor energy storage efficiency.

**Key Performance Indicators**

Shown in Table 5.3 are the KPIs (key performance indicators) for material and mass symmetric cells containing Sigma PAC, they are derived from CCCD and EIS analysis. It should be noted that sample A has been pre-emptively excluded from the calculation of mean and RSD% (relative standard deviation); this was due to the obvious differences this sample presents in CCCD, CV and EIS analysis. It is possible these differences arose due to a manufacturing defect in cell construction (e.g. moisture contamination or poorly dispersed binder additive).

From Table 5.3 it is possible to see that the mean mass specific capacitance of a material and mass symmetric cells containing Sigma PAC is 15.0 F g⁻¹ by CCCD analysis and 12.5 F g⁻¹ by EIS analysis, the lower value from EIS analysis is attributed to it being conducted at 0 V and agrees with CV analysis. Both values have a RSD% of about ±2.5 % which indicates good agreement between samples. As there is material and mass symmetry it is reasonable to use the knowledge that the mass specific capacitance of a half-cell will be four times higher than a full-
cell (as per Equation (2.10), Section 2.3.1), this infers that the mass specific capacitance of a single Sigma PAC electrode is 60.3 F g⁻¹.

Table 5.3 KPIs for material and mass symmetric cells containing Sigma PAC.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(1:1)</td>
<td>15.1 F g⁻¹</td>
<td>12.1 F g⁻¹</td>
<td>7.8 Ω cm²</td>
<td>5.9 Ω cm²</td>
<td>99 %</td>
<td>84 %</td>
<td>11.4 W h kg⁻¹</td>
<td>16.0 kW kg⁻¹</td>
</tr>
<tr>
<td>Sample A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1:1)</td>
<td>15.5 F g⁻¹</td>
<td>13.0 F g⁻¹</td>
<td>6.1 Ω cm²</td>
<td>3.8 Ω cm²</td>
<td>97 %</td>
<td>88 %</td>
<td>12.5 W h kg⁻¹</td>
<td>21.0 kW kg⁻¹</td>
</tr>
<tr>
<td>Sample B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1:1)</td>
<td>14.9 F g⁻¹</td>
<td>12.2 F g⁻¹</td>
<td>4.5 Ω cm²</td>
<td>2.4 Ω cm²</td>
<td>97 %</td>
<td>89 %</td>
<td>12.3 W h kg⁻¹</td>
<td>34.5 kW kg⁻¹</td>
</tr>
<tr>
<td>Sample C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1:1)</td>
<td>14.7 F g⁻¹</td>
<td>12.5 F g⁻¹</td>
<td>3.2 Ω cm²</td>
<td>1.6 Ω cm²</td>
<td>96 %</td>
<td>88 %</td>
<td>12.2 W h kg⁻¹</td>
<td>48.8 kW kg⁻¹</td>
</tr>
<tr>
<td>Sample D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>15.0 F g⁻¹</td>
<td>12.5 F g⁻¹</td>
<td>4.6 Ω cm²</td>
<td>2.6 Ω cm²</td>
<td>97 %</td>
<td>88 %</td>
<td>12.3 W h kg⁻¹</td>
<td>34.8 kW kg⁻¹</td>
</tr>
<tr>
<td>Relative Standard Deviation</td>
<td>±2.9 %</td>
<td>±3.1 %</td>
<td>±31 %</td>
<td>±41 %</td>
<td>±0.60 %</td>
<td>±0.65 %</td>
<td>±1.6 %</td>
<td>±39.9 %</td>
</tr>
</tbody>
</table>

With regards to areal resistance of samples B, C and D: CCCD analysis presents a mean value of 4.6 Ω cm² with RSD% of ±25% and EIS analysis presents a mean value of 2.6 Ω cm² with a RSD% of ±34%. From both analysis methods, the RSD% values are significant; this may be related to individual cell configurations but is more likely associated with the method by which coin cells were connected to the analysis instrument (crocodile teethed clips were used which is not ideal considering the non-planar surface contact). Regardless, the values presented here are in good agreement with those stated in a recent (2011) publication on using CR2032 coin cells for EDLC electrode material testing [272]. As such, while the results may not be entirely in agreement, they still provide a good representation of areal resistance.

Charge storage efficiency, derived by CCCD analysis up to 2.5 V, has a mean value of 97% and a RSD% of ±1 % between samples B, C and D. This indicates consistent charge transfer during both charge and discharge with minimal charge loss. Interestingly, the little loss which is
experienced corroborates with the findings from CV analysis, in which a short period within
the charge cycle (between 2.25 and 2.5 V) appears to be experiencing a chemical reaction. Such
a value is non-ideal but approaches the values found in commercial cells [273].

Energy storage efficiency, derived by CCCD analysis up to 2.5 V, has a mean value of 88%
and a RSD% of ±1.1 % between samples B, C and D. While this indicates consistency between
samples it also shows that energy storage efficiency is significantly less than charge storage
efficiency. This decrease is attributed predominantly to the electronic resistance as per Equation
(2.4) in Section 2.2.1; a visual indication of this in the CCCD plot is the voltage drop upon the
initiation of discharge. Again, such a value is non-ideal but is better than some reported for
commercial cells [273].

The mass specific energy density, calculated from CCCD discharge, has a mean value of
12.4 W h kg⁻¹ and a RSD% of ±1.6 %; it should be noted that this value is for the mass of two
electrodes. If Equation (2.8) is implemented (i.e. only 75% of energy is available), and assuming
that extending the voltage can be extended to 2.7 V under ideal conditions (i.e. maximum
energy efficiency), then a material and mass symmetric cell containing Sigma PAC could
potentially achieve a usable mass specific energy density of 10.3 W h kg⁻¹ with respect to the
mass of two electrodes, this agrees well with the lower estimates of Section 2.4.1 i.e. a real world
EDLC full cell using AC electrodes and organic electrolytes, such as TEA⁺BF₄⁻ in ACN, should
achieve between 9.5 W h kg⁻¹ and 28.5 W h kg⁻¹.

The mass specific power density, calculated from CCCD analysis and assuming matched
load conditions, has a mean value of 34.2 kW kg⁻¹ and a RSD% of 33.2%. This value is for the
mass of two electrodes and affirms the significant power capabilities which are expected from
capacitive materials. The significant RSD% is associated with the variation in resistance as
previously discussed.

Shown in Table 5.4 are the KPIs for material and mass symmetric cells containing Kynol
ACC, they are derived from CCCD and EIS analysis. It should be noted that sample C has been
pre-emptively excluded from the calculation of mean and RSD%, this is due to the occurrence
of abnormal behaviour in EIS analysis.

From Table 5.4 it is possible to see that the mean mass specific capacitance of a material
and mass symmetric cells containing Kynol ACC is 29.0 F g⁻¹ by CCCD analysis and 19.0 F g⁻¹
by EIS analysis; as with Sigma PAC, the lower value from EIS analysis is attributed to it being
conducted at 0 V and is general in agreement with CV analysis. Both values have a RSD% of about ±0.71 % which indicates excellent agreement between samples. The mass specific capacitance of a single Kynol ACC electrode can be inferred as 116 F g⁻¹ (as per Equation (2.10), Section 2.3.1).

Table 5.4 KPIs for material and mass symmetric cells containing Kynol ACC.

<table>
<thead>
<tr>
<th>ACC:ACC (1:1)</th>
<th>Mass Specific Cell Capacitance (CCCD)</th>
<th>Mass Specific Cell Capacitance (EIS 10 mHz) a</th>
<th>Areal Resistance (CCCD)</th>
<th>Areal Resistance (EIS 1 Hz) b</th>
<th>Charge storage efficiency (CCCD)</th>
<th>Energy storage efficiency (CCCD)</th>
<th>Mass Specific Energy Density (CCCD)</th>
<th>Mass Specific Power Density c (CCCD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1:1) Sample A</td>
<td>29.2 F g⁻¹</td>
<td>19.0 F g⁻¹</td>
<td>24.3 Ω cm⁻²</td>
<td>33.6 Ω cm⁻²</td>
<td>95 %</td>
<td>66 %</td>
<td>18.2 W h kg⁻¹</td>
<td>1.88 kW kg⁻¹</td>
</tr>
<tr>
<td>(1:1) Sample B</td>
<td>28.7 F g⁻¹</td>
<td>18.8 F g⁻¹</td>
<td>32.3 Ω cm⁻²</td>
<td>56.6 Ω cm⁻²</td>
<td>94 %</td>
<td>59 %</td>
<td>16.1 W h kg⁻¹</td>
<td>1.29 kW kg⁻¹</td>
</tr>
<tr>
<td>(1:1) Sample C</td>
<td>30.3 F g⁻¹</td>
<td>22.4 F g⁻¹</td>
<td>51.8 Ω cm⁻²</td>
<td>71.3 Ω cm⁻²</td>
<td>97 %</td>
<td>53 %</td>
<td>12.7 W h kg⁻¹</td>
<td>0.57 kW kg⁻¹</td>
</tr>
<tr>
<td>(1:1) Sample D</td>
<td>29.1 F g⁻¹</td>
<td>19.2 F g⁻¹</td>
<td>29.1 Ω cm⁻²</td>
<td>46.9 Ω cm⁻²</td>
<td>95 %</td>
<td>64 %</td>
<td>17.0 W h kg⁻¹</td>
<td>1.46 kW kg⁻¹</td>
</tr>
<tr>
<td>Mean d</td>
<td>29.0 F g⁻¹</td>
<td>19.0 F g⁻¹</td>
<td>28.5 Ω cm⁻²</td>
<td>45.7 Ω cm⁻²</td>
<td>95 %</td>
<td>63 %</td>
<td>17.1 W h kg⁻¹</td>
<td>1.54 kW kg⁻¹</td>
</tr>
</tbody>
</table>

Relative Standard Deviation d ±0.86  ±1.13  ±14.1  ±25.2  ±0.61  ±5.72  ±6.12  ±19.7

a EIS conducted at 0V
b Knee frequency is 1 Hz
c Under matched load condition with a maximum voltage of 2.5 V
d Excluding sample C due to significant differences shown in Figures

With regards to areal resistance of samples A, B and D: CCCD analysis presents a mean value of 28.5 Ω cm² with RSD% of ±11.5 % and EIS analysis presents a mean value of 45.7 Ω cm² with a RSD% of ±20.6 %. These values are significantly higher than those of Sigma PAC based samples, but the RSD% is lower. While this may also be attributed to the instrumental setup (i.e. the use of crocodile teethed clips), it is believed to have three other possible sources: the first is restricted ion diffusion due to the predominantly microporous structure, the second is high contact resistance due to the external morphology of Kynol ACC and the third is a lack of stack pressure due to the use of a single spacer.

On one hand, the mean charge storage efficiency at 95% with an RSD% of ±0.50 is in good agreement with Sigma PAC based cells. On the other hand, the mean energy storage
efficiency at 61% with an RSD% of ±4.67 is significantly lower than Sigma PAC based cells. This decrease is attributed to the high areal resistance which causes a large voltage drop upon the initiation of self-discharge; such drop is clearly visible in all samples presented in Figure 5.2 (b). This decrease in mean energy storage efficiency significantly impacts the mean mass specific energy density, while the capacitance of Kynol ACC is almost double that of Sigma PAC the energy density is only 23% greater. Under ideal conditions (i.e. maximal energy storage efficiency) and applying Equation (2.8) up to 2.7 V suggests a material and mass symmetric cells containing Kynol ACC could potentially achieve a usable mass specific energy density of 19.8 W h kg⁻¹ with respect to the mass of two electrodes, this agrees with estimates from Section 2.4.1.

The mean mass specific power density for a material and mass symmetric cells containing Kynol ACC, calculated from CCCD analysis and assuming matched load conditions, is 1.54 kW kg⁻¹ with an RSD% of 16.07%. This is lower than Sigma PAC based cells and corresponds proportionally with the increase in areal resistance.

5.3.3 Conclusion - Material and Mass Symmetric Cells

The properties of Sigma PAC and Kynol ACC used in cells with material and mass symmetry have been assessed. It has been broadly found that Sigma PAC presents high power capabilities with a mean value of 34.2 kW kg⁻¹. In contrast, Kynol ACC presents high energy storage capabilities with a mean value of 16.0 W h kg⁻¹, albeit at only 61% energy storage efficiency. The primary difference in energy storage capability is attributed to the difference in SSA value which leads to differences in mass specific capacitance. The low energy storage efficiency presented by Kynol ACC samples is attributed to three factors:

- Restricted ion diffusion due to the predominantly microporous structure.
- High contact resistance due to the external morphology of Kynol ACC.
- Lack of stack pressure due to the use of a single spacer.

While the first two attributes are intrinsic properties of Kynol ACC, the third attribute is an extrinsic factor which can be changed; this change was attempted in later experimentation involving Kynol ACC.

In the case of both materials the RSD% of mass specific capacitance is consistently low (< 2.5%) between samples and across testing techniques. In contrast, the RSD% of areal resistance
is consistently high (20 to 30%); this possibly indicates that factors external to the intrinsic electrode properties are at influencing results. One possible factor, which influences all cell types, may be the use of crocodile clips for experimental setup.

A fundamental aim of this experiment set was to assess whether the selected material SSA ratio 1:0.52 does indeed provide a capacitance ratio approaching 1:0.54. The mean electrode specific capacitance values of Kynol ACC and Sigma PAC are 116 and 60 F g⁻¹, respectively; this produces a capacitance ratio of 1:0.52 which agrees exactly with the microporous SSA ratio (derived from GCMC) of these materials. This is a significant finding considering that these AC materials have wholly different precursor materials and external morphologies. These materials were deemed fundamentally suitable for testing the hypothesis that capacitance balancing can be achieved through electrode material asymmetry alone.

5.4 Potentiostatic Ageing of Material Symmetric while Mass Asymmetric EDLC Cells

5.4.1 Cell Configurations – Material Symmetric but Mass Asymmetric Cells

The focus of this section is to validate previous work in this field [168], the details of which are discussed in Section 2.4.3 and with respect to the active electrode material Sigma PAC used in the present study. This requires producing cells which are material symmetric but mass asymmetric and with a capacitance ratio of 1:0.54 (i.e. such that the positive electrode accounts for 65% of the total electrode mass [168]) which was found to provide the optimum operational voltage window for electrolyte 1M TEA⁺BF₄ in ACN. Specifically, an increase in positive electrode mass relative to the negative electrode mass (through mass balancing) also increases the extrinsic capacitance of the positive electrode; if an equivalent amount of charge is passed through a more massive electrode its change in voltage will be reduced thus allowing optimal usage of the stable voltage window (found to be ~1 V for the positive electrode and ~ -2 V for the negative electrode [168]). Validation of this work will not only provide sufficient basis that previous work in this field is well founded but will also validate the experimental techniques in use, alongside behaving as a control result for further experiments.

Validation of the work conducted in [168] could be achieved by reproducing the entire data set, but this would be time consuming and detract from the hypothesis at hand; instead, it was elected to pursue specific data points produced in [168]. Of particular interest were the mass ratios m(1:1) and m(1:0.54), the first ratio represents a control cell with no mass balancing and
the second represents the mass ratio at which minimal aging occurred. It was also of interest to appreciate what happens when this optimal ratio is reversed i.e. m(1:2); this point represents an additional specimen of interest as it possesses the opposite configuration of that believed to be optimal.

Three types of material symmetric cell were fabricated which fit with the mass ratios described above. The material selected for this experimentation was Sigma PAC, selected because it demonstrated both reasonable energy and power performance in Section 5.3. Additionally, the material used in [168] was also a form of PAC with a mass specific capacitance of less than 100 F g⁻¹ per single electrode mass.

One aspect of importance is the fact that the ageing in [168] was conducted at a voltage of 3.5 V. Preliminary experimentation was attempted at this voltage but it was found that significant gas evolution occurred, causing coin cells to rupture after only a few hours. The cause of this may be due to the lack of a pressure release vent; in [168] they do not describe their containment method in detail but it is assumed either gas evolution was negligible or a method other than coin cells was used for containment. The suggestion that gas evolution may have been negligible brings into question the purity of electrolyte used in experimentation. In [168] they mention that their TEA⁺BF₄⁻ in ACN electrolyte has a water content of less than 30 ppm; the electrolyte used in this work contained ACN solvent with a water content of less than 0.005% i.e. < 50 ppm. In addition, preliminary experiments involved drying electrodes at 100 °C for 24 h under high vacuum; this was found to be 20 °C lower than in [168]. It is entirely plausible that these small differences brought about the more significant gas evolution experienced in preliminary experimentation. From this finding it was decided to increase the drying temperature to 120 °C as per [168] but also to reduce the ageing voltage down to 2.7 V, the commonly stated maximum voltage for EDLC cells of this configuration [34].

Shown in Table 5.5 are the cell configurations for material but mass asymmetric samples containing Sigma PAC. The areal density and mass values refer to the active material alone i.e. that not including other cell components such as current collector. Two samples of each mass ratio were fabricated. Sample A and B were desired to be m(1:1); samples C and D were desired to be m(1:2) and samples E and F were desired to be m(1:0.54); it can be seen that all samples closely match their desired mass ratio. One item of note is that the combined mass of samples A and B does not match that of samples C, D, E and F; this was not of significant concern due to the use of potentiostatic ageing which, in theory, is dependent only upon the mass ratio. In all
sample cases the electrode mass is approaching or above the desired 10 mg quantity and thickness values range between 165 and 206 μm, which is in good agreement with research aim 5 (section 2.8). All cells contained 1.5 M TEA⁺BF₄⁻ in ACN electrolyte.

**Table 5.5** Cell configurations for material symmetric but mass asymmetric samples containing Sigma PAC; the target mass ratio is defined above sample name. Note that areal density and mass values refer to the active material alone.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Areal Density</th>
<th>Mass</th>
<th>Mass Ratio</th>
<th>Combined Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg cm⁻²</td>
<td>mg</td>
<td>mg(+) : (−)</td>
<td>µm(+) : (−)</td>
</tr>
<tr>
<td>A</td>
<td>4.99 / 4.94</td>
<td>8.81 / 8.72</td>
<td>1 : 0.99</td>
<td>17.54 / 167 / 165</td>
</tr>
<tr>
<td>B</td>
<td>4.90 / 5.05</td>
<td>8.65 / 8.92</td>
<td>1 : 1.03</td>
<td>17.58 / 170 / 174</td>
</tr>
<tr>
<td>C</td>
<td>5.43 / 10.91</td>
<td>9.59 / 19.28</td>
<td>1 : 2.01</td>
<td>28.88 / 179 / 205</td>
</tr>
<tr>
<td>D</td>
<td>5.41 / 10.88</td>
<td>9.56 / 19.23</td>
<td>1 : 2.01</td>
<td>28.80 / 168 / 206</td>
</tr>
<tr>
<td>E</td>
<td>11.09 / 5.83</td>
<td>19.60 / 10.30</td>
<td>1 : 0.53</td>
<td>29.91 / 196 / 160</td>
</tr>
<tr>
<td>F</td>
<td>10.93 / 5.90</td>
<td>19.31 / 10.42</td>
<td>1 : 0.54</td>
<td>29.74 / 190 / 163</td>
</tr>
</tbody>
</table>

**5.4.2 Theoretical Insight – Material Symmetric but Mass Asymmetric Cells**

In section 5.3 the mass specific capacitance for a single electrode based on Sigma PAC was estimated to be 60 F g⁻¹. In the mass asymmetric cells to be constructed both electrodes behave as individual capacitors which are connected in series. Thus, it is possible to estimate the total cell capacitance \( C_T \) based on the capacitance of each electrode, \( C_{E1} \) and \( C_{E2} \), as per equation (2.9). A similar approach can be implemented, through consideration of Equation (2.10), in which it is possible to estimate the total cell mass specific capacitance \( C_{Ts} \) (i.e. that of a two electrode cell) of a cell with two electrodes are of unequal mass (i.e. mass asymmetric); this approach is shown below in Equation 5.1:

\[
\frac{1}{C_{Ts}} = \left( \frac{m_T}{m_{E1}} \right) \frac{1}{C_{E1s}} + \left( \frac{m_T}{m_{E2}} \right) \frac{1}{C_{E2s}}
\]
Where $m_T$ is the total mass of both electrodes, $m_{E1}$ is the mass of electrode one, $m_{E2}$ is the mass of electrode two, $C_{E1s}$ is the mass specific capacitance of electrode one and $C_{E2s}$ is the mass specific capacitance of electrode two; in the case at hand $C_{E1s}$ equals $C_{E2s}$ i.e. 60.36 F g$^{-1}$. Thus, the theoretical mass specific capacitance and has been calculated for cells with electrode mass ratios $m(1:1)$, $m(1:2)$ and $m(1:0.54)$ and is presented in Table 5.6.

Table 5.6 Theoretical mass specific capacitance for cells based on Sigma PAC at both electrodes and electrode mass ratios $m(1:1)$, $m(1:2)$ and $m(1:0.54)$.

<table>
<thead>
<tr>
<th>PAC:PAC</th>
<th>Theoretical Mass Specific Capacitance F g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>m(+ : -)</td>
<td></td>
</tr>
<tr>
<td>$m(1:1)$</td>
<td>15.09</td>
</tr>
<tr>
<td>$m(1:2)$</td>
<td>13.35</td>
</tr>
<tr>
<td>$m(1:0.54)$</td>
<td>13.73</td>
</tr>
</tbody>
</table>

5.4.3 Results and Analysis – Material Symmetric but Mass Asymmetric Cells

Pre-age Testing

The results of CCCD testing at 0.28 A g$^{-1}$ for material symmetric (Sigma PAC) cells with mass ratios of $m(1:1)$, $m(1:2)$ and $m(1:0.54)$ are shown in Figure 5.7 (a). All sample sets appear to show excellent consistency under CCCD testing but it can be seen from the left inset that samples of $m(1:2)$ differ at high voltage; in fact, at this point of difference samples of $m(1:2)$ appear to present non-linear capacitance, an indicator that charge storage is not purely electrostatic in nature. Samples of $m(1:1)$ and $m(1:2)$ versus samples of $m(1:0.54)$ present a difference in the extent of their capacitive response; this is indicated by the time taken for one full charge-discharge cycle to complete. The extent of this difference will be clarified upon viewing the KPIs in Table 5.7 i.e. upon considering mass specific values.
Chapter 5: The impact of electrode capacitance ratio on asymmetric ACC/PAC EDLC electrochemical capacitors utilising organic electrolyte

![Image](image1.png)

**Figure 5.7** Material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54). Results of (a) CCCD testing at 0.28 A g⁻¹ (3rd cycle) and (b) mass specific capacitance-voltage plots derived from CV testing at 5 mV s⁻¹ (3rd cycle).

Figure 5.7 (b) shows the mass specific capacitance-voltage plots derived from CV testing at 5 mV s⁻¹ for material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54). Starting at low voltage (~0 V), it is evident that samples of m(1:2) and m(1:0.54) exhibit an almost identical mass specific capacitance while samples of m(1:1) are marginally higher; this agrees well with the theoretical estimations presented previously. Between 0.5 and 2 V all samples experience an increase in mass specific capacitance but samples of m(1:2) more so. Above 2 V samples of m(1:2) experience a rapid increase in mass specific capacitance, this strongly indicates an adverse chemical reaction is occurring; samples of m(1:1) and m(1:0.54) also experience an increase, with m(1:0.54) experiencing the least.

![Image](image2.png)

**Figure 5.8** Material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54). Results of EIS analysis at 0 V presented as (a) a Nyquist plot and (b) a Bode mass specific capacitance (BMSC) plot. In (a) samples of m(1:0.54) are specifically identified.
Shown in Figure 5.8 (a) are Nyquist plots for material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54). Generally, the results of mass asymmetric cells m(1:2) and m(1:0.54), are in fair agreement with those of mass symmetric cells i.e. m(1:1). One key area of difference is the imaginary impedance at 10 mHz (the upper most point), this differs between samples due to the differing combined electrode mass of samples. The major differences presented are with respect to samples of m(1:0.54); firstly, the electrode/electrolyte resistance is larger for sample F and secondly, both samples appear to present larger Warburg impedance than samples of m(1:1) and m(1:2) which indicates restricted ion diffusion.

The first difference, related to sample F with m(1:0.54), is believed to be due to poor connection with testing equipment. The second difference is interesting; insightful consideration leads the author to believe this is related to the differences in ion size (or more likely solvated ion size) being attracted to each electrode. In the case of m(1:2) and m(1:0.54) the total electrode mass is equivalent but the mass ratio is almost entirely opposite; m(1:2) has 1 g of positive electrode for every 2 g negative electrode while m(1:0.54) has 2 g of positive electrode for every 1.08 g negative electrode. In addition, due to the equivalent total mass of samples the charge being transferred between each electrode was also equivalent. As such, the larger diffusion resistance experienced by m(1:0.54) may be due to the increased ‘demand’ upon the negative electrode i.e. same quantity of charge transfer through a smaller quantity of material, this is compounded by the fact that it electrostatically adsorbs/desorbs the larger TEA⁺ ion. Such effects do not appear to be well defined in literature but while interesting, further assessment of this phenomenon is outside the scope of experimentation.
Shown in Figure 5.8 (b) are BMSC (Bode mass specific capacitance) plots for material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54). At a frequency of $10^3$ Hz all samples experience minor excitation, which corresponds to the initiation of a capacitive response; this point essentially indicates the starting knee frequency of the samples and appears to be a material specific property and unrelated to mass ratio. At frequencies between 10 Hz and 100 mHz the samples experience a rapid increase in capacitance and by 10 mHz the samples appear to have plateaued in terms of their capacitive response. The results of this indicate that m(1:1) possesses the highest capacitance at $\sim 12.5$ F g$^{-1}$, while samples of m(1:2) and m(1:0.54) reach $\sim 11$ F g$^{-1}$; these values are in agreement with the CV plots at 0 V (which is where EIS was conducted) and agree relatively (i.e. by magnitude of variation) with the theoretical mass specific capacitance values.

Shown in Figure 5.9 are BPA plots for material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54); while in reasonably close agreement there are subtle differences between samples. Samples of m(1:1) appear to present a plateau below 100 mHz whereas in samples of m(1:2) and m(1:0.54) this plateau is never fully formed; it has been suggested that this behaviour indicates an aspect of the cells in m(1:2) and m(1:0.54) is not ‘homogeneous’ and this could be related to the mass imbalance [274]. A different explanation can be found when considering that the lowest performing sample in BPA plots is the same sample with the highest resistance, which could indicate that resistance is a strong factor in empirical phase angle. The plot agrees with the BMSC plots in that the knee frequency occurs at $10^3$ Hz and all approach a value of $\Phi_{of} = 85^\circ$, which is close to ideal.

Shown in Table 5.7 are the KPIs for material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54). Mass specific capacitance calculated from CCCD discharge analysis indicates that samples of m(1:1) and m(1:2) possess a similar specific capacitance while samples of m(1:0.54) possess lower values; this is not entirely in agreement with the theoretical estimations, specifically it is samples of m(1:2) that do not agree. At first it was considered that this occurs due to chemical reactions as indicated in CV analysis of m(1:2) samples, but then it was considered that if chemical reactions were occurring during discharge this would lower, not increase, the mass specific capacitance value due to its charge consumption effect. An alternative explanation is that BF$_4^-$ at the positive electrode is being intercalated rather than reactively consumed. This could provide a reason behind the effect of capacitance increase at voltages above 2.25 V, intercalation effectively increasing the available area for charge to be stored (by storing it under the surface). This effect would also arise during discharge (i.e. BF$_4^-$ de-
intercalation), thus providing the unexpected boost in mass specific capacitance. While there is little mention of such a phenomenon in literature, a recent paper (2015) suggested that BF₆⁻ intercalation may occur in AC materials when PC (propylene carbonate) is used as the solvent [275]. In contrast, the mass specific capacitance derived by EIS at 0 V is in fair agreement with the theoretical mass specific capacitance, again indicating that the boost in mass specific capacitance occurs due to phenomenon at higher voltages.

Table 5.7 KPIs for material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54); target mass ratio is defined above sample name.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>14.9</td>
<td>12.2</td>
<td>4.5</td>
<td>2.4</td>
<td>97</td>
<td>89</td>
<td>12.3</td>
<td>34.5</td>
</tr>
<tr>
<td>B</td>
<td>14.7</td>
<td>12.5</td>
<td>3.2</td>
<td>1.6</td>
<td>96</td>
<td>88</td>
<td>12.2</td>
<td>48.8</td>
</tr>
<tr>
<td>C</td>
<td>14.9</td>
<td>10.7</td>
<td>4.5</td>
<td>3.8</td>
<td>91</td>
<td>78</td>
<td>11.7</td>
<td>21.3</td>
</tr>
<tr>
<td>D</td>
<td>14.0</td>
<td>11.4</td>
<td>4.2</td>
<td>3.6</td>
<td>92</td>
<td>79</td>
<td>11.3</td>
<td>22.5</td>
</tr>
<tr>
<td>E</td>
<td>12.8</td>
<td>10.9</td>
<td>4.2</td>
<td>3.8</td>
<td>99</td>
<td>88</td>
<td>10.2</td>
<td>21.9</td>
</tr>
<tr>
<td>F</td>
<td>12.7</td>
<td>11.0</td>
<td>6.4</td>
<td>7.4</td>
<td>98</td>
<td>87</td>
<td>10.1</td>
<td>14.2</td>
</tr>
</tbody>
</table>

a EIS conducted at 0 V.

b Under matched load condition with a peak voltage of 2.5 V and calculated at 0.28 A g⁻¹.

The areal resistance values from CCCD and EIS are in reasonable agreement with sample B m(1:1) achieving the lowest areal resistance and sample F m(1:0.54) achieving the highest; these do not agree with their partner sets but as there are only two samples of each it is not possible to discern which better represents reality. One interesting insight from EIS analysis is that samples of m(1:1), which possess the lowest total electrode mass, are half as resistive as those of m(1:2) and m(1:0.54); this indicates correlation between electrode thickness and areal resistance.

The charge storage efficiency derived from CCCD plots appears to decrease as the mass ratio becomes negative dominated i.e. approaching m(1:2). This is an indication that adverse
chemical phenomena (be they reactions or intercalation) are occurring. In samples of m(1:0.54), the ideal ratio recommended in [168], the charge storage efficiency is almost unity indicating that adverse chemical phenomena are not occurring. This is a promising development which supports the work done in [168]. Energy storage efficiency data derived from CCCD plots for samples of m(1:1) and m(1:0.54) are in good agreement with each other while samples of m(1:2) are notably less efficient; while energy storage efficiency in general is dominated by cell resistance (as per Equation (2.4)) it is also linked to charge storage efficiency.

Energy density was derived from CCCD, with the maximal value being achieved in samples of m(1:1), followed by m(1:2) and finally m(1:0.54) being least. The exact values achieved demonstrate a complex dependency between capacitance and energy storage efficiency; note that these have not been idealized (through Equation (2.7)) and represent true cell values. Power density is maximal in m(1:1) with m(1:2) and m(1:0.54) being lower, sample F stands out as being the lowest but samples C, D and E are all in good agreement. This again highlights the strong relationship between coating areal density, thickness and resistance which has been previously suggested in literature (see Section 2.6).

**Results of Cell Ageing**

Cell ageing was conducted in order to verify that the mass ratio of m(1:0.54) does indeed provide significant lifespan improvements as per [168]. Ageing was studied in cells containing mass ratios of m(1:1), m(1:2) and m(1:0.54); cell configurations and the results of pre-age testing have been detailed previously in this section. All samples experienced potentiostatic ageing at 2.7 V for up to 100 hours as per Section 5.2.3, similar in principle to that in [168]. Due to the complex nature of the ageing process different representations of it been developed:

- **Figure 5.10** – CCCD comparison over 100 hours in 20 hour periods.
- **Figure 5.11** – CV comparison over initial 60 hours in 20 hour periods.
- **Figure 5.12** – Mass specific capacitance and areal resistance as a function of ageing.
- **Figure 5.13** – Charge and energy storage efficiency as a function of ageing.

Each figure contains details for samples of m(1:1), m(1:2) and m(1:0.54); it should be noted that only one sample was used to represent each mass ratio in CV comparison, this was to provide clear comparability and avoid repetitive representation. It is suggested that the reader reviews these figures prior to their upcoming analysis and discussion.
In Figures 5.10 to 5.13 it can be clearly seen that capacitance balancing through application of a mass ratio can achieve significant improvements in cell lifespan performance. On one hand, samples of m(1:0.54) experience minimal loss of mass specific capacitance and maintain low resistance, high charge storage efficiency and high energy storage efficiency. On the other hand, samples of m(1:1) and m(1:2) experience eventual cell failure; this results in negligible mass specific capacitance, up to 80x increase in areal resistance and an eventual reduction to 0% charge and energy storage efficiency. Cells of m(1:1) are considered to fail at around 40 hours while samples of m(1:2) are considered to fail at around 50 hours.

![Voltage vs. Time Graph](image)

Figure 5.10  CCCD performance at 0.28 A\,g\(^{-1}\) (3\textsuperscript{rd} run) relative to potentiostatic ageing at 2.7 V of material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54).
Chapter 5: The impact of electrode capacitance ratio on asymmetric ACC/PAC EDLC electrochemical capacitors utilising organic electrolyte

Figure 5.11 CV performance at 5 mV s\(^{-1}\) (3\(^{rd}\) cycle) after potentiostatic ageing at 2.7 V of material symmetric cells (Sigma PAC). Sample B represents m(1:1), sample C represents m(1:2) and sample E represents m(1:0.54).

Figure 5.12 Mass specific capacitance and areal resistance as a function of potentiostatic ageing at 2.7 V for material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54).
Capacitive Energy Storage: 
Filling the gap

Figure 5.13 Charge storage efficiency and energy storage efficiency as a function of potentiostatic ageing at 2.7 V for material symmetric cells (Sigma PAC) with mass ratios of m(1:1), m(1:2) and m(1:0.54).

Let us first consider the mass specific capacitance of samples of m(1:1) and m(1:2), this noticeably degrades until almost non-existent after 100 hours of potentiostatic ageing at 2.7 V. According to the detailed plotting of mass specific capacitance as a function of ageing (Figure 5.12), this decrease occurs through multiple steps; there is an initial loss followed by a shoulder like plateau followed by a second significant loss until total degradation occurs. Interestingly, samples of m(1:1) degrade slowly at their first loss step and rapidly in the second loss step, whereas samples of m(1:2) degrade significantly in their first loss step and at an accelerating rate in their second loss step. Further, consider areal resistance as a function of ageing; this clearly shows that increased resistance is associated with the second loss step.

As previously stated in section 2.4.3, cell ageing can occur for three reasons: (1) applying high cell voltage, at or beyond the electrolyte’s ESPW, resulting in adverse electrode reduction/oxidation (redox); (2) permanent electrolyte ion intercalation or electrochemical reaction of organic electrolytes, and (3) harsh working conditions, such as high temperatures [34]. The third possibility has been ruled out in all cases as ageing was being conducted in a controlled environment, at a constant temperature of 25 °C. Let us consider the broadest
Chapter 5: The impact of electrode capacitance ratio on asymmetric ACC/PAC EDLC electrochemical capacitors utilising organic electrolyte

Physical impacts of these ageing processes: adverse electrode reduction/oxidation would result in a build-up of material at the electrode surface, permanent ion intercalation would result in reduced ion availability and electrochemical reaction of electrolyte could result in gas generation.

As such, it is possible to suggest that the initial loss in mass specific capacitance is most likely associated with permanent (irreversible) ion intercalation, such a phenomenon could provide a minimal increase in resistance but significantly impact mass specific capacitance. For samples of m(1:1) it may be suggested that the initially high charge storage efficiency does not indicate permanent ion intercalation but it must be reiterated (see Section 2.2.4) that intercalation is fundamentally not a reaction: if an ion becomes intercalated then electrons are not permanently associated with that ion and as such may continue to be transported between electrodes, thus keeping charge storage efficiency high.

From this, the second loss in mass specific capacitance may be associated with either adverse electrode redox and/or reaction of organic electrolytes. Adverse electrode redox reactions may produce excessive surface material which could behave as an electronic insulator or block the microporous structure, while gas bubbles produced by the reaction of organic electrolytes could also block the microporous structure. Of the two, it is believed that reaction of organic electrolytes, in this case TEA⁺BF₄⁻ in ACN is the more likely, due to its reported decomposition to gaseous products at excessive voltages [34].

An interesting aspect of m(1:2) samples is the initial loss (dip) in charge storage efficiency, followed by a temporary increase until it eventually becomes negligible; the point of temporary increase appears to correspond to the total degradation of mass specific capacitance. It is believed that charge storage efficiency can provide a strong indication of any chemical reactions occurring so a dip in charge storage efficiency indicates the point of reaction; this dip appears to correspond with the point at which mass specific capacitance is decreasing.

Samples of m(1:0.54) exhibit a gradual loss in capacitance combined with a gradual increase in areal resistance; this increase in resistance is reflected in energy storage efficiency values, particularly for sample F. There is uncertainty as to what causes the ageing process in these samples as no significant correlations can be drawn. The use of a QRE (quasi-reference electrode) would have been ideal in clarifying this but unfortunately at this point the developed QRE was not yet ready for use in testing.
5.4.4 Conclusion – Material Symmetric but Mass Asymmetric Cells

Testing of material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54) was conducted prior to ageing. In all cases of CCCD and CV testing, the results of sample types were in good agreement with one another. However, there was slight deviation between samples of m(1:0.54) when conducting EIS analysis. Through EIS analysis at 0 V the pre-ageing mass specific capacitance of all samples are in good agreement with the theoretical capacitance values derived in Section 5.4.2. When mass specific capacitance is derived from CCCD and CV analysis there is a significant deviation in samples of m(1:2) from the theoretical values, this is believed to be due to the occurrence of additional electrochemical phenomena such as ion intercalation.

Analysis of Nyquist plots derived by EIS showed that samples of m(1:0.54) exhibited larger Warburg impedance than samples of m(1:1) and m(1:2). This is believed to be due to an increasing dependence upon the charge transfer capability (predominantly in terms of ionic conductivity) of the negative electrode as its mass has not been increased i.e. the same quantity of charge must transfer through a smaller quantity of material, this is compounded by the fact that it electrostatically adsorbs/desorbs the larger TEA\(^+\) ion. Such a finding appears to be unreported in literature.

The areal resistance of pre-aged samples was assessed and found to be broadly equivalent across all sample types. One interesting insight from EIS analysis is that samples of m(1:1), which possess the lowest total electrode mass, are half as resistive as those of m(1:2) and m(1:0.54); this indicates correlation between electrode thickness and areal resistance. Power density was found to be maximal in samples of m(1:1) with m(1:2) and m(1:0.54) being lower. This highlighted the strong relationship between coating areal density, thickness and resistance which has been previously suggested in literature (see Section 2.6).

The subsequent ageing of samples appears to validate the previous work of Cercola et al. in [168] i.e. a mass ratio of m(1:0.54) will provide significant improvements towards cell lifespan. While it has not been conclusively proven that this mass ratio is optimal the experimental results clearly demonstrated that the principle of capacitance balancing to maximize individual electrode voltages without causing chemical reaction can indeed be achieved by implementing electrode mass asymmetry.
In addition to validating previous work it has been shown that the experimental techniques implemented are suitable for clearly showing the difference between cells with and without capacitance balancing. This is invaluable information for preparing later experiments. It was therefore reasonable to attempt next the achievement of capacitance balancing through material asymmetry.

5.5 Potentiostatic Ageing of Material Asymmetric (ACC/PAC) EDLC Cells

5.5.1 Cell Configurations – Material Asymmetric Cells

The focus of this section is to test the hypothesis that appropriately matching different materials at each electrode can result in capacitance balancing with the aim of cell lifespan extension. This is to be achieved in fundamentally the same manner as the preceding validation experiments in order to maintain comparability.

As such, the experimental setup will involve using Kynol ACC and Sigma PAC as the positive and negative electrode materials, respectively. From the electrochemical analysis of these AC materials (Section 5.3) it was found that the mean electrode specific capacitance values of Kynol ACC and Sigma PAC are 116 and 60 F g⁻¹, respectively. As such, these materials could in theory be implemented in a mass symmetric configuration whilst still producing a capacitance ratio of c(1:0.52), which is in excellent agreement with the desired material capacitance ratio of c(1:0.54) (as defined by [168]).

Shown in Table 5.5 are the cell configurations for material asymmetric samples utilizing Sigma PAC as the negative electrode and Kynol ACC as the positive electrode. The intention of this experiment was to assess if samples containing m(1:1) could still achieve capacitance balancing; unfortunately, the mass of Sigma PAC electrodes selected did not match exactly with the mass of Kynol electrodes; this was due to the use of tape casting when fabricating Sigma PAC electrodes which presented a lack of direct control over the areal density. As such, samples A and B were produced with mass ratios of m(1:0.93) which results in a capacitance ratio of c(1:0.48). While not ideal, this arrangement will still provide insight as to whether the hypothesis is supported.
Table 5.8 Cell configurations for material asymmetric samples utilizing Sigma PAC as the negative electrode and Kynol ACC as the positive electrode, descriptive mass values refer to the active material alone.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>12.63 / 11.79</td>
<td>22.32 / 20.84</td>
<td>1 : 0.93</td>
<td>43.16</td>
<td>350 / 225</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>12.11 / 11.35</td>
<td>21.40 / 20.06</td>
<td>1 : 0.93</td>
<td>41.46</td>
<td>350 / 254 b</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>12.90 / 6.69</td>
<td>22.79 / 11.82</td>
<td>1 : 0.52</td>
<td>34.61</td>
<td>350 / 188</td>
<td>95.1</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>12.77 / 6.31</td>
<td>22.56 / 11.14</td>
<td>1 : 0.49</td>
<td>33.70</td>
<td>350 / 172</td>
<td>92.2</td>
<td></td>
</tr>
</tbody>
</table>

a All electrodes were 15 mm disks thus coating area was 176 mm².
b PAC thickness estimated from equation for linear trend line shown in Figure 4.15 due to loss of data.

Further to this, samples C and D were produced with combined material and mass asymmetry. These cells have an average mass ratio of m(1:0.51) and corresponding capacitance ratio of c(1:0.27) but in practice these values differ slightly; as such they will be clearly identified where necessary in the upcoming results section. These samples were included to assess if the capacitance ratio is indeed the sole contributor towards preventing excessive ageing and when related to work completed in [168] and should age faster than Samples A and B. In all samples the thickness and electrode mass are in good agreement with research aim 5 (i.e. between 100 and 200 μm and greater than 10 mg). All cells contained 1.5 M TEA⁺BF₄⁻ in ACN electrolyte and used one coin cell spacer (1 mm in thickness).

5.5.2 Theoretical Insight – Material Asymmetric Cells

In section 5.4.2 it was shown possible to estimate the total cell mass specific capacitance $C_{TS}$ (i.e. that of a two-electrode cell) for a cell with two electrodes of unequal mass (i.e. mass asymmetric); this approach was shown in Equation 5.1. As the mass specific capacitance could be defined for each electrode respectively then Equation 5.1 is also suitable for calculating the total mass specific capacitance of a cell with both material and mass asymmetry. Thus, the theoretical mass specific capacitance has been calculated for material asymmetric ('ACC:PAC) cells with mass ratios of m(1:0.93) and m(0.51) and are presented below:
Table 5.9 Theoretical mass specific capacitance for material asymmetric (+ACC:PAC) cells with mass ratios of $m(1:0.93)$ and $m(0.51)$.

<table>
<thead>
<tr>
<th>$+\text{ACC:PAC}$</th>
<th>Theoretical Mass Specific Capacitance $F , g^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m(1:0.93)$</td>
<td>19.6</td>
</tr>
<tr>
<td>$m(1:0.51)$</td>
<td>16.1</td>
</tr>
</tbody>
</table>

5.5.3 Results and Analysis – Material Asymmetric Cells

**Pre-age Testing**

The results of CCCD testing at 0.28 A g$^{-1}$ for material asymmetric (+ACC:PAC) cells with mass ratios of $m(1:0.93)$ and $m(0.51)$ are shown in Figure 5.14 (a). It is possible to see that all samples slightly differ in performance, with samples of $m(1:0.93)$ being the most consistent. The significant variation in samples C and D can possibly be attributed to their differing mass ratios as previously described. In all cases the samples possess a high voltage drop at the change from charge to discharge, indicating high contact resistance; this was also exhibited in cells containing purely Kynol ACC (Section 5.3) and has been previously attributed to either electrode morphology or the use of a single spacer. This plot is quantitatively analysed in Table 5.10.

![Figure 5.14](image)

Figure 5.14 Material asymmetric (+ACC:PAC) cells with mass ratios of $m(1:0.93)$ and $m(0.51)$. Results of (a) CCCD testing at 0.28 A g$^{-1}$ (3rd cycle) and (b) mass specific capacitance-voltage plots derived from CV testing at 5 mV s$^{-1}$ (3rd cycle).

Shown in Figure 5.14 (b) are the mass specific capacitance-voltage plots derived from CV testing at 5 mV s$^{-1}$ for material asymmetric (+ACC:PAC) cells with mass ratios of $m(1:0.93)$ and $m(0.51)$. It is apparent that samples are strongly in agreement with one another with respect to
the capacitive response; this is possible due to the slow scan rate providing a picture free from significant resistive effects. This picture is contrary to the idea drawn from CCCD plots that the sample variation between C and D caused the differences seen. The mass specific capacitance of each sample type appears to be marginally less than those predicted but are reasonably in agreement. All samples show a rise in capacitance above 2.25 V, which may be attributed to adverse chemical reactions of the two cell types, samples of m(0.51) present a more pronounced rise.

Shown in Figure 5.15 (a) are Nyquist plots for material asymmetric (*ACC:PAC*) cells with mass ratios of m(1:0.93) and m(0.51). All samples present similar solution resistance alongside significant polarization resistance. Samples of m(1:0.93) appear to be in reasonable agreement as to the magnitude of this polarization resistance but samples of m(0.51) differ significantly. As the CV plots of these cells were in excellent agreement it is suggested that these differences are related to either fibrous electrode morphology or the use of a single spacer (which reduces electrode stack pressure). This plot is quantitatively analysed in Table 5.10.

![Nyquist plots](image)

**Figure 5.15** Material asymmetric (*ACC:PAC*) cells with mass ratios of m(1:0.93) and m(0.51). Results of EIS analysis at 0V presented as (a) a Nyquist plot and (b) a Bode mass specific capacitance (BMSC) plot. In (a) samples specifically identified.

Viewing EIS at 0 V from the perspective of a BMSC plot (Figure 5.15 (b)) provides insight as to frequencies between which material asymmetric (*ACC:PAC*) cells with mass ratios of m(1:0.93) and m(0.51) transitions to a capacitive response. At frequencies higher than 10 Hz all cells are completely non-capacitive, at 10 Hz they all begin the transition. This is lower than the material symmetric counterparts i.e. (*PAC:PAC*) and (*ACC:ACC*) which experience the start of transitions at 1 kHz and ~50 Hz, respectively. This transition is completed by ~100 mHz,
which is in agreement with (*ACC:ACC*) samples, but does not result in an ideal plateau region as found in (*PAC:PAC*) samples. The mass specific capacitance values at 10 mHz agree relatively with those theoretically estimated but are still below the theoretical values; this is presumably related to EIS being conducted at 0 V.

Shown in Figure 5.16 is a BPA plot of EIS data acquired at 0 V for material asymmetric (*ACC:PAC*) cells with mass ratios of m(1:0.93) and m(0.51). The high frequency dip associates with the polarization ‘loop’ shown in the corresponding Nyquist plot. The knee frequency was considered discernible in the BMSC plots but according to BPA plots it is not until at a frequency of 1 Hz that the samples become truly capacitive, as such the quantified areal resistance values will be taken at this frequency. At low frequency, all samples of (*ACC:PAC*) behave in a similar fashion to those of (*ACC:ACC*) i.e. not approaching an ideal phase angle of 90 °, this indicates that energy storage efficiency will be low.

![BPA plot of EIS data](image)

**Figure 5.16** Material asymmetric (*ACC:PAC*) cells with mass ratios of m(1:0.93) and m(0.51). Results of EIS analysis at 0V presented as a Bode phase angle (BPA) plot.

Shown in Table 5.7 are the KPIs for material asymmetric (*ACC:PAC*) cells with mass ratios of m(1:0.93) and m(0.51). As stated during the introduction to this chapter, capacitance maximisation is most likely not realizable with the materials selected for producing material asymmetric cells; this agrees with the mass specific capacitance values derived by CCCD analysis i.e. m(1:0.93) are 10% lower than those theoretically predicted. While these values are an improvement on cells containing purely Sigma PAC they do not approach those of cell containing purely Kynol ACC. This is in addition to retaining the high areal resistance, and thus poor energy storage efficiency, of symmetric Kynol ACC cells which results in mediocre mass
specific energy density and power density values. While this may indicate Kynol ACC is a highly resistive material unsuitable for use in EDLC devices, there is equal indication that the electrode stacking pressure may not have been high enough, which could be limiting material performance.

Table 5.10  KPIs for material asymmetric (ACC:PAC) cells with mass ratios of m(1:0.93) and m(0.51), descriptive mass ratio is defined above sample name.

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>17.7</td>
<td>15.3</td>
<td>37.3</td>
<td>56.0</td>
<td>98</td>
<td>60</td>
<td>9.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Sample B</td>
<td>17.7</td>
<td>15.9</td>
<td>33.4</td>
<td>49.4</td>
<td>99</td>
<td>64</td>
<td>9.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Sample C</td>
<td>14.3</td>
<td>12.6</td>
<td>35.8</td>
<td>46.4</td>
<td>99</td>
<td>67</td>
<td>8.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Sample D</td>
<td>14.5</td>
<td>13.5</td>
<td>50.1</td>
<td>77.4</td>
<td>98</td>
<td>60</td>
<td>7.2</td>
<td>0.9</td>
</tr>
</tbody>
</table>

a EIS conducted at 0V  
b Knee frequency is 1 Hz  
c Under matched load condition with a peak voltage of 2.5 V and calculated at 0.28 A g⁻¹

**Results of Cell Ageing**

Cell ageing was conducted to test the hypothesis that appropriately matching different materials at each electrode can result in capacitance balancing with the aim of cell operating lifespan extension. Material asymmetric (ACC:PAC) cells containing mass ratios of m(1:0.93) and m(0.51) have been produced, cell configurations and pre-age testing have been previously detailed. All samples experienced potentiostatic ageing at 2.7 V for up to 100 hours as per Section 5.2.3, similar in principle to that of [168]. Ageing data is presented as:

Figure 5.17 – CCCD comparison over 100 hours in 20 hour periods.

Figure 5.18 – CV comparison over initial 60 hours in 20 hour periods.

Figure 5.19 – Mass specific capacitance and areal resistance as a function of ageing.

Figure 5.20 – Charge and energy storage efficiency as a function of ageing.
Chapter 5: The impact of electrode capacitance ratio on asymmetric ACC/PAC EDLC electrochemical capacitors utilising organic electrolyte

Each figure contains details for samples of m(1:0.93) and m(0.51). It should be noted that only one sample was used to represent each mass ratio in CV comparison, this was to provide clear comparability and avoid repetitive representation. It is suggested that the reader reviews these figures prior to their upcoming analysis and discussion.

Figure 5.17 CCCD performance at 0.28 A g⁻¹ (3rd run) relative to potentiostatic ageing at 2.7 V of material asymmetric (ACC:PAC) cells with mass ratios of m(1:0.93) and m(0.51).
Capacitive Energy Storage: Filling the gap

Figure 5.18  CV performance at 5 mV s\(^{-1}\) (3\(^{rd}\) cycle) after potentiostatic ageing at 2.7 V of material asymmetric (‘ACC:PAC’) cells. Sample A represents m(1:0.93) and sample C represents m(1:0.51).

Figure 5.19  Mass specific capacitance and areal resistance as a function of potentiostatic ageing at 2.7 V for material asymmetric (‘ACC:PAC’) cells with mass ratios of m(1:0.93) and m(0.51).
Chapter 5: The impact of electrode capacitance ratio on asymmetric ACC/PAC EDLC electrochemical capacitors utilising organic electrolyte

![Graphs](image)

Figure 5.20 Charge storage efficiency and energy storage efficiency as a function of potentiostatic ageing at 2.7 V for material asymmetric (‘ACC:PAC’) cells with mass ratios of m(1:0.93) and m(0.51).

The results of ageing material asymmetric (‘ACC:PAC’) cells with mass ratios of m(1:0.93) and m(0.51) were surprising. It is quite apparent that sample A and B containing the mass ratio of m(1:0.93), which corresponds to a capacitance ratio of q(1:0.48) due to its material asymmetric nature, does not present a significantly prolonged lifespan as hypothesized. Both samples A and B present slightly different responses which is apparent in CCCD comparison and mass specific capacitance as a function of ageing. The cause of this difference is not entirely clear but it could be related to the fact that samples A and B possess slightly different combined mass values.

The CV comparison presented in Figure 5.18 shows that sample A, with m(1:0.93), internally contracts (forms a ‘rhombus’ shape) over the ageing process; this corresponds with an increase in areal resistance as shown by Figure 5.19. In contrast, the CV results of sample C, with m(1:0.51), maintain a constant response during the ageing process which corresponds with minimal change in areal resistance.

The time after which cells of m(1:0.93) are considered to fail is between 60 and 70 hours, which is an improvement in comparison to material symmetric samples i.e. (‘PAC:PAC’) of m(1:1) and m(1:2) which failed at around 40 to 50 hours, respectively. This is a mild
improvement indicating that there is some degree of positive effect from material asymmetry. This contrasts with samples which have been optimized through mass balancing i.e. samples of (PAC: PAC) with m(1:0.54) and samples of (ACC: PAC) with m(1:0.51), which both present lifespans beyond the 100 hour ageing experienced. This suggests that the mass of material in use at each electrode is not the sole influencer when it comes to designing cells with prolonged lifespan.

One alternative influence could be the AC material micro-texture i.e. the surface texture of the micropores. It has been noticed in the SSA plots of Sigma PAC and Kynol ACC (presented in Figure 4.9 on page 109) that Kynol ACC possesses micropores of ~1 nm while Sigma PAC does not. This indicates that a new micro-texture (porous structure) has formed alongside the high microporosity (1540 m² g⁻¹) of Kynol ACC. This structure is joined by an increase in pores of 0.5 nm in width also for Kynol ACC. Consideration of these structure changes is hampered by the fact that the PSD (derived from CCVD) is merely an interpretation of a sorption isotherm and does not necessarily represent the reality at hand. This means that the effects of the internal microporous structure cannot be fully understood by these methods, thus limiting the possible understanding of these structural influences.

Another alternative influence could have been the presence of heteroatoms (e.g. oxygen and nitrogen), in Kynol ACC material. To assess this possibility, raw samples of Sigma PAC and Kynol ACC were analysed using thermogravimetric analysis (TGA). Such a technique involves linearly increasing the temperature experienced by a sample material and assessing the mass loss as this temperature is increased; losses occur at specific temperature and correspond to different materials being decomposed. It was conducted using a TGA Q500 instrument manufactured by TA Instruments at temperatures between room temperature and 600 °C under a flow of nitrogen at a rate of 10 °C per minute, the results of this are presented below in Figure 5.21.
Figure 5.21 Thermogravimetric analysis (TGA) of Kynol ACC and Sigma PAC samples between room temperatures of 0 and 600 °C under a flow of nitrogen at a rate of 10 °C per minute.

From Figure 5.22 it can be seen that both AC materials possess similar surface moisture contents, this is indicated by the rapid mass loss below 50 °C. In the case of Kynol ACC this mass loss continues at a lower but steady rate until 400 °C, as there are no sudden variations in mass loss rate during this period it is assumed; this loss is associated purely with moisture content. The reason for loss at a low constant rate could be due to the purely microporous structure of Kynol ACC causing restricted moisture loss. In contrast, Sigma PAC exhibits a similar constant rate mass loss up until 200 °C, after which a significant loss in mass occurs at 250 °C; this is an indication that Sigma PAC contains heteroatoms. According to [276], this specific temperature range may associate with oxygen heteroatoms but there is no mention of this being present in the product specification [228]. After 250 °C the sample appears to level off resulting in a total mass loss equivalent to Kynol ACC. As such, while it was initially considered that the presence of heteroatoms in Kynol ACC may have degraded performance it in fact appears to be its lack of heteroatoms which could have degraded its performance. It should be noted that these heteroatoms are not present in sorption analysis due to the degassing temperature of 305 °C used in sample preparation.

A further possible influence could be derived from the results of TGA (Figure 5.21) of these materials. While moisture in Sigma PAC appears to be fully driven off by 250 °C in Kynol ACC it is not fully driven off until 400 °C. This indicates that moisture retention of Kynol ACC is much stronger than Sigma PAC. While it is often believed degassing at 120 °C for 24 hours under high vacuum is sufficient for degassing, it may be plausible that moisture rapidly returns during transit between the vacuum oven and argon filled glovebox. As moisture is known to
adversely affect electrolyte purity, which leads to a reduced voltage window, it may be that this is a cause for the unexpected deviation from the hypothesized results.

One final consideration was that the lack of binder used in Kynol ACC could have influence results, but upon deeper consideration it was realized that this would result in an improvement as it implied the entirety of the Kynol ACC electrode is AC material whereas in Sigma PAC electrode 5% of the mass is binder. This would skew the ‘true’ mass ratio to being positive heavy i.e. towards m(1:0.54).

5.5.4 Conclusion – Material Asymmetric Cells

Sigma PAC and Kynol ACC possess PSDs (pore size distributions) which are almost identical in structure and differ predominantly in magnitude, they present mass specific capacitance values of 60 and 116 F g⁻¹, respectively. These values produce a capacitance ratio of c(1:0.52) which fits well with the desired material capacitance ratio of c(1:0.54) (as defined by [168]). It was hypothesised that capacitance balancing could be used to maximise a cell's voltage window, thus improving energy storage and power capabilities, whilst minimising degradation when operating at high voltages and thus improving cycle life. As such, the experiments detailed in this section were conducted to test this hypothesis but apparently showed it to be false.

In addition to this, capacitance maximization, which relates to large quantities of pores 0.7 nm in width being present at the positive electrode, was not exhibited (when compared to the theoretical value). This, alongside high resistance, low energy storage efficiency, low mass specific energy density and low power density indicate this combination of materials is not ideal for producing EDLC cells.

Possible explanations of the unexpected deviation from the hypothesized results have been differences in microporous surface textures, heteroatom content of AC materials and moisture contamination. Possible explanations of the high resistance values, which directly influence energy and power capabilities, have been material morphology and use of a single in-cell spacer. As such, due to the limited scope of this study it has been decided that a broader study will be conducted in which two spacers will be used in cell fabrication alongside a wider variety of mass ratios.
5.6 The Impact of Mass Asymmetry on Potentiostatic Ageing of Material Asymmetric (ACC/PAC) EDLC Cells

5.6.1 Cell Configurations – Material and Mass Asymmetric Cells

The previous section found that the hypothesis at test in this chapter i.e. appropriately matching different materials at each electrode (Kynol ACC as the positive electrode and Sigma PAC as the negative electrode), can adequately achieve cell lifespan extension via capacitance balancing, is not necessarily true. This was discovered by producing two sets of material asymmetric cells with a mass ratio of either m(1:0.93) or m(1:0.51) and ageing them for 100 hours at 2.7 V inside an environmental chamber set to 25 °C. This previous experiment had two apparent shortcomings: first was the limited sample base and second was the use of a single spacer in cell construction. The focus of this section is to overcome those shortcomings and further investigate at what mass ratio a material asymmetric cell such as (ACC:PAC) achieves an extended lifespan.

As such, the experimental setup is fundamentally the same as that described in Section 5.5 but differs in the breadth of samples produced, ranging from m(1.27) to m(1:0.36); also, all coin cells will include two CR2032 spacers (1 mm thick) rather than one. Another unique addition to this section is the inclusion of a silver QRE (quasi-reference electrode); this was incorporated into one of the two sample coin cells created for analysis. As cells which possess a QRE necessitated two separators (see Section 4.5.3) it was decided to use two separators in all samples to minimize variability. In essence, this approach reflects that used by Cericola et al. in [168] with the fundamental difference being cells are aged at 2.7 V rather than 3.5 V; the reasoning for this has been explained previously in Section 5.4.1. It is important to recall that further work by the same group [168] suggested the ESPW of AC electrodes using TEA⁺BF₄⁻ in ACN is in the range between 1 V and −2 V relative to a carbon QRE [166].

Shown in Table 5.11 are the cell configurations for material asymmetric samples utilizing Sigma PAC as the negative electrode and Kynol ACC as the positive electrode. Kynol ACC is a cloth material and as such its areal mass was relatively constant; Sigma PAC electrodes were produced by tape casting. One pair of samples in this experiment has mass ratios of m(1:1), something which was not precisely achieved in previous experimentation. The remaining presented mass ratios are m(1:1.27), m(1:0.87), m(1:0.73), m(1:0.50) and m(1:0.36). It should be noted that two samples of each mass ratio were attempted but not all samples fit exactly with the mass ratios desired, as such the values above indicate the sample average.
Table 5.11 Cell configurations for material and mass asymmetric samples utilizing Sigma PAC as the negative electrode and Kynol ACC as the positive electrode; descriptive mass ratio is defined above sample name. Note that areal density and mass values refer to the active material alone.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ACC: PAC m(+: -)</th>
<th>Areal Density (+/-)</th>
<th>Mass (+/-)</th>
<th>Mass Ratio (+/-)</th>
<th>Combined Mass</th>
<th>Average Thickness (+/-)</th>
<th>Combined Volume a</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(1:1.27)</td>
<td>12.13 / 15.37</td>
<td>21.44 / 27.15</td>
<td>1 : 1.27</td>
<td>48.59</td>
<td>350 / 282</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>Sample B b</td>
<td>12.14 / 15.60</td>
<td>21.45 / 27.56</td>
<td>1 : 1.28</td>
<td>49.01</td>
<td>350 / 290</td>
<td>113</td>
</tr>
<tr>
<td>C</td>
<td>(1:1.00)</td>
<td>12.19 / 12.25</td>
<td>21.54 / 21.65</td>
<td>1 : 1.00</td>
<td>43.54</td>
<td>350 / 263 c</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td>Sample D b</td>
<td>12.13 / 12.29</td>
<td>21.43 / 22</td>
<td>1 : 1.01</td>
<td>43.45</td>
<td>350 / 263 c</td>
<td>108</td>
</tr>
<tr>
<td>E</td>
<td>(1:0.87)</td>
<td>12.00 / 10.33</td>
<td>21.21 / 18.26</td>
<td>1 : 0.86</td>
<td>39.47</td>
<td>350 / 243</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>Sample F b</td>
<td>12.03 / 10.71</td>
<td>21.26 / 18.92</td>
<td>1 : 0.89</td>
<td>40.18</td>
<td>350 / 247</td>
<td>105</td>
</tr>
<tr>
<td>G</td>
<td>(1:0.73)</td>
<td>12.41 / 8.98</td>
<td>21.93 / 15.86</td>
<td>1 : 0.72</td>
<td>37.79</td>
<td>350 / 228</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>Sample H b</td>
<td>12.17 / 8.95</td>
<td>21.50 / 15.82</td>
<td>1 : 0.74</td>
<td>37.32</td>
<td>350 / 227</td>
<td>102</td>
</tr>
<tr>
<td>I</td>
<td>(1:0.50)</td>
<td>12.10 / 6.38</td>
<td>21.38 / 11.27</td>
<td>1 : 0.53</td>
<td>32.65</td>
<td>350 / 192 c</td>
<td>95.8</td>
</tr>
<tr>
<td></td>
<td>Sample J b</td>
<td>12.03 / 5.78</td>
<td>21.26 / 10.22</td>
<td>1 : 0.48</td>
<td>31.48</td>
<td>350 / 183 c</td>
<td>94.1</td>
</tr>
<tr>
<td>K</td>
<td>(1:0.36)</td>
<td>11.96 / 4.32</td>
<td>21.13 / 7.63</td>
<td>1 : 0.36</td>
<td>28.76</td>
<td>350 / 158 c</td>
<td>89.8</td>
</tr>
<tr>
<td></td>
<td>Sample L b</td>
<td>12.01 / 4.27</td>
<td>21.23 / 7.54</td>
<td>1 : 0.36</td>
<td>28.77</td>
<td>350 / 157 c</td>
<td>89.7</td>
</tr>
</tbody>
</table>

a All electrodes were 15 mm disks thus coating area was 176 mm².
b Sample contains silver quasi-reference electrode.
c PAC thickness estimated from equation for linear trend line shown in Figure 4.15 due to loss of data (see Section 4.4.5).

5.6.2 Theoretical Insight – Material and Mass Asymmetric Cells

In section 5.4.2 it was shown possible to estimate the total cell mass specific capacitance \( C_{TS} \) (i.e. that of a two electrode cell) for a cell with two electrodes of unequal mass (i.e. mass asymmetric); this approach was shown in Equation 5.1. As the mass specific capacitance could be defined for each electrode respectively, Equation 5.1 is also suitable for calculating the total
mass specific capacitance of a cell with both material and mass asymmetry. Thus, the theoretical mass specific capacitance has been calculated for material and mass asymmetric (ACC:PAC) cells with a range of mass ratios and presented in Table 5.12.

Table 5.12 Theoretical mass specific capacitance and electrode specific capacitance and voltage values for material and mass asymmetric (ACC:PAC) cells with a range of mass ratios. Note that electrode specific voltage values are calculated by assuming an EDLC cell is charged from 0 to 2.5 V.

<table>
<thead>
<tr>
<th>ACC:PAC m(+ : -)</th>
<th>Theoretical Mass Specific Capacitance</th>
<th>Theoretical Capacitance Ratio c(+ : -)</th>
<th>Theoretical Peak Positive Electrode Voltage</th>
<th>Theoretical Peak Negative Electrode Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1:1.27)</td>
<td>20.3 F g⁻¹</td>
<td>1 : 0.66</td>
<td>0.99</td>
<td>-1.51</td>
</tr>
<tr>
<td>(1:1.00)</td>
<td>19.8 F g⁻¹</td>
<td>1 : 0.53</td>
<td>0.87</td>
<td>-1.63</td>
</tr>
<tr>
<td>(1:0.87)</td>
<td>19.3 F g⁻¹</td>
<td>1 : 0.46</td>
<td>0.79</td>
<td>-1.71</td>
</tr>
<tr>
<td>(1:0.73)</td>
<td>18.4 F g⁻¹</td>
<td>1 : 0.38</td>
<td>0.69</td>
<td>-1.81</td>
</tr>
<tr>
<td>(1:0.50)</td>
<td>15.9 F g⁻¹</td>
<td>1 : 0.25</td>
<td>0.50</td>
<td>-2.00</td>
</tr>
<tr>
<td>(1:0.36)</td>
<td>13.4 F g⁻¹</td>
<td>1 : 0.19</td>
<td>0.40</td>
<td>-2.10</td>
</tr>
</tbody>
</table>

a Assumed capacitance of a single electrode is four times two electrode capacitance (as per Equation (2.10)).
b Total peak cell voltage is assumed to be 2.5 V.

As some samples in this section also contained a silver QRE it was deemed appropriate to calculate the theoretical peak electrode voltage when the total peak cell voltage is assumed to be 2.5 V (a value selected due to its comparability with the experiments at hand), these theoretical values can subsequently be compared to the actual values calculated through the use of a silver QRE. The mean electrode specific capacitance values of Kynol ACC and Sigma PAC have been found to be 116 and 60 F g⁻¹, respectively. As such, the capacitance ratio can be inferred from the mass ratio and is presented in Table 5.12.

Calculating the corresponding theoretical peak voltage of a single electrode in a two electrode cell can be achieved by considering that the capacitance ratio (part-to-part) essentially defines the total voltage ‘fraction’ of each electrode e.g. if a cell of c(1:2) is charged to 3 V then one electrode will be 1 V while the other will be 2 V. A simplistic approach to this is converting the ratio (part-to-part) into a ratio (part-to-whole) such that the example above becomes c(1:3) for one part and c(2:3) for the other. Subsequently, multiplying this ratio (part-to-whole) by the maximum voltage provides the voltage of that electrode part. This has been put into the form
of Equation (5.2) where the electrode of interest is E1 and \(C_{E1\text{part}}\) is the numerator and \(C_{\text{whole}}\) is the denominator of a part-to-whole capacitance ratio.

\[
V_{E1} = V_{\text{max}} \frac{C_{E1\text{part}}}{C_{\text{whole}}} \tag{5.2}
\]

Thus, the theoretical peak voltage of both the positive and negative electrodes has been calculated for each descriptive mass ratio; these theoretical values are presented in Table 5.12.

5.6.3 Results and Analysis – Material and Mass Asymmetric Cells

Pre-age Testing

The results of CCCD testing at 0.28 A g\(^{-1}\) for material asymmetric (*ACC:PAC*) cells with material and mass asymmetric (*ACC:PAC*) cells with a range of mass ratios (presented in Figure 5.22), the full set of quantified results are presented later in Table 5.13. Shown in Figure 5.22 are the results of CCCD testing for samples which possess a QRE; this provided knowledge of electrode potential relative to this QRE which was subsequently normalized to the total cell voltage. It is important to understand what this normalization means; as previously mentioned in Section 3.3.3, a QRE lacks thermodynamic equilibrium thus it must be calibrated. While this calibration in an ideal situation was successful, it was found that when implemented in coin cells the electrode voltage relative to that QRE was not the same in all cells e.g. if the total cell voltage was 0 V the voltage of the positive and negative electrodes relative to a QRE could differ by up to 0.5 V between cells, this is believed to be due to differing QRE positions between cells. For further clarity, an example of this phenomenon is presented in Appendix 11. It can clearly be stated that if the total cell voltage is 0 V then the voltage between the positive and negative electrodes will also be 0 V. As such, results are presented relative to 0 V rather than to the original QRE derived result.
Chapter 5: The impact of electrode capacitance ratio on asymmetric ACC/PAC EDLC electrochemical capacitors utilising organic electrolyte

Figure 5.22 Results of CCCD analysis for material and mass asymmetric (‘ACC:PAC) cells with a range of mass ratios at 0.28 A g⁻¹ (3rd cycle), this includes the electrode specific potential as determined by the incorporated silver QRE.

The results shown above (Figure 5.22) are related only to samples which contained a silver QRE. It can clearly be seen that as the mass ratio decreases so does the time taken for a full CCCD cycle to complete, this indicates reduced charge storage. One other clearly noticeable property is the significantly reduced voltage drop in all samples in comparison to samples fabricated in the previous experimentation. This has been attributed to the use of two spacers (each 1 mm thick) rather than one, indicating that electronic resistance was indeed a major factor.
in the previous results. The areal resistance, efficiency, energy density and power density have all been quantified and are presented in Table 5.13 which is located after EIS analysis.

With regards to total cell voltage it appears that m(1:1.27) and m(1:0.36) possess nonlinear regions at their peaks, these correspond to chemical reactions occurring. In the case of sample B of m(1:1.27) it appears this reaction originates at the positive electrode (Kynol ACC) as indicated by its inward arching charge plot (i.e. increasing capacitance); interestingly, the negative electrode appears to compensate by outwardly arching i.e. the positive electrode capacitance is increasing while the negative electrode capacitance is decreasing. This phenomenon appears to reverse when discharge is occurring. A similar but much less noticeable phenomenon occurs in sample L of m(1:0.36) as the negative electrode approaches ~2 V i.e. an edge of the ESPW for such a system under investigation [166].

While the cause of the reaction at an electrode is understood to be either adverse electrode chemical reactions, permanent electrolyte ion intercalation or electrochemical reaction of organic electrolytes, it is not certain as to why this also results in a change in capacitance for an opposing ‘unreactive’ electrode. One possible explanation is that ion intercalation or degradation produces an imbalanced electrolyte i.e. where the number of opposing ions is not equal. This could affect ion diffusion dynamics across the separator resulting less ionic charge being locally available for the ‘unreactive’ electrode to electrostatically adsorb, thus resulting in an increase electrostatic potential at that electrode.

As this is a matter of interest, a novel method of visualizing CCCD data, in which the potential of both electrodes is known, was developed. This visualization is presented in Figure 5.23 and involves calculating the temporal stepwise mass specific capacitance for each electrode i.e. local capacitance values rather than a single global value; this was done for each sample which contained a silver QRE.

It is clearly visible from Figure 5.23 that the mass specific capacitance of Kynol ACC increases during charging while for Sigma PAC it remains relatively constant at the predetermined average value of 60 F g⁻¹. Sample B with m(1:1.27) shows a dramatic rise in ‘mass specific capacitance’ above 0.5 V on the positive electrode, as previously stated this is not believed to purely represent a capacitive response but also that of a chemical reaction response; the negative electrode in sample B responds by decreasing in capacitance until a value of ~1.25 V at which it starts increasing again, this is associated to the ‘outwardly arching’ response presented in standard CCCD plots.
Chapter 5: The impact of electrode capacitance ratio on asymmetric ACC/PAC EDLC electrochemical capacitors utilising organic electrolyte

Figure 5.23 Temporal stepwise mass specific capacitance for each electrode versus electrode voltage for material and mass asymmetric (ACC:PAC) cells with a range of mass ratios. Derived from CCCD charge analysis of a cell incorporating a quasi-reference electrode (QRE) such as the relative potential of each electrode could be determined.

Samples D and F of m(1:1) and m(1:0.87), respectively, appear to develop a chemical reaction above 0.8 V on the positive electrode; this is indicated by the plot knee at this voltage. Below this voltage electrode potential is also increasing but this is not necessarily associated with a chemical reaction. Firstly, this voltage appears too low for a chemical reaction to occur and as such it may be associated with a physical phenomenon. Consider that Kynol ACC consists of cylindrical fibres, ions must penetrate through the outer radial structure to reach the inner radial structure i.e. fibre core, in order to satisfy changes in electronic charge. Recall that Kynol ACC does not possess a mesoporous structure, that which aids ion transport to/from microporous charge storage sides; this has been shown previously by EIS testing (Section 5.3) to produce restriction of ion transfer. As such, ion penetration to the fibre core is not instantaneous and may take time; during this time the available electrode surface area is effectively being underutilized, the core may for some time be starved of ions thus not facilitating charge storage.
Thus, the initially increasing mass specific capacitance at the positive electrode (Kynol ACC) of samples D and F of m(1:1) and m(1:0.87) can be associated with restricted ion transport.

A contradiction to the model above can be found when further examining samples F, H, J and to some extent L which associate with mass ratios of m(1:0.87), m(1:0.73), m(1:0.50) and m(1:0.36), respectively. In these samples the mass specific capacitance of the positive electrode (Kynol ACC) decreases after CCCD initiation; this phenomenon appears to correspond with an increase in mass specific capacitance of the negative electrode (Sigma PAC). A concerning aspect about this is that the increase in mass specific capacitance at the negative electrode occurs at between -0.5 and -1 V, which is thought significantly lower than the potentials required for electrolyte decomposition to occur and might indicate water contamination.

![Graph showing electrode voltage versus cell mass ratio for material and mass asymmetric ('ACC:PAC') cells. X is mass of the negative electrode relative to the mass of the positive electrode.](image)

Figure 5.24  Electrode voltage versus cell mass ratio for material and mass asymmetric ('ACC:PAC') cells. X is mass of the negative electrode relative to the mass of the positive electrode.

From CCCD testing conducted with a QRE it has been found possible to discern the effect mass ratio has upon the maximum voltage of each electrode when a cell is charged to 2.5 V, quantification of these maximum positive/negative electrode voltages has been presented comparatively in Figure 5.24 against those found theoretically in Section 5.6.2. It can be seen from Figure 5.24 that the respective electrode voltage is in reasonable agreement with the theoretical value derived from understanding the mass specific capacitance of each material. There is a slight positive shift of all samples except that which represents m(1:1.27), which indicates that the mass specific capacitance of the positive electrode material (i.e. Kynol ACC) is less than 116 F g⁻¹ which is in agreement with Figure 5.23. A significant consequence of this is that the hypothesis was tested on this value and as such, if this value is not true then the
Chapter 5: The impact of electrode capacitance ratio on asymmetric ACC/PAC EDLC electrochemical capacitors utilising organic electrolyte

original testing in Section 5.5 may not have adequately achieved the desired capacitance ratio of c(1:0.54) thus providing further justification for the ageing experiment.

![Mass specific capacitance-voltage plots derived from CV testing at 5 mV s⁻¹ (3rd cycle) for material and mass asymmetric ('ACC:PAC') cells with a range of mass ratios.](image)

Figure 5.25 Mass specific capacitance-voltage plots derived from CV testing at 5 mV s⁻¹ (3rd cycle) for material and mass asymmetric ('ACC:PAC') cells with a range of mass ratios.

Shown in Figure 5.25 are mass specific capacitance-voltage plots derived from CV testing at 5 mV s⁻¹ for material asymmetric ('ACC:PAC') cells with a range of mass ratios; the results presented are for those cells which contain a silver QRE. It can be seen that samples which represent the extreme mass ratios (i.e. m(1:1.27), m(1:50) and m(1:0.36)) present rising mass specific capacitance above 2 V; this indicates that a chemical reaction is occurring.
Figure 5.26 Nyquist plot from EIS testing at 0 V for material and mass asymmetric (‘ACC:PAC’) cells with a range of mass ratios.

Figure 5.27 Bode mass specific capacitance (BMSC) plot from EIS testing at 0 V for material and mass asymmetric (‘ACC:PAC’) cells with a range of mass ratios.
Figure 5.28 Bode phase angle (BPA) plot from EIS testing at 0 V for material and mass asymmetric (‘ACC:PAC’) cells with a range of mass ratios.

Shown in Figure 5.26, Figure 5.27 and Figure 5.28 are Nyquist plots, BMSC plots and BPA plots, respectively, for material asymmetric (‘ACC:PAC’) cells with a range of mass ratios, all samples are displayed. The most noticeable difference between these plots and those of previous material asymmetric experimentation (Section 5.5.3), and indeed the plots of Kynol ACC based samples (Section 5.3.2), is the minimal polarization loop in Nyquist and BPA plots. This is attributed to the use of two cell spacers rather than just the single used in previous experimentation, clearly this has produced a higher stacking pressure which enabled better electronic contact between Kynol ACC and the coin cell casing. The minimal polarization loop is most clearly presented in BPA plots as a high frequency downward bump. Note, the Kynol ACC electrode did not utilise any form of current collector and directly interfaced with the coin cell components.

Because of this improved electronic conductivity, all cells now approach the ideal phase angle of 90°, albeit they do not achieve this precise value. While quantified areal resistance values have been derived and presented in Table 5.13, it qualitatively appears that Sample H of m(1:0.73) possesses a disproportionate amount of solution resistance as indicated by the differing point at which this plot crosses 0–Zm. This could possibly indicate that sample H was electrolyte starved and thus had insufficient wetting during fabrication; this sample also contained the QRE for this pair of mass ratio samples and as such the ageing results of this sample may not be
indictive of actual performance at this mass ratio. Regardless of this, sample H of m(1:0.73) presents a mass specific capacitance which is in agreement with its sample pair. Quantitative values for mass specific capacitance at 10 Hz have been derived and presented in Table 5.13.

Table 5.13 KPIs for material and mass asymmetric (‘ACC:PAC’) cells with a range of mass ratios, descriptive mass ratio is defined above sample name.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(1:1.27) Sample A</td>
<td>19.42 F g⁻¹</td>
<td>17.59 F g⁻¹</td>
<td>4.31 Ω cm²</td>
<td>4.53 Ω cm²</td>
<td>97 %</td>
<td>86 %</td>
<td>15.32 W h kg⁻¹</td>
<td>12.61 kW kg⁻¹</td>
</tr>
<tr>
<td>(1:1.27) Sample B</td>
<td>18.92 F g⁻¹</td>
<td>17.10 F g⁻¹</td>
<td>4.75 Ω cm²</td>
<td>2.84 Ω cm²</td>
<td>95 %</td>
<td>79 %</td>
<td>14.74 W h kg⁻¹</td>
<td>11.36 kW kg⁻¹</td>
</tr>
<tr>
<td>(1:1) Sample C</td>
<td>18.96 F g⁻¹</td>
<td>17.43 F g⁻¹</td>
<td>3.72 Ω cm²</td>
<td>2.15 Ω cm²</td>
<td>92 %</td>
<td>78 %</td>
<td>15.28 W h kg⁻¹</td>
<td>16.52 kW kg⁻¹</td>
</tr>
<tr>
<td>(1:1) Sample D</td>
<td>19.32 F g⁻¹</td>
<td>16.97 F g⁻¹</td>
<td>3.72 Ω cm²</td>
<td>3.03 Ω cm²</td>
<td>99 %</td>
<td>90 %</td>
<td>15.44 W h kg⁻¹</td>
<td>16.57 kW kg⁻¹</td>
</tr>
<tr>
<td>(1:0.87) Sample E</td>
<td>16.86 F g⁻¹</td>
<td>16.60 F g⁻¹</td>
<td>3.31 Ω cm²</td>
<td>2.84 Ω cm²</td>
<td>99 %</td>
<td>91 %</td>
<td>13.70 W h kg⁻¹</td>
<td>20.56 kW kg⁻¹</td>
</tr>
<tr>
<td>(1:0.87) Sample F</td>
<td>18.57 F g⁻¹</td>
<td>16.27 F g⁻¹</td>
<td>4.00 Ω cm²</td>
<td>4.03 Ω cm²</td>
<td>99 %</td>
<td>91 %</td>
<td>14.87 W h kg⁻¹</td>
<td>16.57 kW kg⁻¹</td>
</tr>
<tr>
<td>(1:0.73) Sample G</td>
<td>17.50 F g⁻¹</td>
<td>15.75 F g⁻¹</td>
<td>5.25 Ω cm²</td>
<td>6.49 Ω cm²</td>
<td>99 %</td>
<td>91 %</td>
<td>14.02 W h kg⁻¹</td>
<td>13.32 kW kg⁻¹</td>
</tr>
<tr>
<td>(1:0.73) Sample H</td>
<td>17.85 F g⁻¹</td>
<td>15.99 F g⁻¹</td>
<td>9.99 Ω cm²</td>
<td>10.37 Ω cm²</td>
<td>99 %</td>
<td>88 %</td>
<td>13.68 W h kg⁻¹</td>
<td>6.80 kW kg⁻¹</td>
</tr>
<tr>
<td>(1:0.50) Sample I</td>
<td>14.62 F g⁻¹</td>
<td>13.42 F g⁻¹</td>
<td>3.68 Ω cm²</td>
<td>3.31 Ω cm²</td>
<td>98 %</td>
<td>89 %</td>
<td>11.89 W h kg⁻¹</td>
<td>23.27 kW kg⁻¹</td>
</tr>
<tr>
<td>(1:0.50) Sample J</td>
<td>15.21 F g⁻¹</td>
<td>13.86 F g⁻¹</td>
<td>4.62 Ω cm²</td>
<td>5.18 Ω cm²</td>
<td>98 %</td>
<td>89 %</td>
<td>12.33 W h kg⁻¹</td>
<td>17.67 kW kg⁻¹</td>
</tr>
<tr>
<td>(1:0.36) Sample K</td>
<td>12.33 F g⁻¹</td>
<td>11.47 F g⁻¹</td>
<td>5.03 Ω cm²</td>
<td>4.93 Ω cm²</td>
<td>96 %</td>
<td>85 %</td>
<td>9.89 W h kg⁻¹</td>
<td>18.46 kW kg⁻¹</td>
</tr>
<tr>
<td>(1:0.36) Sample L</td>
<td>12.23 F g⁻¹</td>
<td>11.47 F g⁻¹</td>
<td>4.62 Ω cm²</td>
<td>3.87 Ω cm²</td>
<td>98 %</td>
<td>87 %</td>
<td>9.78 W h kg⁻¹</td>
<td>20.16 kW kg⁻¹</td>
</tr>
</tbody>
</table>

a EIS conducted at 0V
b Knee frequency is 10 Hz
c Under matched load condition with a peak voltage of 2.5 V and calculated at 0.28 A g⁻¹

Shown in Table 5.13 are the KPI (key performance indicators) for all samples fabricated for investigating the mass ratio at which material asymmetric cell such as (‘ACC:PAC’) achieves an
extended lifespan. Firstly, the mass specific capacitance has been derived from CCCD analysis and EIS analysis at 0 V; the values derived from EIS are again lower than those of CCCD due to the testing voltage of 0 V. It can clearly be seen that as the mass of the positive electrode relative to the negative electrode increases, the mass specific capacitance value drops. At this point it is of interest to see how the theoretical value compares to the real-world value; in both cases the values have been derived from CCCD plots thus making the comparison fair.

![Graph showing mass specific capacitance relative to mass ratios for material and mass asymmetric (ACC:PAC-) cells. Theoretical values are presented in Table 5.12 and actual values are presented in Table 5.13.](image)

There is excellent agreement between theoretical and actual mass specific capacitance values, the predominant difference is that the actual values are all lower than the theoretical value again indicating that there are no beneficial capacitive interactions between ion size and pore size in this experimental case. The only apparent outlier with respect to CCCD derived mass specific capacitance is Sample E for m(1:0.87); this difference is not reflected through EIS analysis nor in other KPIs and as such its source is not certain. In relation to this is mass specific energy density, which also decreases as mass specific capacitance decreases. Without cell ageing it is difficult to define a mass specific energy density value which best represents the capabilities of a material asymmetric (ACC:PAC-) cell but it can be described that the median value of all cells is 13.86 W h kg\(^{-1}\) which is 12 % greater than the average material and mass symmetric Sigma PAC value but 19% less than the average material and mass symmetric Kynol ACC value.

With respect to areal resistance, there is reasonable agreement between samples. The majority of samples present an areal resistance value < 2 \(\Omega\) cm\(^2\) from either CCCD or EIS analysis. Interestingly both samples of m(1:0.73) possess the highest areal capacitance values indicating that there was an issue in the Sigma PAC fabrication of these electrodes. Regardless,
there has been a dramatic decrease in areal resistance, this is attributed to the use of two spacers rather than one. Charge storage efficiency appears to be highest between mass ratios of m(1:0.87) and m(1:0.73) and often associates with the highest energy efficiencies (91 %). This could be an indication that the optimal mass ratio is lower than the hypothesized m(1:1), but it could also be associated with the significantly decreased areal resistance as sample D of m(1:1) also possesses high energy storage efficiency. Also related to areal resistance is mass specific power density, this has also dramatically improved when compared to previous experimental configurations. The average areal power density (excluding the anomalous sample H of m(1:0.73)) is 17 kW kg⁻¹ which is approximately half that achieved on average by material and mass symmetric cells containing Sigma PAC.

**Results of Cell Ageing**

Cell ageing of material and mass asymmetric ('ACC:PAC) cells with a range of mass ratios was achieved in an almost identical fashion to that used in previous work (see Section 5.2.3) with the only difference being that ageing was conducted in 5 hour periods with CCCD and CV cycles after each period, this done in the hope of achieving a higher temporal resolution of the ageing process, and was conducted over a 75-hour ageing period.

The results are surprising. Examine Figure 5.30 which presents a CCCD comparison over 50 hours in 10 hour periods for samples of m(1:1) and m(1:0.50). From this figure it is possible to visually appreciate that despite the significant difference in mass ratio samples of both types ultimately exhibit similar responses. The most drastic response is presented by sample C for m(1:1) after 10 hours ageing in which the cell initially behaves like a capacitor but transfers into a resistor i.e. constant current, constant voltage, constant resistance. Sample C continues in this fashion until 40 hours, after which it begins to behave as a highly resistive capacitor. There are aspects of this behaviour in Sample D for m(1:1) in which a non-linear CCCD plot is formed between 10 to 30 hours of ageing. This indicates that a significant chemical reaction is occurring in samples which were not present in the work previously conducted. Either the increased electrode stacking pressure, or inclusion of a QRE or unknown contamination could have caused this.
Chapter 5: The impact of electrode capacitance ratio on asymmetric ACC/PAC EDLC electrochemical capacitors utilising organic electrolyte

Figure 5.30 CCCD performance at 0.28 A g\(^{-1}\) (3\(^{rd}\) run) relative to potentiostatic ageing at 2.7 V of material asymmetric ('ACC:PAC') cells with mass ratios of m(1:1), m(0.53) and m(0.48).

Figure 5.31 CV performance at 5 mV s\(^{-1}\) (3\(^{rd}\) cycle) after potentiostatic ageing at 2.7 V for material asymmetric ('ACC:PAC') cells with mass ratios of m(1:1), m(0.53) and m(0.48).
Figure 5.32  CV performance at 5 mV s\(^{-1}\) (3\(^{rd}\) cycle) after potentiostatic ageing at 2.7 V for material asymmetric (‘ACC:PAC’) cells with mass ratios of m(1:1), m(0.53) and m(0.48).

Figure 5.31 and Figure 5.32 present CV comparisons at 5 mV s\(^{-1}\) over the initial 30 hours in 10 hour periods for samples of m(1:1) and m(1:0.50). Again, the samples of each mass ratio present differing responses and as such it is not possible to deduce the truth; this is blamed upon the limited sample size which, while apparently satisfactory for previous experimentation does demonstrate limitations when supposedly identical samples vary dramatically. Again, either the increased electrode stacking pressure, inclusion of a QRE or unknown contamination could have caused this premature ageing as it must be considered that the values presented above are a reasonable reflection of those previously tested.

The broadest representation has been saved for last, Figure 5.33 shows mass specific capacitance, areal resistance, charge storage efficiency and power efficiency as functions of potentiostatic ageing at 2.7 V. While the previous two figure sets focus on samples of m(1:1) and m(1:0.50), this figure presents information for all samples except sample A for m(1.27) which failed after only 10 hours of ageing. It is noticeable that the charge storage efficiency and energy storage efficiency generally increase as the mass ratio becomes more negative electrode heavy, and this culminates with sample M for m(1:0.36) behaving almost ideally. This is interesting because it is significantly lower than the mass ratio of m(1:0.51) used in previous work which presented almost ideal behaviour over periods longer than those used here; as such, this is another indication that either the increased electrode stacking pressure, inclusion of a QRE or unknown contamination has induced premature ageing.
Chapter 5: The impact of electrode capacitance ratio on asymmetric ACC/PAC EDLC electrochemical capacitors utilising organic electrolyte

Figure 5.33 Part A (left) Mass specific capacitance and areal resistance as a function of potentiostatic ageing at 2.7 V and (right) charge storage efficiency and energy storage efficiency as a function of potentiostatic ageing at 2.7 V for material asymmetric ('ACC:PAC') cells with a range of mass ratios.
Capacitive Energy Storage: Filling the gap

Figure 5.36 Part B (left) Mass specific capacitance and areal resistance as a function of potentiostatic ageing at 2.7 V and (right) charge storage efficiency and energy storage efficiency as a function of potentiostatic ageing at 2.7 V for material asymmetric ('ACC:PAC') cells with a range of mass ratios

Let us further consider the possibility of stacking pressure causing premature ageing. One possible impact of additional pressure may be that reactions generally occur faster [277] but it is important to discern where pressure is being applied. It is the author's belief that the introduction of a second spacer has not increased the pressure of the electrolyte as during the crimping process the cell base is initially depressed into the cell can (causing excess electrolyte to be ejected) and finally crimped. The crimping does not provide additional axial pressure but instead radially deforms the cap rim to ensure it cannot slip past the base, thus sealing the cell. It is believed the ejection of excess electrolyte in this process acts as a form of electrolyte pressure control.

Another possible impact is that increased electrode stack pressure has deformed the porous structure of either Sigma PAC or Kynol ACC such that it is more susceptible to reactions. Such a phenomenon has been previously investigated by Gourdin et al. [278], in which electrodes
containing AC materials with SSA values of between 2,000 and 1,500 m² g⁻¹ experienced increasing electrode stack pressures until the porous structure was deemed to have deformed. Firstly, it was found that this structure deformation occurred suddenly (i.e. a collapse), this would imply that if the additional cell spacer had resulted in electrode collapse then the cell would have not functioned at all. Secondly, the minimum pressure at which this collapse was found to occur was 191 kg cm⁻², which is almost three times higher than the pressure applied during the crimping process. As such, the additional spacer is not deemed the source of reduced cell performance.

Let us consider the possibility that performance has been influenced through the inclusion of a QRE device. This device consisted of a silver strip and two parts of Kapton® tape. The silver is believed to be intrinsically unreactive as is the primary Kapton® material, but there is uncertainty as to what effect the adhesive used on this tape may have upon an electrolyte system. This electrolyte contained acetonitrile which is known to be a powerful solvent and as such it may have also dissolved the adhesive material which may have negatively impacted performance. The reason this is not thought to be true is that QREs were only included in one sample of each mass ratio type, and it would have been expected that only cells which contain a QRE would present poor performance, per Figure 5.33 this is not the case. For example, sample F for m(1:0.87) performs worse than sample G for m(1:0.87) despite sample G containing a QRE.

As such, the remaining plausible explanation for the decrease in cell performance is contamination. In this case, it is deemed most likely that this contamination is water. Sources of this contamination will now be considered. The cell casing materials and separation material had been dried and placed into the argon glovebox at the onset of the experiments described in Section 5.3. This is also true for electrolyte materials which were immediately transferred upon arrival into the glovebox environment. The only materials which were prepared specifically for this experiment were the electrodes; while these were certainly dried at 120 °C for 24 hours there is doubt that they were transferred quickly enough into the glovebox environment, this was believed to be due to the last-minute gathering of appropriate QRE materials which were to be incorporated into this cell set.
5.6.4 Conclusion – Material and Mass Asymmetric Cells

The aims of this section were to overcome the short comings of previous experimentation and further investigate at what mass ratio a material asymmetric cell such as (‘ACC:PAC’) achieves an extended lifespan. This included incorporating a silver QRE into some of the samples in order to assess each electrode individually and the addition of double spacers.

The inclusion of a silver QRE has been considered successful, it provided a stable reference point within the electrode/electrolyte system and apparently did not hinder cell performance. This proves the effectiveness of the QRE design modifications i.e. to use kapton tape rather than a PTFE coating. The QRE device enabled mass specific capacitance values for each electrode to be defined which provided invaluable insight as to the electrochemical response of each electrode. Specifically, the Kynol ACC material used as the positive electrode demonstrated an increasing mass specific ‘capacitance’ at high voltages, indicating a chemical reaction. This material also appeared to present intriguing responses at lower voltages which appeared to be associated with reactions occurring across both electrodes, this is believed to indicate the reduction/oxidation of water contamination.

The addition of double spacers produced a significant improvement in cell resistance, energy storage efficiency and power performance when compared to the results of Section 5.5. This indicates that CR2032 coin cells in their standard configuration i.e. one spacer, are not suitable at all for testing high power electrochemical capacitors. Upon further investigation, it was found that this phenomenon had already been reported by Stoller et al. [272] who suggested that the use of two spacers is mandatory when testing electrochemical capacitors using coin (button) cells.

The adjustment of the mass ratio produced mass specific capacitance values for both a two-electrode device and for each individual electrode, these generally agreed with the values theoretically calculated using knowledge derived from prior two electrode measurements (see Section 5.3). Both CCCD and CV clearly showed a decrease in overall capacitance as the mass ratio was shifted further towards positive heavy i.e. low x value in m(1:x). It is unfortunate that the materials proved non-conducive towards beneficial capacitive behaviour which could have arisen by using materials with significantly different PSDs (pore size distributions) i.e. other than just differences in magnitude.
With respect to the assessment of cell ageing, this experimentation has been considered a failure. It is not possible to draw a satisfactory conclusion from the results as samples of the same configuration present significant differences in performance. Samples which should be comparable to those developed in Section 5.5 do not present even remotely similar responses. The reasoning behind this appears to be water contamination during the transfer process from vacuum oven to glovebox, this could be overcome in future work through the use of a dedicated dry room (one with negligible moisture content) which contains both pieces of equipment.

5.7 Discussion

The experimental work detailed in this chapter aimed to assess the hypothesis that appropriately matching different materials at each electrode i.e. Kynol ACC as the positive electrode and Sigma PAC as the negative electrode can adequately achieve capacitance balancing for cell lifespan extension. This was assessed by firstly electrochemically analysing the suitable materials, validating that previous work related to this field holds true, and ultimately testing the hypothesis at hand. All work was conducted using the electrolyte 1.5M TEA⁺BF₄⁻ in ACN and was conducted using CR2032 coin cells.

The first step i.e. electrochemical assessment, has been generally deemed successful and provided full cell mass specific capacitance values for Kynol ACC (116.16 F g⁻¹) and Sigma PAC (60.36 F g⁻¹). Thus, if these materials were placed mass symmetrically they in theory should produce a capacitance ratio of c(1:0.52), almost precisely what was required in order to adequately achieve capacitance balancing for lifespan extension [168]. While the capacitance values derived were relatively consistent between samples it was found that power capabilities varied by around 40 %; this is believed to be partially down to the use of crocodile clips when connecting coin cells to the testing apparatus. In the case of Kynol ACC the use of a single spacer significantly increased the contact resistance thus decreasing power capability, energy storage efficiency and consequently overall energy storage. Ultimately, this first stage of experimentation provided some of the information required in order to properly design material asymmetric cells and also verified the suitability of the experimental techniques at hand.

The subsequent step towards testing the hypothesis at hand involved validating previous work related to this field [168]. This was necessary to firstly ensure that the hypothesis rests on firm understanding but also ensured that the ageing techniques used were effective when assessing cell ageing. This work was deemed successful in reproducing the effects described in
[168] using Sigma PAC i.e. a capacitance ratio of c(1:0.54) does indeed prolong cell lifespan. One aspect of this work that differed from [168] was that potentiostatic ageing was conducted at 2.7 V rather than 3.5 V as used in the prior research, this was due to higher electrolyte impurities and differing cell containment methods. Regardless, this approach taken validated the previous finding that a capacitance ratio of approximately c(1:0.54) can maximise the ESPW of a material symmetric cell by extending the potential of the negative electrode through mass balancing i.e. m(1:0.54). The work done in this step also validated the ageing process which was found to present a clear picture of how cells aged under potentiostatic ageing conditions.

The third step of testing the hypothesis at hand was split into two parts. The first part should be considered preliminary and involved the use of Kynol ACC and Sigma PAC as the positive and negative electrode materials, respectively. These materials in theory enable a mass symmetric cell configuration whilst still producing a capacitance ratio of c(1:0.52), which is in excellent agreement with the desired material capacitance ratio of c(1:0.54), as defined by [168]. Cell containing mass ratios of m(1:0.93) and m(1:0.51), which correspond to theoretical capacitance ratios of c(1:0.48) and c(1:0.27), were produced and it was found that significant ageing still occurs in samples of m(1:0.93) regardless of its appropriate (but not exact) capacitance ratio. In samples of m(1:0.51) the ageing process was significantly reduced indicating that although these materials possess apparently ideal capacitance values they may not result in balanced capacitance with equal electrode mass as was hypothesized.

The second part of this step was aimed at advancing upon all prior and preliminary findings in order to produce a final set of conclusive evidence. While the initial testing of this using a recently developed silver QRE was achieved satisfactorily, the ageing process indicated that samples had been contaminated with moisture. As such, the desired conclusive evidence did not materialize. Regardless, interesting insight can be gathered from this result. The fact that the capacitance ratio is not the sole influencer upon the ageing process raises the question as to what exactly influences the ageing process.

Examination of a recent (2016) paper related to this matter, ‘Design of activated carbon/activated carbon asymmetric capacitors’ [279], indicates that the AC porous texture and surface chemistry also play a significant role in the ageing process. The AC porous texture is a phenomenon which is dictated by the activation process and precursor materials; in [91] it is shown that two types of AC, Super 50 (Norit) and Maxsorb (Kansai) which respectively possess SSA values of 1283 and 1754 m² g⁻¹ and similar chemical and PSD structures, do not behave
similarly under cyclic ageing. Both AC materials were subjected to 3000 CCCD cycles at 650 mA g\(^{-1}\) between 0 and 2.5 V, Super 50 retained 90% of its charge capacity while Maxsorb retained only 50%. This indicates that high SSA AC materials exhibit a reduced cycle life, possibly because of a reduced ESPW. The author has considered this and proposes the following hypothesis as to how this may work.

Apparently, as the SSA value in AC materials increases, their susceptibility to chemical reaction also increases [91, 43, 34, 45]. This is believed to be related more so to the changes in porous texture than the SSA value explicitly. Let us simplify the possible porous carbon texture into three fundamental structures, a protruding tip which is ideally one atomic layer thick (i.e. graphene) (Figure 5.34 (A)), a planar surface with extensive depth (Figure 5.34 (B)), and a pore extensively surrounded by carbon and wide enough for ions to enter (Figure 5.34 (C)). This simplification represents only the most extreme structures and a wide variety of carbon surfaces exists between them [280].

![Figure 5.34 Schematic representations of carbon/electrolyte interfaces (A) a protruding tip which is ideally one atomic layer thick (i.e. graphene), (B) a planar surface with extensive depth, (C) a pore extensively surrounded by carbon and wide enough for ions to enter.](image)

Subsequently, consider that these surfaces are interacting with an electrolyte such that an electric double layer is formed at the carbon/electrolyte interface, such a situation has been represented in Figure 5.34 but has been simplified to only show a basic Helmholtz double-layer. In the case of (A), the protruding tip possesses high surface area with electrolyte accessibility on both sides; in the case of (B), the planar surface can accept ions on one side and in the case of (C), the electrolyte will be surrounded by carbon on both sides.

Now, the main focus for this avenue of consideration is the voltage (electrostatic potential), both in a global sense e.g. that detected across a two-electrode device and in a local sense e.g. that experienced between local nanostructure of carbon and the electrolyte. In a global sense, there is always just one voltage value but in a local sense there could be a distribution of values
depending on the local carbon nanostructure. It is well known that sharp protruding edges e.g. tips, can present more exposed electric fields (large field gradients); this is due to the way electronic charge distributes across a surface, sharp edges offer minimal repulsion due to the lack of surrounding structure and as such charge tends to congregate excessive at these points.

As such, if an electrode is polarized i.e. charged, then these sharp protruding edges will experience an above average electron density. Conversely, a pore may experience below average electron density while a planar surface may experience normal density. As such, it is possible to hypothesize that while the global voltage of an electrode may be one value the local voltage may be distributed across many values, this could take the form of a normal bell-curve distribution but may also be strongly associated with the PSD which often does not present a normal distribution. Considering this, it is possible to envision that these sharp edges/tips/points will endure higher voltages and as such, may be more susceptible to chemical reaction.

Returning to the experiments at hand, it is possible that the higher SSA of Kynol ACC also presents a higher content of sharp nanocarbon edge/tips/points which in turn reduce the global voltage (ESPW) of the electrode material as a whole. It could indeed be this which caused samples of material asymmetric (+ACC:PAC) to behave differently from the theorized response.

5.8 Summary and Outlook

The primary aim of the experiments detailed in this section was to develop and characterise an EDLC (electrical double layer capacitor) type EC (electrochemical capacitor) device which possesses a stable high voltage (2.7 V) using capacitance balancing by material asymmetry (research aim 1, section 2.8). Multiple experimental steps were required to do this.

The first step was characterisation of intrinsic properties possessed by the AC materials (Sigma PAC and Kynol ACC) used in this study (see Section 5.3). This was achieved by producing symmetric material and mass cell configurations which utilised the electrolyte 1.5 M TEA^+BF_4^- in ACN. It was found that Kynol ACC and Sigma PAC possess mass specific capacitance values of 116 and 60 F g^-1 respectively; this produces a capacitance ratio of 1:0.52 which agrees exactly with the microporous SSA ratio (derived by GCMC). This is a significant finding considering that these AC materials have wholly different precursor materials and external morphologies, albeit, without a broader range of material data it is difficult to rule out coincidence. The average mass specific energy density of Kynol ACC and Sigma PAC was found to be 17.1 and 12.4 W h kg^-1 when discharge from 2.5 V at a constant current density of
Chapter 5: The impact of electrode capacitance ratio on asymmetric ACC/PAC EDLC electrochemical capacitors utilising organic electrolyte

0.28 A g⁻¹. The average mass specific power density of Kynol ACC and Sigma PAC was found to be 1.54 kW kg⁻¹ and 34.8 kW kg⁻¹, respectively, but it should be noted that samples containing only Sigma PAC had two spacers while samples with Kynol ACC had only one spacer; later experiments in Section 5.5 indicated that the use of two separators would have significantly improved the power performance of cells containing only Kynol ACC.

Once basic characterisation had been completed it was possible to test the validity of previous work in this field [168]. Specifically, it had been previously stated that a mass ratio of m(1:0.54) should be used i.e. the positive electrode mass is approximately double the negative electrode mass when using TEA⁺BF₄⁻ in ACN with the same material at both electrodes. Such an approach was taken and found to be true (see Section 5.4), the resulting effect of this configuration was a prolonged cell lifespan when aged potentiostatically at 2.7 V. While it was not proven that the mass ratio is optimal, the experimental results clearly demonstrate that the principle of capacitance balancing can indeed be achieved by implementing electrode mass asymmetry. From other literature, such as [169, 170], it is believed that the same approach can be simply applied to a myriad of other cell configurations; the impact will be optimised cells with maximised voltage capabilities resulting and result in increased energy, power and cycle life capabilities.

The subsequent step in this study was to test the hypothesis at hand i.e. that capacitance balancing by material asymmetry could be used to maximise a cell’s voltage window, thus resulting in the same improvements as those presented when capacitance balancing by mass asymmetry. The experiments conducted in Section 5.5 indicate this hypothesis is not entirely true. Cells were produced in which a capacitance ratio close to c(1:0.54) was obtained by material asymmetry (i.e. Kynol ACC as the positive electrode material and an appropriate mass of Sigma PAC as the negative electrode material). This was believed to be due to differences in the microporous surface textures, heteroatom content of the AC materials and possible moisture contamination. A further result was lower than expected power and energy capabilities; this may have been due to differences in material external morphology and the use of a single in-cell spacer.

Based upon the results of the study was to propose a final broad investigation in which a wider variety of mass ratios of (ACC:PAC) are tested, alongside the use of two spacers and the incorporation of a QRE into some samples. The inclusion of a QRE was considered successful (meeting RA 7, see supplement A), it provided a stable reference point within the
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Filling the gap

electrode/electrolyte system and apparently did not hinder cell performance; it enabled the occurrence of chemical reactions to be identified, including the possible reduction/oxidation of water contamination. The use of double spacers produced a significant reduction in cell areal resistance resulting in improved energy and power performance (comparative to the results of Section 5.5).

Pre-ageing assessment of samples with a wide variety of mass ratio (with an asymmetric material configuration) was conducted; it was found through CCCD and CV analysis that a decrease in capacitance occurs as the mass ratio shifts towards being positive heavy i.e. low x value in m(1:x). From prior theoretical insight (section 5.6.2) this was expected to occur.

Ageing of samples was conducted potentiostatically (i.e. at constant voltage) but the results were inconclusive. Sample which should have been comparable to those developed in Section 5.5 did not present even remotely similar responses. The reasoning behind this appeared to be water contamination which occurred during the electrode transfer from vacuum oven (for drying) to the glovebox. For future work it is suggested that cells are immediately transferred without any delay, or a dedicated dry room (i.e. one with negligible moisture content) is used to house both the drying facility and glovebox.

That the results of this extended study were inconclusive is a disappointment, but prior testing of the hypothesis still stands and is believed to be experimentally valid. The hypothesis was thus proven to be not true and an extensive discussion as to why this is so has been conducted in Section 5.7. It has been identified that the micro-texture of activated carbon plays a significant role in its chemical stability at high voltages. On the one hand, it is believed Kynol ACC possesses a higher content of ‘sharp’ nanotexture (edges/tips/points) which in turn increase its susceptibility to chemical reaction; on the other hand, Sigma PAC is believed to possess a smoother surface texture (possibly indicated by its lower SSA or mesoporous content) and is thus less susceptible to chemical reaction. Broadly speaking, consideration for such matters should be taken when cells are to be fabricated with material asymmetry.
6 AN INVESTIGATION OF USING A SILICON BASED NEGATIVE ELECTRODE IN LITHIUM ION CAPACITORS

6.1 Introduction

The primary aim of the research detailed in this section is to develop and quantify an LIC (lithium ion capacitor) type EC (electrochemical capacitor) device which possesses a silicon based negative electrode. Such a device should also be compared against current state-of-the-art LICs which utilise graphite based negative electrodes (research aim 2, section 2.8). Experimentation in this area focuses around the use of Li⁺PF₆⁻ (lithium hexafluorophosphate) in EC/DEC (ethylene carbonate/diethyl carbonate) 50/50 (v/v), an industry standard electrolyte for LIC and LIB (lithium ion battery) research. In addition to this, industry standard coin cell casings are used. Both approaches are aimed at satisfying research aim 6 i.e. to use materials and techniques which are closely related to current industrial standards. Prior to commencing this investigation, the reader should have a comprehensive understanding of how an LIC type EC device functions; a basic schematic of such a device can be found in Figure 2.13 on page 32 while advanced considerations toward such a device can be found in Section 2.5.

In essence, an LIC variety of EC device appears to offer substantial benefits over more classical EC devices, such as those based on purely EDLC (electrical double-layer capacitor) charge storage (see Section 2.5). An LIC combines an EDLC positive electrode with a lithium intercalative negative electrode; this allows an LIC to operate between substantially higher voltages (3 to 4.5 V) than those found in more classical devices, thus improving energy storage. In addition, LICs have been found to retain good power capability, high energy storage efficiency, long cycle lives and slow self-discharge rates [10, 38, 86]. As such, an LIC is an extremely desirable device for filling the gap between traditional batteries and capacitors.

At present, the state-of-the-art in an LIC type EC device is to use graphite as the intercalative negative electrode [91, 86]; the novel approach followed during this investigation
is to instead use silicon for this purpose. It has been found that silicon possesses significantly higher charge capacity versus graphite (372 A h g⁻¹ for graphite, 4,200 A h g⁻¹ for silicon) but it also possesses an intercalation potential ~0.35 V lower than that of graphite, thus reducing the maximum EPSW (electrochemical potential stable window). Together, these properties result in a silicon based LIC device which theoretically achieves a similar mass specific energy storage density as a graphite based LIC device when both electrodes are maximally charged i.e. fully utilised. Interestingly, it was found in Section 2.5 that if the negative electrode of a silicon based LIC device is not maximally charged during standard operation i.e. underutilised, then it still presents a mass specific energy storage density which is comparable to a fully utilised device. The author proposes that this dynamic could be exploited to achieve an improvement in power capability while maintaining high energy density and minimizing volumetric expansion.

6.2 Methodology

6.2.1 Experimental Overview

Firstly, it is appropriate to provide an overview of what is required in order to assess the author’s proposal that implementing a silicon based negative electrode in an LIC device could achieve an improvement in power capability while maintaining high energy density over the previous state-of-the-art graphitic material:

1. Produce LICs which use the current state-of-the-art graphitic material as the negative electrode. Firstly, this will confirm if LIC type EC devices can indeed be fabricated using the available instruments and techniques. Secondly, it will allow for electrochemical testing of traditional devices in order to validate their stated performance; such devices can subsequently be used to benchmark the performance of LICs which possess a silicon based negative electrode.

2. Produce LICs which use a silicon based negative electrode. A core aspect of this will be to produce cells with varying degrees of charge capacity utilisation of the negative silicon based electrode. This will confirm if such an electrode does indeed function in an LIC device, it will also provide insight as to the relationship between gravimetric (i.e. mass specific) cell energy density and power density of such an LIC device which uses a silicon based electrode. A similar procedure was followed in [91] when investigating LICs using graphitic negative electrodes.
In both cases, initial theoretical calculations were conducted in order to identify what material mass ratio would produce the negative electrode charge capacity utilisation desired for investigation. As such, mass ratios will be stated in the form of m(x:1), where x is value of the positive electrode relative to that of the negative electrode i.e. the ratios are part-to-part. Note that this opposes the terminology used in Section 5 due the necessity that the positive electrode be significantly heavier than that of the negative electrode in this work, this runs counter to the work conducted in Section 5.

6.2.2 Materials and Experimental Control

To produce high quality and trustworthy results it is necessary to establish control over experiment variables. In this work the core variables are:

- Positive/negative electrode – Material(s), thickness, areal density, preparation method and deposition method, current collector.
- Electrolyte – Salt, solvent, molar concentration, fabrication method, quantity.
- Cell separation material.
- Cell containment materials and method.
- Temperature

With regards to positive/negative electrode materials: A novel silicon based electrode was acquired from an external company which specialises in silicon electrode development; it has been designated the title NXA-513. Full material specifications have been detailed in Section 3.3.2 but essentially this electrode came prefabricated with active material having been deposited onto copper foil followed by compaction under a pressure of 483 kPa. The binder used is stated as PVDF but the precise quantity is not defined. The areal density of deposited material is stated as 3.55 mg cm\(^2\); 2.45 mg cm\(^2\) is stated as silicon and thus 1.10 mg cm\(^2\) accounts for binder and additives.

NXA-513 was investigated through SEM analysis, EDX analysis and nitrogen sorption measurement (see Section 4.2). From SEM it was identified that individual particle sizes are about 10 \(\mu m\) and possess a ‘hairy’ surface, the presence of MWCNTs (multi-walled carbon nanotubes), silver nanoparticles and PVDF were also identified through the use of EDX analysis. According to the manufacturer, the MWCNT content is present in order to improve electronic conductivity and silver was used in the Si preparation procedure but the particle found is in fact unintended residue (but may also provide improved electronic conductivity). The quantity of
PVDF binder in this electrode is believed to be 10 wt%. From nitrogen sorption measurement and GCMC analysis it was found that NXA-513 possesses a purely mesoporous structure with an SSA (specific surface area) value of 4.55 m² g⁻¹, and a SPV (specific porous volume) value of 0.0680 cm³ g⁻¹ which associated predominantly with slit shaped pores 30 nm in width.

The other materials required for this investigation are graphite, ACs and a carbon black additive. With regards to graphite, full manufacturer specifications have been detailed in Section 3.3.2 but essentially it is a high purity synthetic graphitic powder with particles of major dimensions below 44 μm, this has been qualitatively confirmed through SEM analysis (see Section 4.2). From nitrogen sorption measurement and GCMC analysis it was found that this graphite powder possesses a purely mesoporous structure with an SSA (specific surface area) value of 2.32 m² g⁻¹, and a SPV value of 0.00854 cm³ g⁻¹ which associated predominantly with slit shaped pores 8 nm in width.

To maintain some semblance of comparability with the experiments conducted in Chapters 5 and 7, the same AC materials were also implemented i.e. Sigma PAC (powdered activated carbon) and Kynol ACC (activated carbon cloth). The full manufacturer specifications of Sigma PAC and Kynol ACC can be found in Section 3.3.2 while full SEM and nitrogen sorption analysis data can be found in Section 4.2.

Sigma PAC is an acid washed PAC with a particle size distribution where 10-15% is believed to be greater than 74 μm while 70-75% is greater than 10 μm, this has been qualitatively confirmed by SEM analysis. The manufacturer specification states it has an SSA of 1,000 m² g⁻¹ (derived from BET analysis) which has been confirmed through nitrogen sorption testing; the more appropriate values are those derived from GCMC analysis (with a slit pore assumption) which defines Sigma PAC as both a mesoporous and microporous material. With regards to mesoporous structure, it possesses an SSA value of 42 m² g⁻¹, and an SPV value of 0.158 g cm³ which associates with pores between 7.5 and 12.5 nm in width while with regards to microporous structure, it possesses an SSA value of 801 m² g⁻¹, an SPV value of 0.340 g cm³ which associate with a bimodal PSD (pore size distribution) with peaks at ~0.7 nm and ~1.35 nm. Electrochemical analysis of this material in a mass symmetric configuration with 1.5 M TEA⁺BF₄⁻/ACN electrolyte has been conducted in Section 5.3 and it was inferred that the mass specific capacitance of a single Sigma PAC electrode is 60 F g⁻¹, such a configuration also presented excellent power capabilities of 34.80 kW kg⁻¹ on average.
Kynol ACC is a woven textile of individual ACF (activated carbon fibres); these fibres possess a diameter of the order of 10 \( \mu \text{m} \) which has been verified qualitatively by SEM analysis. The manufacturer specifications state it possesses an areal mass of 120 g m\(^{-2}\) which has been confirmed in Section 5.3; the specifications also state the material possesses a thickness of 500 \( \mu \text{m} \) but this was for an uncompressed sample, under compression the thickness was reduced to an average of 350 \( \mu \text{m} \) in thickness. Note, this reduction in thickness was measured using a micrometer with 10 \( \mu \text{m} \) resolution; the compressed state was taken as the point at which the micrometer could not be further tightened. GCMC analysis (using a slit pore assumption) of nitrogen sorption measurements were conducted and defined Kynol ACC as a microporous material with trace amounts of mesoporosity. With regards to microporous structure, it possesses an SSA value of 1540 m\(^2\) g\(^{-1}\) and an SPV value of 0.666 g cm\(^{-3}\) which associates with a bimodal PSD (pore size distribution) with peaks at \( \sim 0.7 \) nm and \( \sim 1.35 \) nm. With regards to mesoporous structure, it possesses an SSA value of 20 m\(^2\) g\(^{-1}\) and an SPV value of 0.0210 g cm\(^{-3}\) which associates with pores between 2 and 3 nm in width. Electrochemical analysis of this material in a mass symmetric configuration has been conducted in Section 5.3 and it was inferred that the mass specific capacitance of a single Kynol ACC electrode is 116 F g\(^{-1}\); unfortunately, this analysis configuration utilized only a single spacer and as such the power capabilities were poor. Later use of such a material with two spacers, albeit in a material asymmetric configuration, demonstrated modest power capabilities of 17 kW kg\(^{-1}\).

Only Sigma PAC and graphite powder possess electrode thickness and areal density variability as NXA-513 arrived prefabricated and Kynol ACC is a cloth material. As such, Sigma PAC and graphite powder coatings were fabricated by the tape casting method defined in Section 4.4, it should be noted that Sigma PAC electrodes were fabricated from a large quantity of material (\( \sim 300 \) ml) while graphite electrodes were fabricated from a small quantity of material (\( \sim 20 \) ml). The areal density is the property of most interest as it is this which can be used to define negative electrode utilization, a fundamental aspect of the research at hand.

TIMCAL Super P\(^{\text{\textregistered}}\)-Li carbon black was purchased for use in graphite based electrodes as a conductive additive, this material is specified as having a density of 160 kg m\(^{-3}\) and an SSA of 62 m\(^2\) g\(^{-1}\).

Each graphite based electrode contained 92.5 m\% graphite, 5 m\% SBR./CMC binder, 2.5 m\% Super P\(^{\text{\textregistered}}\)-Li conductive additive. The precise manufacturing procedure (tape casting) for graphite based electrodes can be found in Section 4.4.
For the CC (current collector) of the negative electrode copper foil was used as the lithium based electrolyte can chemically react with aluminium foils at voltages lower than the intercalation voltage, therefore NXA-513 was also deposited onto copper foil; as such, a copper foil of 20 μm thickness and 9 mg cm\(^{-2}\) areal density was used. For the CC of the positive electrode i.e. that of AC, the same 30 μm Tostal Carbo® as used previously in Section 5 was also used.

The electrolyte used for all experiments in this chapter was 1.0M Li\(^+\)PF\(_6\) in EC/DEC 50/50 (v/v); this electrolyte was procured premixed (see Section 3.3.1). The only issue of concern is that the quantity of electrolyte could not be directly measured. Even with a fixed volume pipette it was found that any excess electrolyte could be squeezed from the cell during crimping, thus causing a difference between the quantity deposited and the quantity contained. As such, cell materials were cumulatively weighed prior to initiation of the cell fabrication process, upon completion of fabrication the cell could be wiped clean of excess liquid and reweighed thus telling the quantity of electrolyte which was contained within (see Section 4.5.3).

Attempts were made to hold constant the variables related to cell separation material and cell containment method. Cell separation was achieved with a 60 μm NKK TF40-60 cellulose membrane and cell containment employed industry standard CR2032 coin cell cases; the precise containment procedures followed are detailed in section 4.5.3. Note, QRE refinement was not established until work on LICs containing silicon based negative electrode were conducted. The temperature was held constant at 25° C for all experimentation using an environmental chamber.

### 6.2.3 Electrochemical Analysis and Key Performance Indicators

The electrochemical analysis techniques to be used in the following experimentation are CCCD (constant current charge discharge) and CV (cyclic voltammetry); see section 3.4.3 for detailed understanding of these techniques. In the case of CCCD the current density (A g\(^{-1}\)) can be stated with respect to the mass of positive electrode, mass of negative electrode or total electrode mass. In the case of the experiments at hand, the mass of the positive electrodes was varied at some points but the negative electrode i.e. that of graphite or silicon, will remain constant. As such, the CCCD current density has been defined with respect to the negative electrode mass with tests being conducted at 0.1, 0.25, 0.5, 1 and 2.5 A g\(^{-1}\). These tests were conducted between two voltage windows, one between 1.5 and 4 V and the other between 3 and 4.5 V. In all cases of CCCD analysis three cycles were conducted in order to produce a stabilized plot, the third cycle was selected to represent performance of that current density.
CV analysis was conducted at a scan rate of 5 mV s\(^{-1}\) between the same two voltage windows as defined above i.e. one between 1.5 and 4 V and the other between 3 and 4.5 V. This technique allows for definition of adverse chemical reactions at higher voltages while also providing a qualitative view of cell performance. It should be noted that CV analysis is not used for deriving any quantitative properties, as they are difficult to derive and lack substantial definition; a min/average/max capacitance derived from CV bears little meaning in comparison to the definite capacitance values, which can be derived from CCCD.

EIS was attempted but difficulty arose in reaching a stable current, this pertains to complications in how EIS is conducted using a Solartron 1255B FRA (frequency response analyses). Essentially, prior to EIS analysis cells could either be held at constant voltage or in open circuit condition; the latter option was selected during experimentation as it was believed that holding cells at high voltage may cause uneven chemical reactions across different samples. The consequence of this was that samples were not in a steady voltage state when EIS was initiated and as such the response was often non-steady, it is for this reason that EIS results have been discounted from the analysis process. With hindsight, it would have been preferable to hold cells at a constant low voltage rather than trying to assess performance purely at higher voltages.

The quantitative properties of interest in the following experiments are:

- Mass Specific Capacitance
- Areal Resistance
- Charge storage efficiency
- Energy storage efficiency
- Mass Specific Energy Density
- Mass Specific Power Density

Using these properties, it will be possible to definitively identify trends in the gathered results. It should be noted that resistance will be presented specific to electrode area; while all electrodes in this work do possess an equal area, it aids in comparing results to those found in literature. All electrochemical analysis was conducted at a constant 25 °C. Note: the capacitance is derived per total active material mass of both electrodes within the cell.
6.2.4 Pre-lithiation Technique – Formation Cycling

All LIC devices require pre-lithiation in order to overcome the initial high charge-transfer resistance present in low lithiation states [178]; in this work pre-lithiation was achieved through the use of formation cycles which was developed by Khomenko et al. [91]. The cell was repeatedly driven to high voltage followed by long periods of self-discharge. Initial work towards using formation cycles was actually conducted whilst using silicon based electrodes in LIC devices (see Section 6.4); from this initial work an advanced type of formation cycling was developed and applied across all LIC cell types (both using graphite and silicon based electrodes). This advanced type of formation cycling involved two initial formation cycles at 3.5 V followed by a further two formation cycles at 4 V, these cycles consisted of a high current ramp to the desired voltage followed by a relaxation period in an open circuit condition for three hours. In order to assess the effect such a process has upon cell performance it was decided that CV analysis would be conducted at the start, middle and end of the pre-lithiation process. An example of the ultimate formation cycling procedure developed for use in this work is shown in Figure 6.1.

![Formation Cycling Diagram](image_url)

**Figure 6.1** Example of the formation cycling technique implemented for LIC research. In essence, the cell is repeatedly driven to high voltage followed by long periods of self-discharge.

In principle, this process should shift the intrinsic potential of the negative electrode to a lower potential i.e. a high lithiation state, than that with which it started with. One item of uncertainty in this matter is how lithiation will occur in the presence of a finite quantity of electrolyte, it was for this reason that the quantity of electrolyte used in an LIC was monitored.
6.3 LIC Using a Graphite Based Negative Electrode

6.3.1 Theoretical Insight – LIC with Graphite Based Negative Electrode

The aim of this section is to produce LICs which use the current state-of-the-art graphitic material as the negative electrode. It has been elected that Sigma PAC will be used as the positive electrode due to the flexibility offered during electrode fabrication i.e. the thickness and thus areal density can be defined.

Prior to producing LIC devices it is necessary to establish their theoretical properties based upon what is known about the materials intended for use. The techniques used here have been previously presented in Section 2.5 when considering hypothetical materials, now they will be applied to the materials at hand.

![Relative power and energy density as a function of the mass ratio of the electrodes for LICs utilizing AC as positive electrode and graphite as negative electrode. Note, this graph associates only with the materials used in [91].](image)

Figure 6.2 Relative power and energy density as a function of the mass ratio of the electrodes for LICs utilizing AC as positive electrode and graphite as negative electrode. Note, this graph associates only with the materials used in [91].

It has been found previously by Khomenko et al. [91] that implementing a highly underutilised GC electrode may present improved power capabilities; this is presented clearly in Figure 6.2 taken from [91]. An important aspect about this figure is to note that it only associates with the materials used in [91]; specifically, the AC material was Super 50 which was found to have a mass specific capacitance of 76 F g⁻¹ using 1.0M TEA⁺BF₄⁻ in ACN (acetonitrile) and 90 F g⁻¹ when using 1.0M Li⁺PF₆⁻ in EC/DEC, the first value was derived by EIS analysis at 2.5 V while the second value was derived by CV analysis at voltages between 2 and 4 V versus a lithium QRE. The graphitic material used in [91] was SLC1025 which was declared to possess a charge capacity of 380 mA h g⁻¹.
Using the value of 90 F g⁻¹, Khomenko et al. proposed that a Super 50 AC electrode which operates between 2 and 5 V will possess a specific capacity of ~75 mA h g⁻¹, the method of this conversion is presented in Appendix 3. Thus, the mass ratio of AC to graphite should be 5:1 i.e. 380 mA h g⁻¹ divided by 75 mA h g⁻¹, in order to fully utilize the charge capacity of the graphite electrode, this reflects the maximum ratio found in Figure 6.2. Ideally, a similar approach would have been taken in this work but at the point of experiment initiation an effective QRE device had not yet been established. As such, it was initially elected to use the capacitance value of 60 F g⁻¹ for Sigma PAC established in Section 5.3 using 1.5M TEA⁺BF₄⁻ in ACN. While this value was not ideally representative of the system to be fabricated, it did provide an initial indication as to what the mass specific capacitance will be.

At this point, discussion arose as to the exact change in voltage experienced by the positive AC electrode. Khomenko et al. [91] demonstrated that a graphite based LIC cell, where the charge capacity of both electrodes is fully utilised, the positive AC electrode can experience a change in voltage of 3 V between 2 V and 5 V versus a lithium QRE. Later in [91], Khomenko et al. showed that for a graphite based LIC which uses an underutilised graphite electrode the minimum voltage between which the device will operate effectively is close to 3 V, thus decreasing the available potential window to between 3 V and 5 V versus a lithium QRE. Further in [91], Khomenko et al. showed that a graphite based LIC cell which operates up to 5 V versus a lithium QRE will experience a 35 % loss of capacity over 10,000 CCCD cycles at 650 mAg⁻¹ (per mass of one electrode) while a graphite based LIC cell which operates up to 4.5 V versus a lithium QRE loses only 10 % loss in capacity over 10,000 CCCD cycles at the same current density.

As such, based upon the finding above it was decided that the actual operating window of the AC electrode in a graphite based LIC device is 3 V to 4.5 V i.e. a change of 1.5 V. Incidentally, this appears to agree with the figures presented by Naoi and Nagano in their recent publication (2013) [86]. Thus, it was decided that calculations in this work would assume a change of 1.5 V at the positive AC electrode compared to 3 V used in the initial calculations of Khomenko et al. This resolves the issue of the change in voltage experienced by the positive AC electrode and agrees with previous understanding (see Section 2.5) that GC remains close to 3 V relative to its initiation potential [86, 173, 174].

From these findings, it was determined that devices in which GC was 50% utilised should be fabricated, according to Figure 6.2 this presents a 50% increase in power density alongside a
15% loss in energy density, this appears to be a reasonable trade-off. Thus, using the calculations provided in Appendix 3 as described in Section 2.5, alongside the understanding that Sigma PAC presents a mass specific capacitance of 60 F g\(^{-1}\) while graphite presents a charge capacity of 380 mA h g\(^{-1}\), it is possible to calculate the theoretical mass specific energy density as a property of both electrode utilization and mass ratio. Such a calculation has been done with the results presented in Table 6.1; it should be noted that this calculation makes some idealized assumptions. It has been assumed that the lithiation of GC occurs at a constant voltage, this runs counter to the fact that approximately the first 20% of the lithiation process in GC occurs at a varying voltage. In relation to this, it has been assumed that the intercalation potential of GC is 3 V, in reality the true intercalation potential will be approximately 0.2 V lower than this, especially during the discharge phase [174]. Regardless, the calculations provided in Table 6.1 are broadly indicative of the expected cell performance and the production of cells with this configuration (mass ratio) was sought.

Table 6.1 Theoretical energy density of an LIC device which contains Sigma PAC as the positive electrode and graphitic carbon as the negative electrode. The negative electrode charge capacity utilization has been defined as 50%. The peak cell voltage has been taken as 4.5 V.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>PAC Charge Capacity (1.5 V) (a)</th>
<th>GC Charge Capacity (3 V) (b)</th>
<th>PAC Charge Capacity Utilisation</th>
<th>GC Charge Capacity Utilisation</th>
<th>Mass Ratio</th>
<th>Theoretical Mass Specific Energy Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Sigma) PAC : GC (\Sigma)</td>
<td>25.0 A h g(^{-1})</td>
<td>380 A h g(^{-1})</td>
<td>100 %</td>
<td>50 %</td>
<td>7.44 : 1</td>
<td>82.64 W h kg(^{-1})</td>
</tr>
</tbody>
</table>

\(a\) Sigma PAC charged from 0 to 1.5 V

\(b\) Graphitic carbon charged at a constant 3 V.

One aspect to note about the calculations presented in Table 6.1 is that the peak cell voltage has been taken as 4.5 V. There is concern that this voltage may extend beyond the theoretical ESPW limits presented in [86] and as such testing will also be conducted up to 4 V. As such, theoretical calculations have been pursued (using the methods described previously in Section 2.5) which assume the Sigma PAC is charged between 0 and 1 V while the GC electrode is charged at 3 V, this presenting a maximum cell voltage of 4 V. The results of these calculations are presented in Table 6.2 and indicate that a reduction in voltage window of 0.5 V results in a 38% reduction in theoretical mass specific energy density.
Capacitive Energy Storage: Filling the gap

Table 6.2. Theoretical energy density of an LIC device which contains Sigma PAC as the positive electrode and graphitic carbon as the negative electrode. The electrode mass ratio is pre-defined by the results presented in Table 6.1. The peak cell voltage has been taken as 4 V.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>PAC Charge Capacity (1 V) a</th>
<th>GC Charge Capacity (3 V) b</th>
<th>PAC Charge Capacity Utilisation</th>
<th>GC Charge Capacity Utilisation</th>
<th>Mass Ratio</th>
<th>Theoretical Mass Specific Energy Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC : GC</td>
<td>16.7</td>
<td>380</td>
<td>100</td>
<td>33.0</td>
<td>7.44 : 1</td>
<td>51.4</td>
</tr>
</tbody>
</table>

a Sigma PAC charged from 0 to 1 V
b Graphitic carbon changed at a constant 3 V.

6.3.2 Cell Configurations – LIC with Graphite Based Negative Electrode

Based upon theoretical calculations and experimental insight of [91] it was deemed necessary to fabricate Sigma PAC and GC based LIC cells with a mass ratio of m(7.44:1). This ratio should in theory provide a series of cells with which further investigations can be compared.

As such, three sets of circular 1.767 cm² Sigma PAC and GC electrodes were fabricated using the tape casting technique described in Section 4.4. Attempts were made to produce GC electrodes with a comparable mass to the silicon based electrode (NXA-513) under investigation, this was done so to minimise variability. Ultimately, the mass of the GC electrodes was approximately 15% less than the silicon content of NXA-513 which was deemed acceptable. The precise mass and thickness of each GC electrodes is defined in Table 6.3 and presents an average mass of 3.6 mg and average thickness of 53 μm, these values are lower than those required to meet research aim 5 in section 2.8 but there is reasoning behind this; if a high GC electrode mass were to be used then the mass of the AC electrode must also be significantly higher. Consider the possibility that GC electrodes were fabricated with the desired minimum mass of 10 mg, the PAC electrode would need to be 74.4 mg or, in relation to the 1.767 cm² electrode disks used, 42.1 mg cm². Per the linear fit of Figure 4.15, the electrode thickness would be over 1 mm thick, this value is totally unreasonable and quite possibly unattainable with available fabrication instruments and processes, it is for this reason that the GC electrode mass was kept well below the desires of research aim 5.

To achieve the desired mass ratio, electrodes of Sigma PAC were required to be 27.9 mg (as the GC electrodes possess an average mass of 3.6 mg). This was achieved to a high degree of accuracy as shown in Table 6.3; the average Sigma PAC electrode mass was 27.5 mg. These
corresponded with electrode thicknesses between 255 and 281 μm and as such these electrodes agree with the targets defined by research aim 5. The resulting mass ratio of all cells is in excellent agreement with the theoretical requirements set out in the previous section.

All electrodes were then placed as appropriate in CR2032 coin cells which also contained two spacers, prior to the addition of electrolyte cell materials were cumulatively weighed; subsequently, three droplets of LiPF₆ in EC/DEC electrolyte were added (onto the separator) prior to sealing, as described in Section 4.5.3. The final cell was wiped clean of any ejected electrolyte and reweighed, the total electrolyte content was thus calculated and is displayed in Table 6.3.

Table 6.3 Cell configurations and sample identification for LIC devices using a graphite based negative electrode and a Sigma PAC based positive electrode. Note that areal density and mass values refer to the active material alone.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Series/Sample</th>
<th>Sample Identification</th>
<th>Areal Density (+/-)</th>
<th>Mass (+/-)</th>
<th>Mass Ratio</th>
<th>Average Thickness (+/-)</th>
<th>Combined Volume a</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC-LIC A</td>
<td>16.19 / 2.09</td>
<td>28.61 / 3.69</td>
<td>7.76 : 1</td>
<td>281 / 48</td>
<td>58.2</td>
<td>72.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC-LIC B</td>
<td>15.34 / 2.05</td>
<td>27.10 / 3.63</td>
<td>7.48 : 1</td>
<td>266 / 58</td>
<td>57.2</td>
<td>73.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC-LIC C</td>
<td>15.07 / 1.97</td>
<td>26.63 / 3.49</td>
<td>7.63 : 1</td>
<td>255 / 54</td>
<td>54.7</td>
<td>81.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a All electrodes were 1.5 cm disks thus coating area was 1.767 cm².

One aspect of concern was with regards to the quantity of lithium ions in the electrolyte available for lithiation. Consider that if the electrolyte does not contain enough lithium ions to adequately fill the GC electrode to 50% of its charge capacity, or in other words lithiation state, then cell performance will be degraded. As such, it was deemed necessary to calculate the number of lithium ions available in the electrolyte and compare this to the quantity of carbon atoms available in the GC electrode. As it is believed that there is a singular lithiation state of graphite i.e. LiC₆, it is possible to evaluate if the electrolyte present is sufficient.

Such evaluation is numerically cumbersome and as such has been presented in Appendix 12. Essentially, the process towards the calculation was to break the electrolyte down into its atomic content and then calculate the mass percent of each atomic component, this can be achieved because the atomic weight of each atomic component is known. Ultimately, it was found that Li ions account for 0.534% of the mass of 1M LiPF₆ EC/DEC 50/50 (V/V).
6.3.3 Results and Analysis – LIC with Graphite based Negative Electrode

At this point all three cells were put to test using the standard test procedure defined previously in Section 6.2.3. Unfortunately, it must be stated that sample GC-LIC C did not function at all; it is believed this is due to a short circuit between opposing electrode which may have occurred due to movement of the separator during fabrication, but this is not certain as the equipment for de-sealing a CR2032 coin cell was not available.

As such samples GC-LIC A and GC-LIC B were subjected to the advanced type of formation cycling, described in Section 6.2.4, as is suggested in [91]; the results of CV analysis pre, mid and post formation are presented in Figure 6.3. There is a stark difference between the two apparently identical samples: GC-LIC A appears to exhibit extremely poor performance regardless of formation cycling, this is indicated by the low current density. Subsequent CCCD tests were conducted upon sample GC-LIC A but it was found that it exhibited an extreme amount of electronic resistance; the results exemplifying this can be found in Appendix 13. As such, this sample was excluded from further analysis.

Sample GC-LIC B presents better performance; consider the 1st CV cycle, it is noticeable that the results of CV analysis differ significantly from those of an EDLC type EC device (Chapter 5), this is due to the chemical nature of an LIC type EC device. In essence, at low voltages below 2.5 V there is almost no charge transfer between electrodes, above 2.5 V charge transfer increases in two clearly defined regions, between 2.5 and 3 V there is a linear slope and between 3.5 and 4 V there is another linear slope of increased gradient but careful observation indicates this gradient is decreasing. Upon discharge there is a delayed shift from positive to negative current, this indicates that the scan rate of 5 mV s⁻¹ is too fast for equilibrated charge transfer to occur. The cause of this is most likely slow lithium ion diffusion through the GC electrode. The discharge curve peaks at approximately 3.2 V and sharply declines below 3 V,
this indicates that by this point the majority of lithium ions which were absorbed (lithiated) were de-lithiated from the GC electrode by 3 V.

Concerning the 2\textsuperscript{nd} and 3\textsuperscript{rd} CV i.e. mid and post formation cycling, there is a reduction in charge transfer at the peak voltage of 4 V and a slightly less pronounced charge transfer at voltages below 3 V. Incidentally, it is close to 3 V at which the graphite electrode is believed to experience intercalation thus providing proof that formation cycling has pushed the GC electrode to a higher lithiation state.

Further CV analysis at 5 mV s\textsuperscript{-1} was conducted between 3 and 4.5 V on sample GC-LIC B, which theoretically possesses a 50% utilized GC negative electrode; the results of this are presented in Figure 6.4 alongside post-formation CV analysis between 1.5 and 4 V. It is quite clear to see that charging between different, but overlapping, voltage windows presents wholly different CV responses. The results of CV between 1.5 and 4 V has been discussed previously above. The use of a 3 to 4.5 V voltage window presents an interesting response, above 4 V on the upward sweep there appears to be a significant reaction occurring. This has been partially identified as the formation of an SEI layer which had not previously formed due the lack of high voltage formation cycling. On the downward sweep a section between 3.8 and 4.2 V
experiences a bulge, this indicates that the reaction may be partially reversible but there is uncertainty as to how this associates with the second bulge at lower voltages.

![Graph](image)

Figure 6.4 Results of CV testing at 5 mV s\(^{-1}\) (3rd cycle) of a single LIC type EC device using Sigma PAC as the positive electrode and graphitic carbon as the negative electrode combined with a LiPF\(_6\) EC/DEC 50/50 (v/v). The negative electrode charge capacity utilization has been previously calculated as 50%.

In order to further investigate this phenomenon CV was conducted at 100 mV s\(^{-1}\), the results of this are presented comparatively against those at 5 mV s\(^{-1}\) in Figure 6.5. Firstly, it is interesting to note that the magnitude of current is relatively similar despite the drastic increase in scan rate, this indicates that the system is restricted in some manner. One possible reason for this restriction is lithium intercalation into the graphite structure, it is known that this can be a slow process which depends greatly on graphite particle size [91]. The second interesting aspect of this high scan rate is the dramatic irreversible charge transfer above 4.3 V, this is in agreement with the theoretical limits presented in [86] but is lower than the experimental setup presented in [91] albeit this setup did present a 10% degradation of initial capacity over 10,000 charge-discharge cycles.

![Graph](image)

Figure 6.5 Results of CV testing at 5 mV s\(^{-1}\) (3rd cycle) and 100 mV s\(^{-1}\) of a single LIC type EC device using Sigma PAC as the positive electrode and graphitic carbon as the negative electrode combined with a LiPF\(_6\) EC/DEC 50/50 (v/v).
Figure 6.6 CCCD testing at 0.1 A g⁻¹ (3rd cycle) of a single LIC type EC device using Sigma PAC as the positive electrode and graphitic carbon as the negative electrode combined with a LiPB EC/DEC 50/50 (v/v). The negative electrode charge capacity utilization has been previously calculated as 50%.

Shown in Figure 6.6 are the results of CCCD testing at 0.1 A g⁻¹ of a single LIC type EC device using Sigma PAC as the positive electrode and graphitic carbon as the negative electrode, the cell was charged between 1.5 and 4 V in one instance and between 3 and 4.5 V in another. It appears in both cases that charge storage initiates around 3 V, suggesting that the GC electrode is pre-lithiated, and rises non-linearly to 3.5 V at which point linear charge storage occurs. This linear charge associates with the positive AC material behaving as an EDLC while the negative GC electrode remains at a relatively constant potential.

The charge transferred during both the charge and discharge steps has been calculated: it can be seen that extending the upper voltage window limit by 0.5 V allows almost double the charge transfer. This is not entirely surprising considering the device only being to function fully above 3.5 V thus extending from 4 to 4.5 V is also doubling the effective voltage window.

Table 6.4 Charge transfer during CCCD testing at 0.1 A g⁻¹ (3rd cycle) at differing CCCD voltage windows. Input refers to the charging process while output refers to the discharging process.

<table>
<thead>
<tr>
<th>CCCD Voltage Window</th>
<th>Charge Input</th>
<th>Charge Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 to 4 V</td>
<td>0.93</td>
<td>0.89</td>
</tr>
<tr>
<td>3 to 4.5 V</td>
<td>1.74</td>
<td>1.49</td>
</tr>
</tbody>
</table>
Table 6.5 KPIs derived from CCCD testing at 0.1 A g\(^{-1}\) (3\(^{rd}\) cycle) at differing CCCD voltage windows. All values correspond to the discharge phase unless explicitly stated otherwise.

<table>
<thead>
<tr>
<th>CCCD Voltage Window</th>
<th>Mass Specific Capacitance (^{a}) (Charge) F g(^{-1})</th>
<th>Mass Specific Capacitance (^{a}) (Discharge) F g(^{-1})</th>
<th>Areal Resistance (\Omega ) cm(^{2})</th>
<th>Charge storage efficiency %</th>
<th>Energy storage efficiency %</th>
<th>Mass Specific Energy Density Wh kg(^{-1})</th>
<th>Mass Specific Power Density kW kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 to 4 V</td>
<td>48.5</td>
<td>44.1</td>
<td>76.4</td>
<td>97</td>
<td>91</td>
<td>27.9</td>
<td>2.96</td>
</tr>
<tr>
<td>3 to 4.5 V</td>
<td>50.9</td>
<td>48.5</td>
<td>164</td>
<td>86</td>
<td>80</td>
<td>50.3</td>
<td>1.71</td>
</tr>
</tbody>
</table>

\(^{a}\) Calculated between 0.7 and 0.8 \(V_{\text{max}}\) and assuming only the positive Sigma PAC electrode is capacitive i.e. taken relative to mass of the PAC electrode.

\(^{b}\) Under matched load condition with a peak voltage of taken as that of the voltage window.

An item of interest in this matter is the mass specific capacitance; as previously stated, the mass specific capacitance of the Sigma PAC material was assumed to be equivalent to that of a system using TEA\(^+\)BF\(_4\) in acetonitrile i.e. 60 F g\(^{-1}\). From the CCCD testing, if an assumption is taken that the capacitive response i.e. voltage increase/decrease over time, is related purely to the Sigma PAC based EDLC electrode then the mass specific capacitance value of this electrode can be calculated. These values have been calculated during the liner charge/discharge phase and presented in Table 6.5 alongside other KPIs (key performance indicators) derived from CCCD testing at 0.1 A g\(^{-1}\). It is clear to see that the mass specific capacitance values are between 16 and 26 % lower than those originally assumed in theoretical calculations and cell design.

In the work conducted by Khomenko et al. [91], it was found that Super 50 AC (which has an SSA value of 1283 m\(^2\) g\(^{-1}\) calculated by CO\(_2\) sorption analysis) combined with 1M LiPF\(_6\) in EC/DMC possesses a mass specific capacitance of 86 F g\(^{-1}\). Considering that Sigma PAC possess a microporous SSA of 801 m\(^2\) g\(^{-1}\), and assuming that mass specific capacitance is linearly correlated with material SSA, Sigma PAC may possess a mass specific capacitance of 54 F g\(^{-1}\). Such a value is slightly higher than the results derived above and may be attributed to differing SSA measurement methods or the difference in electrolyte solvent.

Shown in Table 6.5 are the areal resistance values derived from CCCD at 0.1 A g\(^{-1}\); these values are significantly higher than those of EDLC devices presented in Section 5. The source of this increased areal resistance is not entirely clear; the cells involved in this work contained two spacers and as such contact resistance is not the issue. Also, recall that these cells included Super P\(^{\circ}\)-Li carbon black as a conductive additive, thus further mystifying the high resistance. One possible explanation is the low quantity of coating slurry produced; this low quantity
prohibited using an overhead stirrer and as such mixing was achieved using a magnetic stirrer (see Section 4.4.2) which may have resulted in an inhomogeneous mixture. Such inhomogeneity could also be the explanation as to why sample GC-LIC A failed to perform as expected.

One other matter of interest regarding areal resistance is its variation depending on voltage window; this finding is believed to have links to the method of calculation combined with the fact that above 4.3 V the cell experiences extensive chemical reaction (see Figure 6.5). In the case where the cell reaches a peak voltage of 4.5 V it is effectively outside the ESPW of the system; upon initiating discharge, there are thus two effects on the system, one due to the discharge current (ohmic losses) and one due to the rate at which charge is consumed in chemical reaction. This combined effect causes a larger voltage drop in the CCCD plot than that which happens when the cell is discharged within the ESPW. As such, the result of 164 Ω cm² is considered unrealistic while the value of 76.4 Ω cm² better reflects reality.

The charge storage efficiency of the two voltage windows backs up the findings above, when the cell is charged up to 4.5 V its charge storage efficiency decreases by over 10 %. The low charge storage efficiency and abnormal resistance combine to also reduce the energy storage efficiency for the higher voltage window. The lower voltage window of 1.5 to 4 V is thus deemed to better reflect true device performance.

A further consequence of high areal resistance values is the apparently low power density of these devices. Using similar approaches Khomenko et al. [91] achieved maximum power densities of 10 kW kg⁻¹ but it should be noted that this value was achieved at a current density far above 0.1 A g⁻¹ (believed to be around 10 A g⁻¹ as values are not explicitly stated). As such further testing was conducted across a broad range of current densities 0.1, 0.25, 0.5, 1 and 2.5 mA g⁻¹, the power densities derived from this approach are presented comparative to the derived mass specific energy density in the form of a Ragone plot as presented in Figure 6.7. From this, it can be seen than a peak power density of ~3 kW kg⁻¹ was achieved from both voltage windows but it must be noted that this value also corresponded to poor mass specific energy density.
The mass specific energy density of this device is interesting; this is because it does not fit with the theoretically calculated results of 51.42 and 82.64 W h kg\(^{-1}\) for voltage windows of 1.5 to 4 V and 3 to 4.5 V which have been found experimentally to in fact be 27.91 and 50.33 W h kg\(^{-1}\), respectively. The author will now discuss the possible causes of this difference.

The simplest aspect to note is that the theoretical calculations are ideally efficient while reality is not. Modification of the experimental results in order to account for energy storage efficiency yields 30.67 and 62.91 W h kg\(^{-1}\), an improvement but still not equivalent to the theoretical results.

A further aspect of how reality may significantly differ from theory is the use of formation cycles i.e. pre-lithiation techniques. These cycles are used to shift the GC electrode to a higher lithiation state in order to overcome the resistance presented at low lithiation states [178]. For the initial theoretical calculations the entirety of the GCs charge capacity was utilised but by the nature of pre-lithiation this is not the reality, some of the charge capacity is occupied prior to the initiation of CCCD testing thus reducing charge capacity. Alongside making adjustments for the mass specific capacitance, which will be taken as the value derived during the charging process, it has been found that assuming 25 % of GCs charge capacity is occupied prior to CCCD initiation results in theoretical mass specific energy densities of 32.32 and 55 W h kg\(^{-1}\), values which are close to those found experimentally. Unfortunately, due to the lack of QRE incorporated into this device there is no data to confirm or deny this assumption.
As such, it has been deemed appropriate to further consider how theoretical results are derived. One avenue of interest are the voltages at which each electrode operates; during initial theoretical calculations it was taken that the negative GC electrode operates at 3 V while the positive PAC electrode operates between 0 and 1.5 V i.e. such that total cell voltage is 4.5 V. According to CCCD plots in Figure 6.6 the ‘capacitive’ phase does not start until 3.5 V, after which the electrochemical response is capacitive in nature. This capacitive phenomenon has been attributed purely to the PAC electrode as Li intercalation in to GC should occur at a relatively constant voltage, the only region which runs counter to this is when the cell is operating between 3 and 3.5 V, between these voltages it appears both electrodes are undergoing changes in potential which may suggest that the GC electrode is not in a lithiated state as previously considered. Such a proposal runs contrary to prior assumption that 25 % of GCs charge capacity if occupied prior to CCCD initiation.

An in-depth investigation of the literature has found other valuable insights. Although it was previously known that an SEI (surface electrolyte interface) is formed on graphite when used as an anode in LIC devices (see Section 2.5), it was not appreciated that this results in a reduction of charge capacity with some estimates putting this reduction at around 10% [281]. When such a reduction is taken into consideration it is possible to arrive at the theoretical estimations of 37.61 and 63.36 W h kg⁻¹ for cells with voltage windows of 1.5 to 4 V and 3 to 4.5 V. These values are slight over estimates of those derived (with efficiency adjustment) from the experiments at hand.

6.3.4 Conclusion – LIC with Graphite Based Negative Electrode

The aim of this section is to produce LICs which use the current state-of-the-art graphitic material as the negative electrode. Although only a single working device was achieved it was found that this device is relatively comparable in terms of energy density to the possible theoretical values. The maximum energy density was found to be 50.33 W h kg⁻¹ when operating between 3 and 4.5 V; according to Khomenko et al. [91] this is a reasonable voltage window but CV investigations found that chemical reactions occur above 4.3 V.

An interesting correlation regarding this reaction has been drawn between the findings of [91] and [281]. In [91] the devices were operated up to 4.5 V and experienced a 10 % degradation from the initial charge capacity value over 10,000 cycles; in [281] the formation of an SEI layer on graphite is also stated to reduce charge capacity by 10 %. As such, it is quite possible that the reaction presented in Figure 6.5 at 4.3 V is the formation of this SEI layer.
Ultimately, this chemical reaction could be avoided by operating below 4.3 V but this will negatively impact upon mass specific energy density.

Device performance with regards to mass specific power density was lower than anticipated, this was despite the use of two spacers in coin cell fabrication and the inclusion of a conductive additive in the graphite electrode. From [91] it was expected that a graphite based LIC device, particularly one which implements an underutilised electrode, would have presented 10 kW kg⁻¹ or more but the results presented a peak power value of 3 kW kg⁻¹ which was also tied with poor energy performance. This led the author to speculate that there was an issue with electrode fabrication, possible related to poor mixing of the slurry prior to deposition.

While the fact that a single sample is insufficient for drawing significant conclusions, the high mass specific energy density is encouraging. Alongside the results of [91], this finding leads the author to believe that LICs can offer a viable method for filling the performance gap between traditional EDLC type EC devices and lithium-ion batteries. The next aspect of this investigation is to see if an LIC device using a silicon based negative electrode can further improve LIC performance.

6.4 LIC Using a Silicon Based Negative Electrode

6.4.1 Initial Theoretical Insight – LIC with Silicon Based Negative Electrode

The aim of this section is to produce LICs which use a novel silicon based material as the negative electrode. It has been elected for this investigation to try both Sigma PAC and Kynol ACC as the positive electrode material; Sigma PAC due to the flexibility offered during electrode fabrication i.e. the thickness and thus areal density can be defined and Kynol ACC due to its high mass specific capacitance value.

A novel silicon based electrode was acquired from an external company which specialises in silicon electrode development; it has been designated NXA-513. This material has been described previously (see Section 6.2.2 for details) but its composition is believed to be of most interest; the total areal density is 3.55 mg cm⁻² of which 2.45 mg cm⁻² is known to be silicon and 1.10 mg cm⁻² is known to be binder and additives. The binder used is PVDF and is believed to account for 10 % of the total areal density (see Section 4.2.1) i.e. 0.355 mg cm⁻², this leaves 0.745 mg cm⁻² as additives. These additives have been identified as primarily carbon based either of a Si surface coating or independent MWCNT content.
Chapter 6: An investigation of using a silicon based negative electrode in lithium ion capacitors

The combination of both silicon and carbon materials will make this investigation problematic as both behave as Li intercalative materials. The highest lithiation state of Si is Li$_2$Si, which offers a charge capacity of 4200 mA h g$^{-1}$, whilst GC (graphitic carbon) possesses a singular lithiation state of LiC$_6$, which offers a charge capacity of $\sim$380 mA h g$^{-1}$. The lithiation states of MWCNTs depends upon their diameter and wall number; as such, it has been found that the charge capacity will be between 200 and 380 mA h g$^{-1}$ depending on purity [282].

As such prior to electrochemical examination it has been deemed appropriate to theorise the outcomes of such examination, this will be conducted in a similar manner to that of Section 6.3.1 but accounting for the fact that lithiation occurs at a higher potential than GC relative to a lithium reference electrode ($\sim$ 0 V vs Li for GC, $\sim$4 V vs Li for Si). The impact of this is a lower cell voltage due to the limited operating window, further details on this aspect are provided in Section 2.5.

The mass specific capacitance of Sigma PAC will be taken as 50 F g$^{-1}$ which is in line with experimental results from Section 6.3.3; this material is expected to operate between 0 and 1.5 V for a cell with a maximum voltage of 4.1 V, which accounts for the lower intercalation voltage of Si. A limiting factor in the fabrication of these devices has been identified; in Section 2.5 it was found that a fully utilised device requires a mass ratio in the order of m(100:1) or greater, as the areal density of the silicon content in NXA 513 is 2.45 mg cm$^{-2}$ Sigma PAC would need to be at least 245 mg cm$^{-2}$ to fully utilize the Si material. Such an PAC areal loading would theoretically result in a thickness of $\sim$3,600 µm according to the linear fit of Figure 4.15, a value which is far beyond the capabilities of the tape casting method used in Sigma PAC electrode fabrication. As such, mass ratios of m(7.5:1), m(5:1) and m(2.5:1) will be used in theoretical calculations for devices which use Sigma PAC; these values are similar to those used in the analysis of GC, thus providing an element of direct comparability between results, and provide reasonable fabrication targets.
Table 6.6 Theoretical properties of a LIC device which contains Sigma PAC as the positive electrode and silicon based NXA-513 as the negative electrode. The peak cell voltage has been taken as 4.1 V.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>PAC Charge Capacity (1.5 V)</th>
<th>Si Charge Capacity (2.6 V)</th>
<th>PAC Charge Capacity Utilisation</th>
<th>Si Charge Capacity Utilisation</th>
<th>Mass Ratio</th>
<th>Theoretical Mass Specific Energy Density</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>PAC : Si</em></td>
<td>mA h g⁻¹</td>
<td>mA h g⁻¹</td>
<td>%</td>
<td>%</td>
<td>m(+) : (-)</td>
<td>W h kg⁻¹</td>
</tr>
<tr>
<td>m(7.5 : 1)</td>
<td>20.83</td>
<td>4200</td>
<td>100</td>
<td>3.72</td>
<td>7.5 : 1</td>
<td>61.48</td>
</tr>
<tr>
<td><em>PAC : Si</em></td>
<td>mA h g⁻¹</td>
<td>mA h g⁻¹</td>
<td>%</td>
<td>%</td>
<td>m(+) : (-)</td>
<td>W h kg⁻¹</td>
</tr>
<tr>
<td>m(5 : 1)</td>
<td>20.83</td>
<td>4200</td>
<td>100</td>
<td>2.48</td>
<td>5 : 1</td>
<td>58.16</td>
</tr>
<tr>
<td><em>PAC : Si</em></td>
<td>mA h g⁻¹</td>
<td>mA h g⁻¹</td>
<td>%</td>
<td>%</td>
<td>m(+) : (-)</td>
<td>W h kg⁻¹</td>
</tr>
<tr>
<td>m(2.5 : 1)</td>
<td>20.83</td>
<td>4200</td>
<td>100</td>
<td>1.24</td>
<td>2.5 : 1</td>
<td>49.85</td>
</tr>
</tbody>
</table>

a Sigma PAC charged from 0 to 1.5 V
b Si changed at a constant 2.6 V.

Shown in Table 6.6 are the theoretical properties of a LIC device using NXA 513 as the negative electrode and Sigma PAC as the positive electrode, note the low mass ratios correspond to extremely low Si utilisation values but interestingly they result in rather impressive theoretical mass specific energy densities especially considering the theoretical value for a 4 V LIC using GC was found to be ~35 W h kg⁻¹ after consideration of experiments.

The use of Kynol ACC as the positive electrode will also be attempted. Such a material has a single areal density of 12 mg cm⁻²; this limits the possible mass ratio to m(4.9:1). It is also important to recall that Kynol ACC has a mass specific capacitance of 116.16 F g⁻¹ when used with 1.5M TEA-BF₄ in ACN; in the case of Sigma PAC the mass specific capacitance when used with 1M LiPF₆ in EC/DEC was approximately 17% lower than estimated from using 1.5M TEA-BF₄ in ACN and as such it has been deemed appropriate to assume a similar case will occur with Kynol ACC. Thus, the mass specific capacitance of Kynol ACC will be assumed as 97 F g⁻¹. Other than this difference, the theoretical calculations will use the same underlying assumptions as those for cells which use Sigma PAC.
Table 6.7  Theoretical properties of a LIC device which contains Kynol ACC as the positive electrode and silicon based NXA 513 as the negative electrode. The peak cell voltage has been taken as 4.1 V.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>ACC Charge Capacity (1.5 V)</th>
<th>Si Charge Capacity (2.6 V)</th>
<th>ACC Charge Capacity Utilisation</th>
<th>Si Charge Capacity Utilisation</th>
<th>Mass Ratio</th>
<th>Theoretical Mass Specific Energy Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACC : Si m(4.9:1)</td>
<td>40.33</td>
<td>4200</td>
<td>100</td>
<td>4.71</td>
<td>4.9 : 1</td>
<td>112.22</td>
</tr>
</tbody>
</table>

\( a \) ACC charged from 0 to 1.5 V

\( b \) Si charged at a constant 2.6 V.

Table 6.7 shows the theoretical properties of a LIC device which contains Kynol ACC as the positive electrode and silicon based NXA 513 as the negative electrode. The theoretical mass specific energy density is over double that predicted for LIC devices which use Sigma PAC at an equivalent mass ratio, this is obviously due to the increase in material mass specific capacitance. Note that the Si charge capacity utilization is the higher than any viable Sigma PAC electrode. Such a finding suggests that the underlying restriction in these devices is the mass specific capacitance of the positive electrode.

6.4.2 Cell Configurations – LIC with Silicon Based Negative Electrode

Based upon the known restrictions in electrode fabrication, it has been deemed appropriate to investigate LIC devices which broadly fit with the theoretical findings of both materials. While the electrode utilisation values are vastly different from those of GC samples it is believed by the author that the similar mass, ratios will provide excellent comparability with previous results.

The fabrication procedures are equivalent to those used previously in Section 6.3; Sigma PAC based electrode fabrication is detailed in Section 4.4 and cell fabrication is detailed in Section 4.5. By this point in the experimental work a silver QRE had been developed which was appropriate for use in coin cell devices; consequentially, QREs were incorporated into some (but not all) of the samples using the methods described towards the end of Section 4.5.3.

Based upon the theoretical findings, LIC device configurations containing NXA-513 as the negative electrode and either Sigma PAC or Kynol ACC as the positive electrode were fabricated. With regards to LIC devices containing Sigma PAC, four device types were fabricated which each approximately represented mass ratios of m(1.72:1), m(3.67:1), m(5.83:1)
and m(7.31:1); these device types are labelled as type A, B, C and D, respectively. With regards to LIC devices containing Kynol ACC, one device type was fabricated which approximately represented a mass ratio of m(1.5:17); this type of device was labelled as type E. Three samples of each cell type were produced; it should be noted that the third sample of each type contained a silver QRE device. The detailed configuration of each sample is presented in Table 6.8, it should be noted that in the case of NXA-513 the areal density and mass represents the silicon content alone.

All electrodes were then placed as appropriate in CR2032 coin cells which also contained two spacers. Prior to the addition of electrolyte cell materials were cumulatively weighed; subsequently, three droplets of LiPF6 in EC/DEC electrolyte were added prior to sealing, as described in Section 4.5.3. The final cell was wiped clean of any ejected electrolyte and reweighed, the total electrolyte content was thus calculated and is displayed in Table 6.8. From this it can be clearly seen that there is a great deal of variability in electrolyte quantity. Sample B-1 has the lowest quantity with 61 mg while sample E-2 has the highest at 158 mg; it should be noted that samples containing Sigma PAC possess less electrolyte on average (84 mg) than samples of Kynol ACC (127 mg), this is due to Kynol ACC being highly absorbent thus requiring more electrolyte to be fully wetted. As sample E-1 possesses significantly less electrolyte than samples E-2 and E-3 it will be possible to assess the impact of electrolyte quantity between similar samples.

As with the cell configurations of Section 6.3.2, there was concern with regards to the quantity of lithium available in the electrolyte; this concern is particularly prominent considering the high charge capacity of silicon (4200 mA h g⁻¹). Using the approach detailed previously Section 6.3.2 it has been found that sample B-1, which possesses the lowest electrolyte quantity of 61 mg, will contain 2.8 x 10⁹ lithium ions. Assuming that the silicon content in NXA-513 is the primary intercalative material infers that the quantity of lithium ions required for 100 % Si utilization is 2.8 x 10⁹. Thus, it is possible to theorize that the lithium available in the least amount of electrolyte added to a sample can allow for 8.12 % Si utilization, a value above the maximum expected utilization value. Regardless, this finding raises an interesting question as to how LIC cells which contain high charge capacity materials could ever attempt to fully utilize their electrodes. Such a question will be further considered during the discussion section of this chapter.
Table 6.8 Cell configurations and sample identification for LIC devices using a silicon based negative electrode (NXA-513) and either Sigma PAC or Kynol ACC based positive electrode. Note that areal density and mass values refer to the active material alone. In the case of NXA-513 the areal density and mass represents only the silicon content.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Sample Identification</th>
<th>Type-Sample</th>
<th>Areal Density a (+ / -)</th>
<th>Mass a (+ / -)</th>
<th>Mass Ratio (+ : -)</th>
<th>Average Thickness (+ / -)</th>
<th>Combined Volume b</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC : Si Type A</td>
<td>Si LIC A-1</td>
<td>4.19 / 2.45</td>
<td>7.40 / 4.33</td>
<td>1.71 : 1</td>
<td>132 / 55</td>
<td>33.0</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si LIC A-2</td>
<td>4.26 / 2.45</td>
<td>7.53 / 4.33</td>
<td>1.74 : 1</td>
<td>139 / 55</td>
<td>34.3</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si LIC A-3 c</td>
<td>4.19 / 2.45</td>
<td>7.40 / 4.33</td>
<td>1.71 : 1</td>
<td>129 / 55</td>
<td>32.6</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>PAC : Si Type B</td>
<td>Si LIC B-1</td>
<td>8.82 / 2.45</td>
<td>15.58 / 4.33</td>
<td>3.60 : 1</td>
<td>191 / 55</td>
<td>43.5</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si LIC B-2</td>
<td>9.16 / 2.45</td>
<td>16.18 / 4.33</td>
<td>3.74 : 1</td>
<td>183 / 55</td>
<td>42.0</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si LIC B-3 c</td>
<td>9.02 / 2.45</td>
<td>15.94 / 4.33</td>
<td>3.68 : 1</td>
<td>184 / 55</td>
<td>42.2</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>PAC : Si Type C</td>
<td>Si LIC C-1</td>
<td>14.35 / 2.45</td>
<td>25.36 / 4.33</td>
<td>5.86 : 1</td>
<td>251 / 55</td>
<td>54.1</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si LIC C-2</td>
<td>14.05 / 2.45</td>
<td>24.82 / 4.33</td>
<td>5.73 : 1</td>
<td>264 / 55</td>
<td>56.3</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si LIC C-3 c</td>
<td>14.49 / 2.45</td>
<td>25.60 / 4.33</td>
<td>5.91 : 1</td>
<td>266 / 55</td>
<td>56.7</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>PAC : Si Type D</td>
<td>Si LIC D-1</td>
<td>17.92 / 2.45</td>
<td>31.66 / 4.33</td>
<td>7.31 : 1</td>
<td>323 / 55</td>
<td>66.7</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si LIC D-2</td>
<td>17.83 / 2.45</td>
<td>31.50 / 4.33</td>
<td>7.27 : 1</td>
<td>320 / 55</td>
<td>66.3</td>
<td>114</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si LIC D-3 c</td>
<td>17.99 / 2.45</td>
<td>31.78 / 4.33</td>
<td>7.34 : 1</td>
<td>325 / 55</td>
<td>67.1</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>ACC : Si Type E</td>
<td>Si LIC E-1</td>
<td>12.76 / 2.45</td>
<td>22.55 / 4.33</td>
<td>5.21 : 1</td>
<td>350 / 55</td>
<td>71.6</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si LIC E-2</td>
<td>12.62 / 2.45</td>
<td>22.30 / 4.33</td>
<td>5.15 : 1</td>
<td>350 / 55</td>
<td>71.6</td>
<td>158</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si LIC E-3 c</td>
<td>12.62 / 2.45</td>
<td>22.31 / 4.33</td>
<td>5.15 : 1</td>
<td>350 / 55</td>
<td>71.6</td>
<td>130</td>
<td></td>
</tr>
</tbody>
</table>

a Negative electrode accounts for Si content only. All Si based electrodes are 70% Si. The remaining 30% consists of binding materials (10%) and carbon additives, such as MWCNTs.
b All electrodes were 15 mm disks thus coating area was 176 mm².
c Sample contains silver quasi-reference electrode.

As the LIC investigation at hand is highly novel, the approach towards electrochemical investigation required development in situ; additionally, such LIC type EC devices incorporate aspects of both battery and EDLC type devices which complicates their testing. As such, it was deemed appropriate to conduct research in stages; these stages are described in detail during the presentation of results but roughly equate to three stages:
1. Sample 1 of each device type e.g. A-1, B-1 etc. experienced CCCD analysis between 0 and 4.6 V at 1 C-rate. This first stage did not involve any formation cycling and was purely to assess initial performance.

2. Based upon the results of the first stage: Sample 2 of each device type e.g. A-2, B-2 etc. experienced a preliminary type of formation cycling up to 4.3 V which experienced low current during the charge phase. This was followed by CCCD analysis between 0 and 4.3 V at a C-rate equivalent to that used in the first stage.

3. The third stage involved refinement of what was learnt from previous stages. All samples of all cell types were subjected to the developed type of formation cycling, described in Section 6.2.4, up to 4 V which occurred at rapid charge.

Note: The C-rate is a measure of the rate at which an electrochemical device is charged or discharged relative to its maximum charge capacity e.g. a device with a charge capacity of 1 A h being charged with a current of 1 A is experiencing charging process of 1 C-rate, this process will take 1 hour.

The theoretical maximum charge capacity of each device has been calculated and presented in Table 6.9; this was done so using the average mass of AC material present in each sample of device configuration and the AC specific charge capacities presented in Table 6.6 and Table 6.7. It has been assumed in doing this that the AC electrode operates between 0 and 1.5 V and as such the charge capacity corresponds to the quantity of charge required to increase the electric potential of the average AC electrode mass by 1.5 V (theoretically setting the maximum cell voltage at 4.1 V). A C-rate of 2 was selected as it was thought to provide an adequate charge-discharge time (theoretically totalling 1 hour); the current associated with this value is presented in Table 6.9.
Table 6.9 Theoretical maximum charge capacity and associated 1 C-rate current for LIC devices using a silicon based negative electrode (NXA-513) and either Sigma PAC or Kynol ACC based positive electrode.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>AC Electrode Mass a</th>
<th>AC Specific Charge Capacity</th>
<th>Maximum Charge Capacity b</th>
<th>Maximum Charge Capacity b</th>
<th>2 C-rate Current c</th>
</tr>
</thead>
<tbody>
<tr>
<td>+PAC : Si- Type A</td>
<td>7.45</td>
<td>20.83</td>
<td>0.155</td>
<td>0.558</td>
<td>0.31</td>
</tr>
<tr>
<td>+PAC : Si- Type B</td>
<td>15.9</td>
<td>20.83</td>
<td>0.331</td>
<td>1.191</td>
<td>0.662</td>
</tr>
<tr>
<td>+PAC : Si- Type C</td>
<td>25.3</td>
<td>20.83</td>
<td>0.526</td>
<td>1.894</td>
<td>1.00</td>
</tr>
<tr>
<td>+PAC : Si- Type D</td>
<td>31.7</td>
<td>20.83</td>
<td>0.660</td>
<td>2.376</td>
<td>1.32</td>
</tr>
<tr>
<td>+ACC : Si- Type E</td>
<td>22.4</td>
<td>40.33</td>
<td>0.903</td>
<td>3.251</td>
<td>1.80</td>
</tr>
</tbody>
</table>

a Average across three samples of device type.
b Maximum charge capacity when AC electrode charged from 0 to 1.5 V.
c At this C-rate a device should theoretically take 1 hour to both charge and discharge.

6.4.3 Results and Analysis – LIC with Silicon Based Negative Electrode

Preliminary CCCD analysis between 0 and 4.6 V

The first stage involved sample 1 of each device type e.g. A-1, B-1 etc; these samples were to experience CCCD analysis between 0 and 4.6 V at 2 C-rate associated with the theoretical maximum charge capacity (see Table 6.9); the results of this are displayed in Figure 6.8. It should be noted that this first stage did not involve any formation cycling and was purely to assess basic performance and the upper voltage limit of 4.6 V was selected to investigate the upper performance limits of such a silicon based LIC device. Prior to this, samples were left in an open circuit state for 5 minutes in order to assess their initial condition; sample A-1 settled at 0.3 V while samples B-1, C-1, D-1 and E-1 all settled between 0 and 0.1 V.

The results shown in Figure 6.8 are interesting. Firstly, it is important to note that the x-axis has been presented in terms of charge (in Coulombs) rather than time, this was done so to better visualise the increasing charge storage capacity (which is a component of test current and time). It has been appreciated that this limits comparability with the results of Section 6.3.3 and as such time taken to reach the theoretical capacity has also been presented in the figures caption;
all cells took \(\sim 31\) minutes to reach the theoretical charge capacity (indicated as vertical blue dash-dot line) but this did not always coincide with the assumed peak cell voltage of 4.1 V (indicated as horizontal red dashed line).

Figure 6.8 CCCD testing at 2 C-rate theoretical charge capacity (5\textsuperscript{th} cycle) from 0 to 4.6 V of differing LIC type EC devices using either Sigma PAC or Kynol ACC as the positive electrode and silicon based NXA-513 as the negative electrode combined with a LiPF\(_6\) EC/DEC 50/50 (v/v). The time taken for samples to complete a full cycle in minutes was (A) 157, (B) 65, (C) 46, (D) 69 and (E) 60.
Chapter 6: An investigation of using a silicon based negative electrode in lithium ion capacitors

Qualitatively, the results of CCCD testing (Figure 6.8) indicate that increasing the charge capacity of the positive electrode, such that a higher portion of the Si based electrode is utilized, produces improvements in cell functionality. This culminates in D-1 and E-1 producing CCCD profiles which are generally equivalent to those using a graphite based negative electrode. The voltage window of each device appears to vary depending on the quantity of silicon utilization, at low values (e.g. in A-1 utilization is theoretically less than 1.2 %) the limiting voltage appears to be 4.1 V, after which abnormal cell behaviour occurs. In contrast, samples D-1 and E-1 for which Si utilization is theoretically 3.7 % and 4.7 %, respectively, apparently present abnormal behaviour above 4.3 V during the charge phase. The discharge phase may tell a different story, recall that the graphite based LIC developed in Section 6.3 presented a significant voltage drop when operated up to 4.5 V, this was partially associated with the occurrence of adverse chemical reactions which also contribute to the voltage drop; such an occurrence may also be true for samples of D-1 and E-1 and may corroborate with sample A-1 in suggesting 4.1 V is the upper voltage limit of this device configuration.

Table 6.10  KPIs derived from CCCD testing at 2 C-rate theoretical charge capacity (5th cycle) from 0 to 4.6 V of differing LIC type EC devices using either Sigma PAC or Kynol ACC as the positive electrode and silicon based NXA-513 as the negative electrode combined with a LiPF₆ EC/DEC 50/50 (v/v). All values correspond to the discharge phase unless explicitly stated otherwise.

<table>
<thead>
<tr>
<th>Series-Sample</th>
<th>Areal Resistance (Ω cm²)</th>
<th>Charge storage efficiency (%)</th>
<th>Energy storage efficiency (%)</th>
<th>Mass Specific Energy Density (charged 0 to 4.1 V) (Wh kg⁻¹)</th>
<th>Mass Specific Energy Density (discharged 4.6 to 0 V) (Wh kg⁻¹)</th>
<th>Mass Specific Power Density (kW kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si LIC A-1</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Si LIC B-1</td>
<td>99.1</td>
<td>35</td>
<td>19</td>
<td>35.60</td>
<td>17.01</td>
<td>4.18</td>
</tr>
<tr>
<td>Si LIC C-1</td>
<td>105</td>
<td>43</td>
<td>30</td>
<td>31.53</td>
<td>19.98</td>
<td>2.66</td>
</tr>
<tr>
<td>Si LIC D-1</td>
<td>132</td>
<td>55</td>
<td>42</td>
<td>56.65</td>
<td>39.01</td>
<td>1.72</td>
</tr>
<tr>
<td>Si LIC E-1</td>
<td>87.3</td>
<td>64</td>
<td>51</td>
<td>97.70</td>
<td>68.05</td>
<td>3.44</td>
</tr>
</tbody>
</table>

a Under matched load condition with a peak voltage of 4.6 V at 2 C-rate.

The CCCD plots for silicon based LIC devices, presented previously in Figure 6.8, have been analysed and KPI have been extracted. The lack of capacitance is due to the predominant lack of a linear region in all but sample E-1. In all cases the areal resistance is substantial but equivalent to those produced when testing GC based LIC at high voltage (Section 6.3.3), this
could be due to a high electronic resistance but it is believed that the method of analysis has been compromised through additional voltage drop caused by adverse chemical reactions. Such a finding is also reflected in the low charge and energy storage efficiency values; it is apparent that the efficiency increases as Si utilisation increases, this matter will be investigated after further experimentation. The high resistance is also reflected by the low mass specific power density of the samples tested; although this is comparable to the values achieved by GC based LIC devices it is believed that the additional MWCNT content should provide a superior conductive, and thus power, performance.

With regards to mass specific energy density it was deemed appropriate to calculate two differing KPIs. The first is a measurement of the energy transferred during the charge process from 0 to 4.1 V; this associates well with theoretical calculations presented in Section 6.4.1 which were calculated up to a maximum cell voltage of 4.1 V. The second uses the standard approach defined in Sections 5 and 6.3 in which mass specific energy density is calculated from the full discharge plot.

The first KPI i.e. mass specific energy density (charged 0 to 4.1 V), indicates that the theoretical calculations of 61.48 and 112.22 W h kg\(^{-1}\) for D-1 and E-1, respectively, are close but not identical to the experimental values. The experimental values are approximately 10 % lower than theoretical values; this could be explained by the predominantly non-linear behaviour of such samples, something which was not accounted for in the theoretical analysis. One other aspect of difference is that the theoretical results were derived between 2.6 and 4.1 V whereas the experiment operated between 0 and 4.6 V but it does appear that charge storage does not effectively start until \(~2.6\) V during charge. Regardless, it is promising that the theory appears to hold true, particularly when considering the precise intersection between assumed voltage, theoretical charge capacity and experimental results present in samples D-1 and E-1 of Figure 6.8. The second KPI i.e. mass specific energy density (discharged 4.6 to 0 V), does not necessarily provide a significant amount of useful information as it includes the voltage drop due to adverse chemical reactions; this makes cells appear less efficient than they may in fact be if operated at a lower voltage.
Chapter 6: An investigation of using a silicon based negative electrode in lithium ion capacitors

Preliminary Formation cycling and CCCD analysis up to 4.3 V

Based upon these initial findings it was decided to pursue formation cycling and CCCD testing up to a maximum voltage of 4.3 V. It was also decided that type A devices were not viable for further testing as they did not present a clearly defined CCCD plot; in addition to this, it is observable that a type A device does not offer sufficient Si utilization. The experiments detailed in this section involved only sample 2 of each device type e.g. B-2, C-2 etc. Prior to analysis, samples were left in an open circuit state for 5 minutes, all of them settled at voltages between 0 and 0.1 V.

The use of formation cycling in this work was considered a preliminary approach as it had not been previously attempted by the author (although used in Section 6.3 it was in fact developed during work with Si based electrode). This preliminary formation cycling method was similar in principle to that of Khomenko et al. [91] i.e. cells are charged to high voltage then left in an open circuit condition. It was decided that a cell should be charged at a slower rate than the previous section, a C-rate of C/20 was selected. Unfortunately, the dramatic extension of experimental time required in order to accommodate this low C-rate was not considered and the default experimental time limit (a feature of the Solartron software used in electrochemical analysis) was not appropriately adjusted; as such, cell charging occurred for only 2.7 hours before the open circuit condition was enabled.

The results of formation cycling are presented in Figure 6.9; note that three formation cycles were conducted but the peak voltage achieved at the end of each cycle was not always equal between cell types, this is due to the aforementioned issue with experimental setup. The impact of this variation in peak voltage might be that some cells experience the formation of SEI layers while others do not, adding an element of undesired variability. Qualitatively, it is quite apparent that as the AC electrode charge capacity increases (from type B up to E) so does the charge retention during open circuit condition; this is indicated by the eventual formation of approximately flat plateaus in the open circuit phase of samples D and E. It is believed by the author that charge retention, when present, indicates successful pre-lithiation of a cell.
Figure 6.9  Three formation cycles performed on differing LIC type EC devices (Table 6.8) using the preliminary technique of charging at C/20 followed by three hours open circuit self-discharge.

Let us consider the physical processes involved with formation cycling and attempt to associate them with the responses seen in Figure 6.9. In a fresh sample, i.e. one just fabricated, the voltage between electrodes in an LIC device, which used NXA-513 as the negative electrode and AC as the positive electrode, has been found to be between 0 and 0.1 V; this implies neither electrode has yet accumulated any significant electric charge which would cause the potential difference (voltage) between them to be higher.

During the charging process, differing physical and chemical phenomena are occurring at each electrode; the positive AC electrode behaves as an EDLC while the negative Si based electrode (with MWCNT addition) behaves as an intercalative electrode. By their nature, an EDLC type electrode associates with the quantity of surface area (see Section 2.4.2) while an intercalative type electrode associates with the quantity of material due to charge storage below the surface (see Section 2.2.4). The fact that intercalative electrodes can store charge below the materials surface is coupled with the fact that ions must take time to diffuse towards those internal charge storage sites [36]. This diffusion occurs when there is a higher concentration of ions.
stored in one area of the material compared to another e.g. a high ion concentration at the material surface and low ion concentration at the materials core.

When formation cycling occurs, a cell is essentially being charged up to a certain voltage followed by a period of relaxation in an open circuit condition. With regards to the materials at hand: during the charge phase, Li ions will be absorbed into the intercalative surface materials of NXA-513 while PF\textsubscript{6} ions will be adsorbed onto the surface of AC based materials. A small quantity of AC material (as in the case of type B devices) may result in few PF\textsubscript{6} ions being adsorbed from the electrolyte which consequently results in few Li ions being absorbed from the electrolyte. Further to this, it has been previously found that electrode mass ratio plays a substantial role in the voltage experienced by each electrode (see Section 5.4); in previous work it was found that the electrode with the lowest mass may present the highest voltage (in the case of a material symmetric cell). The author believes such a concept extends to the LIC devices at hand [283].

Relating to the cell types under investigation, it is possible that in type B the quantity of AC material is low and thus this electrode experiences over charging (i.e. its voltage goes above the stable ESPW). This would cause significant self-discharge upon the initiation of an open circuit condition; such a phenomenon may be presented in Figure 6.9. It is also possible that the small quantity of ions stored at the negative NXA-513 electrode (associated with the small quantity of ions stored at the positive AC electrode) are diffusing away from material surface related high voltage sites to internal low voltage sites, thus balancing the voltage throughout the negative NXA-513 electrode; the consequence of this is a lower, but uniform, voltage overall. It could be this diffusion process which also causes significant self-discharge upon the initiation of an open circuit condition.

At the opposite end of devices tested (with respect to Si utilization) are type E devices in which a relatively high quantity of AC material is present, especially when considering its overall charge storage capacity. This may minimize the possibility of pushing the positive electrode out of its ESPW or it may minimize the requirement for charge to significantly diffuse throughout the negative NXA-513 electrode. At this point it is not possible to attain a deeper understanding of the precise physical and chemical phenomenon due to the lack of knowledge about the voltage of each electrode, such knowledge can be gained upon testing sample 3 of each Si based LIC type due to their inclusion of silver QRE devices.
Capacitive Energy Storage:  
Filling the gap

Figure 6.10  CCCD testing at 0.5 C-rate theoretical charge capacity (5th cycle) from 0 to 4.3 V of silicon based LIC type EC devices with varying silicon utilization, post formation cycling. This is compared against the preliminary ‘fresh’ results taken from sample 1 devices.

CCCD testing was conducted immediately after formation cycling at a C-rate of 0.5 between 1.5 and 4.3 V; the results of this are presented above in Figure 6.10. Also included in Figure 6.10 are the results of CCCD testing upon fresh samples at a C-rate of 2 between 0 and 4.6 V. By the nature of the differing test setups, these results are not directly comparable; however, they do provide a unique insight into the effects of formation cycling, particularly upon the initiation of the charge phase.

From qualitative analysis, it is immediately apparent that formation cycling has had a pronounced effect upon the charge capacity of Si based LIC devices. It appears that charge capacity has been reduced overall while the voltage at which charge transfer initiates has been raised to approximately 3 V, up from 2 V experienced by a fresh cell; this indicates that pre-lithiation has been successful in raising the lithiation state of NXA-513. The reduced charge
capacity can be explained when further consideration is given to the ramifications of formation cycling for pre-lithiation. Consider that for a fresh sample, neither electrode possesses stored charge upon test initiation (confirmed by the negligible open circuit voltage experienced in both samples 1 and 2). As such, the AC electrode, which is essentially the limiting factor in Si electrode utilisation, can fully utilise its entire charge capacity for charge storage. In the case of a cell which has been pre-lithiated, a certain quantity of this charge capacity has been utilised in balancing the pre-lithiation process i.e. if the negative electrode is storing ionic charge, so too is the positive electrode. If one was storing charge but the other was not then there would be an imbalance thus causing charge transfer until the electrodes achieved electroneutrality (see Section 2.6.1). As such, a certain portion of the available charge storage capacity of the AC material should already be filled if the cell is in a pre-lithiated state (particularly true if formation cycles were used as this extracts lithium from the electrolyte causing a perturbation from electroneutrality within that electrolyte); this will reduce the charge storage capacity available for CCCD testing as Figure 6.10 confirms.

The extent to which charge storage capacity is reduced appears to vary significantly between samples. Of the four samples related to formation cycling presented in Figure 6.10, it appears that sample D-2 has the largest reduction in available charge capacity. This could be a consequence of the uneven formation cycling process in which some cells achieved a higher voltage than others. Another possible contributor could have also been the variation in electrolyte quantity, but upon further inspection it was found that this cell received a quantity which was slightly above samples B-2 and C-2 but also 2/3 that of E-2. One final possibility is the Sigma PAC electrode was in some way defective and lacked the desired properties, but this is unlikely as it was taken from the same production batch as the Sigma PAC electrode used in sample D-1.

KPIs have been extracted from the formation cycled CCCD plots (Figure 6.8); these are presented in Table 6.11. From this information, a trend has been observed whereby as Si utilisation is increased (from type B up to E) a reduction in areal resistance occurs. This leads to sample E-2 achieving a mass specific power density of 23.4 kW kg⁻¹, an outstanding value among other LIC research and commercial devices [10, 38, 86, 91]; such an improvement over the results of fresh samples indicates that the use of formation cycling does indeed overcome the high resistance associated with Si devices in low states of charge [178].
Table 6.11 KPIs derived from CCCD testing at 0.5 C-rate theoretical charge capacity (5th cycle) from 0 to 4.3 V of silicon based LIC type EC devices with varying silicon utilization, post formation cycling. All values correspond to the discharge phase unless explicitly stated otherwise.

<table>
<thead>
<tr>
<th>Series-Sample</th>
<th>Areal Resistance (Ω cm²)</th>
<th>Charge storage efficiency (%)</th>
<th>Energy storage efficiency (%)</th>
<th>Mass Specific Energy Density (charged 1.5 to 4.1 V) W h kg⁻¹</th>
<th>Mass Specific Energy Density (discharged 4.3 to 1.5 V) W h kg⁻¹</th>
<th>Mass Specific Power Density kW kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si LIC B-2</td>
<td>41.35</td>
<td>44</td>
<td>30</td>
<td>12.43</td>
<td>7.09</td>
<td>2.78</td>
</tr>
<tr>
<td>Si LIC C-2</td>
<td>12.05</td>
<td>81</td>
<td>68</td>
<td>28.16</td>
<td>29.37</td>
<td>6.95</td>
</tr>
<tr>
<td>Si LIC D-2</td>
<td>12.75</td>
<td>85</td>
<td>70</td>
<td>17.01</td>
<td>18.73</td>
<td>5.39</td>
</tr>
<tr>
<td>Si LIC E-2</td>
<td>3.90</td>
<td>81</td>
<td>70</td>
<td>45.72</td>
<td>50.66</td>
<td>23.4</td>
</tr>
</tbody>
</table>

a Under matched load condition with a peak voltage of 4.3 V at 0.5 C-rate.

An improvement has also been made with regards to charge and energy storage efficiency; in pre-lithiated samples of type D and E there has been improvements of between 20 and 40% compared to fresh samples of these types. With the charge storage efficiency being less than 100% it implies that a chemical reaction is still occurring despite samples previously experiencing periods at high voltage, this could be related to the fact that cells were tested up to 4.3 V but there have been previous indications that 4.1 V may in fact be the maximum stable cell voltage.

The mass specific energy density, both during charge up to 4.1 V and full discharge, has been reduced in all pre-lithiated samples when compared to fresh samples. The most drastic decrease occurred in samples of Type D; this is predominantly associated with the previously discussed reduction in charge capacity. The mass specific energy density of sample E-2 has been reduced in both forms of KPI; it is believed the value associated with the sample being charged from 1.5 to 4.1 V is the most reliable as it is within the assumed ESPW. It should be noted that although CCCD cycling is initiated from 1.5 V, as opposed to 0 V used with fresh samples, there is no evidence of significant energy storage until at least 2 V; this consideration should allow direct comparison between a fresh and pre-lithiated sample of a type E silicon based LIC device. As such, it is believed the pre-lithiation process resulted in a reduction in energy density of over 50% but alongside a significant improvement in power density.
Advanced Formation cycling

Prior to formation cycling, it was reasoned that a fresh sample of type E (E-3) should be compared to sample E-1 which experienced CCCD testing up to 4.6 V, and sample E-2 which experienced preliminary formation cycling and CCCD testing up to 4.3 V; this type has proven to be the best performing thus far and is believed to potentially represent a viable device configuration. This comparison was conducted using CV analysis at a scan rate of 5 mV s⁻¹ for 5 cycles, the results of which are presented in Figure 6.11. The results clearly indicate the negative effects of high voltage (≥ 4.3 V) operation; brief periods at 4.6 V result in a loss of reversible charge storage, indicated by the manner in which samples E-1 and E-3 experience similar upward sweeps but E-3 has a lower current during the downward sweep. Sample E-2 performs very poorly in comparison to the fresh E-3 sample, while the maximum voltage experienced by E-2 was only 4.3 V it was held at or around this voltage for extensive periods of time during preliminary formation cycling. Overall, the manner in which the fresh E-3 sample behaves is intriguing; the upward sweep is a relatively uniform process in which the current increases as voltage increases but the downward sweep experiences multiple ‘bumps’, these could be associated with differing lithiation states with either the silicon or MWCNT material. It is believed the initial bump on the downward sweep is more pronounced due to the lack of equilibrium achieved during CV analysis, this is possibly due to the scan rate being faster than the Li diffusion capability in NXA-513.

![Image](chart.png)

*Figure 6.11  CV analysis at 5 mV s⁻¹ (5th cycle) of type E LIC devices using Kynol ACC as the positive electrode and silicon based NXA-513 as the negative electrode combined with a LiPF₆ EC/DEC 50/50 (v/v). Individual samples have experienced differing degrees of electrochemical testing as stated in the legend.*

At this point of the investigation it was realised that the preliminary formation cycling technique is non-ideal due to the variations in peak cell voltage (albeit caused by an improper experimental setup). It was decided that an advanced type of formation cycling should be
developed, one in which the effects of such a process can be evaluated while minimising variability. This approach has generally been described in Section 6.2.4 and was implemented when assessing the performance of graphite based LIC devices (Section 6.3).

Essentially, this advanced type of formation cycling involved two initial formation cycles at 3.5 V followed by a further two formation cycles at 4 V, these cycles consisted of a high current ramp (10 C) to the desired voltage followed by a relaxation period in an open circuit condition for three hours. In order to assess the effect such a process has upon cell performance it was decided that CV analysis would be conducted at the start, middle and end of the pre-lithiation process; this CV analysis took the form of 5 cycles at 5 mV s\(^{-1}\). Such a process was applied to both the remaining fresh samples i.e. sample 3 of each device type e.g. A-3, B-3 etc. and previous samples which had been tested. From this it was hoped that cell performance could be related to previous electrochemical conditions experienced by an individual cell.

Advanced formation cycling was conducted on sample 3 of each device type e.g. B-3, C-3 etc. It is important to recall that sample 3 of each device type contained a silver QRE, as previously mentioned in Section 6.4.2. This allowed for the voltage of each electrode to be determined relative to this QRE value, these values could then be related to the overall cell voltage between each electrode. Presented in Figure 6.12 are the results of the ultimate two formation cycles (up to 4 V); these results are presented with both the overall cell voltage and the voltage of individual electrodes relative to an Ag QRE. It is clear that as the theoretical Si utilization factor increases (owing to the increase in AC charge capacity) so does charge retention ability during periods of open circuit operation; this is clearly indicated by the concluding cell voltage value which increases from 2.50 V for a type B device up to 3.82 V for a type E device. Of further interest is that in all devices the discharge during open circuit is predominantly dictated by discharge of the AC electrode, this is especially true in type B and C cells which present the lowest theoretical Si utilization. Upon conducting preliminary formation cycling, it was believed possible that the AC material, used as the positive electrode in type B devices, experiences a voltage above the stable ESPW of this system; upon examining the positive electrode potential relative to a silver QRE, such a case has been proven true. This is indicated by the sudden drop in voltage upon the initiation of open circuit condition. This approach to formation cycling is considered superior to the preliminary method due to the apparent testing consistency.
Figure 6.12  Formation cycling of differing Si based LIC type EC devices (Table 6.8) using an advanced method; the initial charge phase was conducted with a current density of 125 mA g⁻¹ (relative to total Si content). Only the last two cycles, those which operate up to 4 V, of this pre-lithiation process are displayed. These devices incorporated Silver (Ag) QREs; the voltage of the positive and negative electrodes have been evaluated relative to this QRE. The concluding voltage at the end of formation cycling is displayed to the right of each plot.
Capacitive Energy Storage:
Filling the gap

To assess the effect such a process has upon cell performance it was decided that CV analysis would be conducted at the start, middle and end of the pre-lithiation processes; this was achieved at a scan rate of 5 mV s\(^{-1}\) between 2 and 4 V. The results of this are presented below in Figure 6.13. Further insight was gained through analysing the quantity of charge transferred during each sweep; from this the cyclic charge storage efficiency was determined, these are presented in Table 6.12.

![Graphs showing CV analysis for Si LIC D-3 and Si LIC E-3](image)

Figure 6.13 Analysis of formation cycling by CV testing at 5 mV s\(^{-1}\) (5th cycle) of differing Si based LIC type EC devices (Table 6.8). The 1\(^{st}\), 2\(^{nd}\) and 3\(^{rd}\) CV plots associate with pre-, mid- and post- formation.

<table>
<thead>
<tr>
<th>Series-Sample</th>
<th>Charge storage efficiency Pre-Formation</th>
<th>Charge storage efficiency Mid-Formation</th>
<th>Charge storage efficiency Post-Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si LIC D-3</td>
<td>92</td>
<td>96</td>
<td>98</td>
</tr>
<tr>
<td>Si LIC E-3</td>
<td>95</td>
<td>97</td>
<td>98</td>
</tr>
</tbody>
</table>

Table 6.12 Effects on charge storage efficiency by formation cycling, calculated from CV plots presented in Figure 6.13. Pre-, mid- and post- formation associate with 1\(^{st}\), 2\(^{nd}\) and 3\(^{rd}\) CV plots.
Chapter 6: An investigation of using a silicon based negative electrode in lithium ion capacitors

The CV plots presented in Figure 6.13 indicate that formation cycling raises the cell potential showing that pre-lithiation is occurring; the overall CV sweep shape is retained in both samples and shifted to higher voltages. The charge storage efficiency has been measured in both cases to increase during formation cycling (see Table 6.12) but it is also observable that sample D-3 initially starts with a lower efficiency than sample E-3; this may further indicate that the use of a positive AC electrode with low charge capacity relative to the negative intercalation electrode causes the AC electrode to experience potentials outside its ESPW.

![Graphs showing voltage relaxation over time for different Si LIC types](image)

Figure 6.14 Formation cycling of differing Si based LIC type EC devices (Table 6.8) using an advanced method. Only the last cycle of this pre-lithiation process, which operates up to 4 V, are displayed.

As advanced formation cycling was conducted upon all samples of type B, C, D and E devices, it is possible to broadly compare the pre-lithiation process between them. All samples experienced this advanced type of formation cycling regardless of prior electrochemical analysis. Figure 6.14 shows the results of the open circuit condition during the 4th formation cycle for all samples. It is quite apparent that sample 2 of each type, those which experienced preliminary formation cycling and CCCD analysis up to 4.3 V, retain the least charge during open circuit
condition. Such a significant loss of charge could indicate that the voltage of the AC materials has been pushed outside its respective ESPW, this could occur if the silicon based NXA-513 experienced significant degradation when the cell voltage was above 4.3 V. With regards to sample 1 of each type, those which experienced only CCCD up to 4.6 V; these samples present reduced charge retention which almost certainly associates with high voltage operation. Although the 4.6 V experienced by these cells is higher than those of sample 2 devices, the extent of time for which cells were at this voltage was less (as formation cycling was not conducted); it is for this reason that these samples outperform sample 2 devices. Ultimately, it is apparent that fresh samples which have not been exposed to excessive voltages (considered above 4.1 V) perform best when formation cycled.

**Advanced CCCD Analysis including QRE interactions**

Post-formation cycling, CCCD analysis was conducted upon all samples at a range of currents; these are described specifically alongside relative to the mass of available silicon content and total mass of a NXA-513 electrode (i.e. current density) in Table 6.13. This differs from previous experiments in which the current was defined as a C-rate value (the C-rate is a measure of the rate at which an electrochemical device is charged or discharged relative to its maximum charge capacity); this is due to the apparent lack of precise charge capacity which occurs after formation cycling which hinders the use of a precise C-rate value.

<table>
<thead>
<tr>
<th>Test Current</th>
<th>Current Density Silicon Only</th>
<th>Current Density NXA-513</th>
</tr>
</thead>
<tbody>
<tr>
<td>mA</td>
<td>mA g⁻¹</td>
<td>mA g⁻¹</td>
</tr>
<tr>
<td>0.4</td>
<td>200</td>
<td>60</td>
</tr>
<tr>
<td>1.1</td>
<td>550</td>
<td>165</td>
</tr>
<tr>
<td>2.2</td>
<td>1,100</td>
<td>330</td>
</tr>
<tr>
<td>4.3</td>
<td>2,150</td>
<td>650</td>
</tr>
<tr>
<td>11</td>
<td>5,500</td>
<td>1,662</td>
</tr>
</tbody>
</table>

The results of CCCD analysis at 200 mA g⁻¹ (relative to total Si content) from 1.5 to 4 V of differing LIC type EC devices (see Table 6.8) using either Sigma PAC or Kynol ACC as the positive electrode and silicon based NXA-513 as the negative electrode are displayed in Figure 6.15. It should be noted that some samples of each device type have experienced prior
electrochemical analysis, these are described in the legend. The results generally show significant differences between device types and samples. Qualitatively, as the theoretical Si utilization value increases (from type B to E) the CCCD shape develops from that similar to an EDLC-type EC device to an LIC-type EC device. This indicates that at low Si utilization the positive AC electrode is the limiting factor.

![Diagram of Si LIC Types B, C, D, and E](image)

**Figure 6.15** CCCD testing at 200 mA g⁻¹ (relative to total Si content) (3rd cycle) from 1.5 to 4 V of differing LIC type EC devices with varying silicon utilization combined with a LiPB, EC/DEC 50/50 (v/v) electrolyte.

Samples of type D and E in Figure 6.15 generally form a voltage plateau at around 3.5 V during the charge phase, this could indicate that NXA-513 electrode has reached its maximal lithiation state while the positive EDLC electrode is then the predominant contributor to voltage change. For sample 2 this plateau does not appear to occur, this may be due to the detrimental effects of previous operation at 4.3 V. The fact that a fresh sample, which has experienced extensive formation cycling up to 4 V, presents maximal performance indicates that operations up to 4 V are below the threshold voltage at which detrimental chemical reactions occur.
The fact that charge and discharge phases present wholly different CCCD responses is of great interest. Further insight in this matter has been gained for sample E-3 through the utilization of a silver QRE device; the total cell voltage and individual electrode voltage has been monitored with resulting data being presented in Figure 6.16 for a CCCD cycle at 200 mA g⁻¹ (relative to total Si content). This plot clearly demonstrates that the voltage response is relatively uniform at both electrodes during the charge phase while distinct steps are formed during the discharge phase, these are indicated by green circles with respect to cell voltage and are clearly visible in fresh samples of type D and E devices (Figure 6.15).

Figure 6.16  CCCD testing at 200 mA g⁻¹ (relative to total Si content) (3rd cycle) from 1.5 to 4 V of the sample type E-3 which contains a Kynol ACC based positive electrode and an NXA-513 based negative electrode. This plot includes data captured through the use of a silver QRE device, as defined by the legend. ● This marker indicates the transition point between differing electrochemical discharge processes.

Figure 6.16, combined with information from Figure 6.15, provides a large amount of information. Firstly, from Figure 6.16 it is possible to see that the transition point between differing electrochemical discharge processes, indicated by green dots, associates predominantly with the positive AC electrode; this is surprising as an EDLC electrode typically has a constant voltage-charge relationship (capacitance). Secondly, from Figure 6.15 it is possible to see that upon operations at higher voltages (as in sample 1) these well-defined transition points are removed. The author believes these results are a consequence of the complex material relationship of NXA-513 which possesses both Si and MWCNT content.

With regards to the Si content of NXA-513: according to a recent (2016) publication by Cao et al [284], the lithiation (i.e. charge phase) of silicon occurs in three distinct stages and is ultimately best described as a reaction limited layer-by-layer process; in this work, it was shown
that lithiation occurs initially at the Si surface and progresses deeper with a ‘reaction front’, such a concept is analogous to that of a ‘wave front’ which may progress through a medium. The processes of forming an SEI layer, the surface lithiation layer and the internal ‘reaction front’ form the three distinct stages during the lithiation of silicon with each pertaining to a specific voltage range. Such phenomenon quite possibly did occur within the Si material but are almost certainly associated with the rapid voltage increase of the negative electrode upon the initiation and termination of CCCD. Further to this, the formation cycling process could have advanced the ‘reaction front’ to a sufficiently deep sub-surface depth thus removing the possibility of this step occurring during CCCD (this is assuming the ‘reaction front’ remains static upon de-lithiation). One final observation from this publication is the fact that lithiation does not necessarily occur throughout the entire Si material instantaneously, this could allay any fears that that there is insufficient electrolyte for Si intercalation to occur as the surface area of NXA-513 is sufficiently low at 4.55 m² g⁻¹. In contrast to this, [285] clearly shows the voltage curve of crystalline silicon which appears to possess multiple voltage plateaus throughout both charge and discharge phases.

With regards to carbon content of NXA-513: While thus far the carbon content has been referred to as predominantly of the MWCNT variety, it was also found through SEM/EDX analysis (Section 4.2.1) that there is possibly significant carbon content surrounding the silicon particles. It has been found that MWCNTs experience lithium intercalation at a constant voltage plateau and de-intercalation with linearly decreasing voltage (dropping by 0.6 V from full charge to negligible charge) [286]. Interestingly, a recent paper (2017) by Ding et. al. [287] discerns the electrochemical lithiation properties of electrodes containing silicon, graphite and CNT content which, by material content, is very similar to NXA-513. In this work they detail the process of growing CNTs by chemical vapour deposition (CVD) followed by encapsulating silicon nanoparticles in few-layer graphene; this combination of materials results in a constant voltage plateau during lithiation and a discharge plot whereby there is an initial decrease in voltage, followed by a brief voltage plateau, followed by further decreases in voltage. This is not wholly different from that presented in Figure 6.16 between the first three markers.

With regards to the positive AC electrode: as previously mentioned, the transition point between differing electrochemical discharge processes, indicated by green dots, associates predominantly with the positive AC electrode. This adds an element of confusion as such a response is not typical of an EDLC which associates with the PF₆ negative ion [288, 91]. As such, the author believes a non-constant electronic or ionic resistance arises during the discharge
process; this could be due to the multiple lithiation sources, as one which less resistivity is depleted (i.e. fully de-intercalated) the remaining sources (which possibly have higher electronic/ionic resistance) become dominant. Such an effect could cause voltage drops in the AC electrode to arise as the rate of de-intercalation may also vary with such changes.

Ultimately, it is the unique similarity between samples of E-1 and E-3 during the charge phase (Figure 6.16) which enables some semblance of a conclusion to be drawn about the electrochemical processes at hand. The fact that these samples behave identically during the charge phase but different during the discharge phase indicates that differing materials are in use during each phase. It is entirely possible that lithium intercalation associates predominantly with the surface carbon content then later diffused through to the silicon particles, this would hold especially true if the Si is indeed encapsulated in carbon as the lithium must pass through this carbon layer. During the high voltage (4.6 V) operation of sample E-1 it appears one element of this system has been degraded, thus causing this sample to de-intercalate at lower voltages compared to E-2, this could be due to the degradation of the Si material which, firstly, is known to have a lower ESPW [175], and secondly, is known to have a multiple lithiation states which appear removed from sample E-1 when compared to sample E-3.

Quantification has taken the form of deriving KPIs from the CCCD plots of fresh samples (3rd) of type B, C, D and E LIC devices, these have been presented in Table 6.14. The areal resistance decreases from type B to type E indicating that this is strongly associated with Si utilization and proper capacity balancing between electrodes. When compared to the Table 6.11, which contains the results of CCCD testing up to 4.3 V, both the charge and energy storage efficiency are significantly improved. The charge storage efficiency being less than 100% indicates that further chemical reactions are occurring, which results in the loss of charge; it is almost certainly associated with the negative NXA-513 electrode. Unfortunately, as the cell did not reach 4.1 V the mass specific energy KPI associated with this value is not available for comparison with previous samples. Regardless, the mass specific energy density during discharge is available; this has dropped by over 50% in all samples which is believed to be predominantly due to the lower operating voltage (recall that energy is dependent on the square of voltage as per equation (2.7)) and partially due to the advanced formation cycling process, this process pre-lithiated samples which reduced their available charge capacity. A similar reduction is also found in mass specific power density which, while reduced, is still significantly higher than that of GC based LIC devices, both those fabricated during this investigation and in literature [91].
Table 6.14 KPIs derived from CCCD testing 200 mA g\(^{-1}\) (relative to total Si content) \(3^{\text{rd}}\) cycle) from 1.5 to 4 V of differing LIC type EC devices with varying silicon utilization. All values correspond to the discharge phase unless explicitly stated otherwise.

<table>
<thead>
<tr>
<th>Series-Sample</th>
<th>Areal Resistance Ω cm(^2)</th>
<th>Charge storage efficiency %</th>
<th>Energy storage efficiency %</th>
<th>Mass Specific Energy Density (discharged 4.0 to 1.5 V) Wh kg(^{-1})</th>
<th>Mass Specific Power Density kW kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si LIC B-3</td>
<td>50.7</td>
<td>90</td>
<td>65</td>
<td>5.13</td>
<td>6.20</td>
</tr>
<tr>
<td>Si LIC C-3</td>
<td>22.4</td>
<td>92</td>
<td>76</td>
<td>10.70</td>
<td>8.50</td>
</tr>
<tr>
<td>Si LIC D-3</td>
<td>23.2</td>
<td>94</td>
<td>80</td>
<td>14.91</td>
<td>9.54</td>
</tr>
<tr>
<td>Si LIC E-3</td>
<td>14.5</td>
<td>96</td>
<td>84</td>
<td>22.53</td>
<td>17.01</td>
</tr>
</tbody>
</table>

*a* Under matched load condition with a peak voltage of 4 V at 200 mA g\(^{-1}\)

As CCCD analysis was conducted at a multitude of test currents (see Table 6.13 and Appendix 14 for CCCD plots) for the \(3^{\text{rd}}\) sample of each type of Si based LIC device (see Table 6.3), it is possible to produce a comprehensive Ragone plot. Such a plot is presented in Figure 6.17, it clearly indicates the relationship between mass specific energy and power density. It is firstly noticeable that energy storage and power capabilities increase with AC charge capacity, this is broadly in agreement with the results presented in Table 6.10, Table 6.11 and Table 6.14. Another interesting aspect is the constant power performance across all current densities, this indicates that the breadth of current densities tested was possibly not enough to encounter the extremes of device performance. Regardless, such a plot provides an excellent comparison of device performance and clearly indicates that type E devices (i.e. those containing a Kynol ACC positive electrode, a silicon based (NXA-513) negative electrode and combined with the electrolyte LiPF\(_6\) in EC/DEC 50/50 V/V) provide the best performance of all Si based LIC devices tested.
6.4.4 Conclusion – LIC with Silicon Based Negative Electrode

The aim of this section was to produce LICs which use a novel silicon based material as the negative electrode. It was elected for this investigation to try both Sigma PAC and Kynol ACC as the positive electrode material; Sigma PAC due to the flexibility offered during electrode fabrication i.e. the thickness and thus areal density can be defined and Kynol ACC due to its high mass specific capacitance value. It was identified from the onset that the charge capacity of the AC material will be a limiting factor; as such, a wide variety of cell types were fabricated (see Table 6.3) to fully understand its influence. Three samples of each device type were fabricated.

Initial tests involved subjecting samples of each type to CCCD cycling at a theoretical C-rate of 2 from 0 to 4.6 V; this resulted in extremely high energy densities of 97 Wh kg\(^{-1}\) during charge up to 4.1 V and 68 Wh kg\(^{-1}\) during discharge from 4.6 to 0 V. Cells presented high areal resistance and consequently poor power capabilities (3.5 kW kg\(^{-1}\)), this was associated with the method of calculation and the fact that adverse chemical reactions at high voltage can influence this calculation. A further consequence of testing at high voltage was the poor charge and energy storage efficiency. It was identified that the ESPW of such a cell may be 4.3 V but also possibly as low as 4.1 V.
Chapter 6: An investigation of using a silicon based negative electrode in lithium ion capacitors

As such, further testing was conducted at 4.3 V; this included the use of formation cycles as described in [91]. As the use of formation cycles was not fully developed at the time of testing, the approach was considered preliminary; not all samples experienced the same formation effect. The results of this formation cycling process, and the use of a lower voltage, were improvements in power capability (up by almost 1000% from previous testing) alongside improvements to charge and energy storage efficiency. Unfortunately, it appears the formation process also reduces the mass specific energy density to 46 W h kg⁻¹ during charge up to 4.1 V and 51 W h kg⁻¹ during discharge from 4.3 to 0 V (note the differing voltage windows associated with these values). Such results were considered promising but low charge storage efficiency indicated that the an electrode was operating outside its ESPW. This was later confirmed when subsequent testing found these cells had degraded significantly compared to fresh samples.

An advanced form of formation cycling was subsequently developed in which all samples experienced the same extent and type of cycling. The consequence of such a process was a shift of cells to higher operating potentials (as indicated by CV plots) and improved charge retention during open circuit (self-discharge) conditions. Such findings were supported through the use of a silver QRE in which it was found that the positive AC electrode is the primary source of voltage loss during self-discharge, this loss was minimized when NXA-513 was combined with a high charge capacity AC material (Kynol ACC).

Ultimately, CCCD testing was conducted on all samples. It was predominantly found that samples of Type E (see Table 6.3) perform the best under all conditions. A sample of this type was analysed using a silver QRE, it was found that the charge process occurs in a consistent manner while the discharge process varies depending on the SoC (state-of-charge). This finding was attributed to the NXA-513 electrode, which contained a combination of silicon and carbon (of graphitic and MWCNT morphologies); although it was not possible to definitively distinguish which material it was associated with it is believed that the silicon content of NXA-513 is the contributor of multiple voltage plateaus during discharge.

6.5 Comparison of Si and GC based LIC devices

At this point it is appropriate to conclude by comparing the Si and GC based LIC devices fabricated and tested in this section and the previous alongside GC based LIC devices fabricated in literature [91]; this comparison is presented in Table 6.15. The only device comparable to that fabricated in [91] is the GC based LIC device operated up to 4.5 V; this device fails to match literature with respect to both mass specific and power density. It is reasonable to firstly
question the extent of this comparability; the Sigma PAC used in this study exhibited a mass specific capacitance in relation to PF$_6$ ions of $\sim 50$ F g$^{-1}$ whereas in [91] the Super 50 PAC presented a capacitance in relation to PF$_6$ ions of 90 F g$^{-1}$, more akin to that of Kynol ACC. It is quite possible that using Kynol ACC would have significantly improved device performance as such a case was exhibited when testing Si based LIC devices, this could have brought it more in line with the results of [91].

Table 6.15 Comparison of Si and GC based LIC devices fabricated and tested during this investigation alongside a GC based LIC devices fabricated in literature [91].

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>GC based LIC (4 V)</th>
<th>GC based LIC (4.5 V)</th>
<th>GC based LIC (4.5 V) From [91] $^a$</th>
<th>Si based LIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode Materials</td>
<td>Graphitic Carbon (-) Sigma PAC (+)</td>
<td>Graphitic Carbon (-) Sigma PAC (+)</td>
<td>Graphitic Carbon (-) Super 50 PAC (+)</td>
<td>NXA-513 (-) Kynol ACC (+)</td>
</tr>
<tr>
<td>Electrolyte Materials</td>
<td>1 M LiPF$_6$ in EC/DEC</td>
<td>1 M LiPF$_6$ in EC/DEC</td>
<td>1 M LiPF$_6$ in EC/DMC</td>
<td>1 M LiPF$_6$ in EC/DEC</td>
</tr>
<tr>
<td>Storage Mechanism</td>
<td>Li Intercalation (-) Electrostatic (+)</td>
<td>Li Intercalation (-) Electrostatic (+)</td>
<td>Li Intercalation (-) Electrostatic (+)</td>
<td>Li Intercalation (-) Electrostatic (+)</td>
</tr>
<tr>
<td>E (W h kg$^{-1}$)</td>
<td>27.91</td>
<td>50.33</td>
<td>103.8</td>
<td>22.53</td>
</tr>
<tr>
<td>P (kW kg$^{-1}$)</td>
<td>2.96</td>
<td>1.71</td>
<td>10</td>
<td>17.01</td>
</tr>
<tr>
<td>Energy storage efficiency (%)</td>
<td>91</td>
<td>80</td>
<td>?</td>
<td>84</td>
</tr>
<tr>
<td>Time Constant $^b$</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Cycle Life (cycles) $^c$</td>
<td>?</td>
<td>?</td>
<td>$&gt; 10^4$</td>
<td>?</td>
</tr>
<tr>
<td>ESPW (V)</td>
<td>$\sim 4.5$</td>
<td>$\sim 4.5$</td>
<td>$\sim 4.5$</td>
<td>$\sim 4$</td>
</tr>
<tr>
<td>Self-Discharge $^d$</td>
<td>0.15 V over 3 hours</td>
<td>?</td>
<td>0.75 V over 4 hours</td>
<td>0.20 V over 3 hours</td>
</tr>
</tbody>
</table>

a Uncertainty as to whether values related to a cell which has experienced formation cycling or not.
b Not entirely applicable as process is not purely capacitive (see Equation (2.11)).
c Not tested in this investigation.
d Estimated from final open circuit condition of formation cycling.

Another possible comparison can be drawn between GC and Si based LIC devices operated up to a maximum of 4 V. In this case, it appears the mass specific energy density of Si based LIC devices is $\sim 25$ % lower than that of GC based LIC devices; such a finding are certainly due to the precise configurations of each device rather than intrinsic material properties. If higher capacitance or mass AC electrodes were used in either case then the results could have been
significantly different (consider the progressive performance increases presented in Si based LIC devices).

With regards to power performance it is almost certainly not a fair comparison due to the presence of differing conductive additives in the negative electrode of each device type (MWCNT in NXA-513 based electrodes, TIMCAL Super P®-Li carbon black in GC based electrodes). It is also notable that NXA-513 has been manufactured by a commercial enterprise which specializes in silicon material fabrication; as such, the design and fabrication of this device may be considered superior to the GC based electrodes fabricated during this investigation. As such, the NXA-513 based LIC device possesses a power performance approximately a third of the maximum achieved (48.83 kW kg⁻¹) for EDLC devices fabricated in Section 5 while improving their energy density by a minimum of 25 %.

![Graph of voltage vs. minutes](image)

**Figure 6.18** Comparison of CCCD testing at 4 mA (3rd cycle) of GC and Si based LIC devices. Note that GC based LIC devices contained a Sigma PAC negative electrode while the Si LIC device contained a Kynol ACC negative electrode.

The energy storage efficiency of these devices is considered reasonable but unfortunately this value was not provided in [91], as such a full comparison cannot be completed. One matter of interest is the low energy storage efficiency of Si based LIC devices; to fully appreciate this, it has been deemed necessary to provide a comparative representation of CCCD at the same current (4 mA) for each device. From Figure 6.18 it is possible to visualise the reason for poor energy storage efficiency, note the similarity between GC and Si based LIC devices during the
charge phase but the dissimilarity between them during the discharge phase; the GC presents a consistent decline in voltage while the Si based LIC presents an inconsistent decline in voltage. A consequence of this inconsistency is the loss of energy.

The final, but not definitive, comparison between these devices can be found in the form of a Ragone plot presented in Figure 6.19. Whilst a useful comparison, it lacks information about the cyclic stability of these devices, an extremely important aspect of device performance. This plot reflects the results where it visually represents the comparison presented in Table 6.15 but include high current performance. It is clear that NXA-513 based LIC retains its high-power performance even while approaching 5 A g⁻¹, albeit with a small drop in mass specific energy density.

![Ragone Plot](image)

Figure 6.19 Comparative Ragone Plot between the GC and Si based LIC devices fabricated in this study. Test current densities were 100 (right), 250, 500, 1000 and 2500 (left) mA g⁻¹ of graphite material and 200 (right), 500, 1000, 2000 and 5000 (left) mA g⁻¹ of silicon material.

### 6.6 Summary and Outlook

The primary aim of the research detailed in this section was to develop and quantify and LIC type EC device which uses a novel silicon based negative electrode (NXA-513); this task has been successfully achieved and compared against current state-of-the-art LICs which use graphite based negative electrodes. It was hypothesised that the novel silicon based electrode could provide an improvement in power capability while maintaining high energy density and minimising volumetric expansion. Experiments were conducted using an industry standard electrolyte for LIC and LIB research, Li⁺PF₆⁻ in EC/DEC 50/50 (V/V). In both cases a pre-
lithiation technique called *formation cycling* was used, this was developed by Khomenko et al. [91].

It was found that a traditional LIC device using a graphite based negative electrode can achieve an energy density of 50.33 W h kg\(^{-1}\) (post formation cycling) when operating between 3 and 4.5 V; according to Khomenko et al. [91] this is a reasonable voltage window but CV investigations found that chemical reactions occur above 4.3 V. The power capability of such a device was found to be 3 kW kg\(^{-1}\), less than the 10 kW kg\(^{-1}\) exhibited by similar devices in [91]; this is despite using two spacers in coin cell fabrication and the inclusion of conductive additive (Timcal Super P-\(\text{Li}\)) within the electrode. The author speculates that reduced power performance may be related to the poor mixing of electrode slurry prior to deposition.

An investigation of LICs which use a novel silicon based electrode material (NXA-513) was conducted. It was identified from the onset of experimentation that the charge capacity of the AC materials will be a limiting factor in performance; as such, a wide variety of cell types were fabricated using either Sigma PAC or Kynol ACC as the positive electrode material.

Initial tests in this investigation did not involve formation cycling. The highest performing device utilised Kynol ACC as the positive electrode, it achieved an energy density of 97 W h kg\(^{-1}\) during charge from 0 to 4.1 V and 68 W h kg\(^{-1}\) during discharge from 4.6 to 0 V; the charge–discharge processes were conducted at a theoretical C-rate of 2. It was found that cells operated under this charge–discharge regime exhibited poor power capability (3.5 kW kg\(^{-1}\)), this was associated with the method of calculation (from the voltage drop during CCCD testing) and the fact that adverse chemical reactions at high voltage can influence its calculation. It was identified that chemical reactions certainly occur above 4.3 V and possible above 4.1 V.

A preliminary type of formation cycling was used in further experiments and the maximum voltage was limited to 4.3 V; the result of this was a significant improvement in power capability with sample containing Kynol ACC achieving 23.4 kW kg\(^{-1}\), this was combined with improvements in charge and energy storage efficiency. Unfortunately, the use of formation cycling appears to also reduce the mass specific energy density to 46 W h kg\(^{-1}\) during charge up to 4.1 V and 51 W h kg\(^{-1}\) during discharge from 4.3 to 0 V. Upon detailed analysis it was noted that charge efficiency was sub-optimal, indicating that cells were operating outside their stable voltage window. This was later confirmed when subsequent testing found cells had degraded significantly compared to fresh samples.
An advanced type of formation cycling was subsequently developed and the final samples of each device type were tested. It was found that the baseline operating voltage (i.e. the voltage at which charge storage starts to significantly occur) was increased, charge retention during open circuit (self-discharge) conditions was also improved across all samples.

Silver QRE devices were incorporated into the final samples of each device type. It was found that the positive AC based electrode is the primary source of voltage loss during self-discharge. This loss could be minimised by using materials with high intrinsic capacitance (and thus high charge capacity) as the positive electrode, such as Kynol ACC. Subsequent analysis using the QRE device showed that the charge phase of the silicon based negative electrode occurs at a constant voltage, during discharge its voltage is dependent upon the SoC of the electrode. This phenomenon was associated with the silicon content of NXA-513.

A comparison between silicon and graphite based electrodes has been presented, this included the results of this work and that presented in [91]. It was shown that while the energy density of cells created in this study did not approach those presented in [91], there was a significant improvement in power capability (up from 10 to 17 kW kg⁻¹). A more accurate comparison can be made if comparisons are confined to the results of cells fabricated in this work only; it was found that the silicon based NXA-513 can achieve comparable energy density comparable with graphite whilst providing an improvement of almost 1000 % in power density.

Broadly speaking, the results of this chapter indicate that LIC type EC devices provide a significant improvement in energy density compared to traditional EDLC type EC devices. The author sees the current state-of-the-art graphite based devices as a stepping stone to more advanced devices which incorporate novel silicon based electrodes; but more research in this field is required. Specifically, it would be desirable to use more of the available charge capacity present in silicon based negative electrodes; this will almost certainly hinge upon finding high charge capacity positive electrodes. Other lithium intercalative electrodes, such as tin, may also be used [289, 290]. Conversely, other intercalative ions, such as sodium, could also be used instead of lithium [291].
7 A STUDY OF MULTILAYER SPRAY DEPOSITION FOR COMPOSITE CARBON ELECTRODES

7.1 Introduction

The primary aim of the research detailed in this section was to utilise spray deposition i.e. the process in which a slurry is atomised (converted into fine droplets) and sprayed onto a substrate material, in producing targeted multi-layer electrode coatings (research aim 4, section 2.8). The main electrode material used in this work was Sigma PAC whilst a conductive additive of Elicarb MWCNTs (multi-walled carbon nanotubes) was also included, the binder was SBR/CMC based; precise material descriptions can be found in Section 3.3.2. Experimentation took the form of spray depositing electrode coatings in which each layer was of the same material composition and coatings in which the material composition of each layer differs through the inclusion of conductive additives (research aim 3, section 2.8). The author proposed that introducing MWCNTs at specific locations within an otherwise standard PAC based electrode (e.g. at the base layer or top layer) may in fact bring the benefits of lower electrode resistance without excessive use of MWCNTs, potentially lowering the cost and environmental impact of fabricating high power electrodes. Further benefits of spray deposition are that it does not involve direct contact with the substrate and electrode coatings can be applied to uneven surfaces and irregular shapes [207].

Spray deposition of electrode material was achieved by using an airbrush i.e. pneumatic atomisation (see Section 2.6.3); these formed electrode coatings which were implemented in a purely EDLC type EC device. Contrary to previous experiments conducted, samples were material symmetric with the mass ratio between positive and negative electrodes held constant at 1:1. Although this did not allow for the maximisation of ESPW (see Chapter 5), it did allow for a simple and fair comparison between electrodes produced by spray deposition. Specifically, rather than combining electrodes from different spray sessions (to achieve different mass electrodes), the electrodes produced during the same spray session were used together, thus allowing for clearer definition of cause and effect. Further to this, MWCNTs were combined
with AC materials in varying quantities and at targeted locations (e.g. at the base layer or top layer); this was to assess if MWCNTs exhibited a high-quality dispersion during spray deposition and, if so, what effect this may have upon an electrode’s resistance.

7.2 Methodology

7.2.1 Experimental Overview

It is firstly appropriate to provide an overview of what was required to assess the author’s proposal that introducing MWCNTs at specific locations within an otherwise standard PAC based electrode (e.g. at the base layer or top layer) may in fact bring the benefits of reduced electrode resistance without excessive use of MWCNTs.

1. Utilise a spray deposition process to fabricate electrodes coatings. This involved the preparation of a dilute electrode slurry containing the desired material compositions; such a slurry was then spray deposited onto a suitable CC (current collector). The entire spray deposition result set was subsequently analysed by SEM (scanning electron microscopy) and EDX (energy dispersive x-ray).

2. Electrochemically test multi-layer spray-deposited electrodes consisting of 95 % Sigma PAC and 5 % SBR/CMC binder. Electrolyte, general materials and cell containment were kept the same as those used previously in Section 5.3; this allowed for a controlled comparison between tape casting and spray deposition techniques.

3. Electrochemically test multi-layer spray deposited electrodes consisting predominantly of Sigma PAC alongside varying degrees of Elicarb MWCNT additive, the binder was held constant at 5 % SBR/CMC. This test will assess the impact the addition of MWCNTs has upon cell resistance and power capability.

4. Electrochemically test electrodes fabricated with targeted MWCNT deposition. Such depositions took the form of electrodes in which either the base or top layer coatings contained significant MWCNT content. This test will enable assessment of the effects targeted MWCNTs placement has upon cell resistance and power capability.
7.2.2 Materials and Experimental Control

To produce high quality and trustworthy results it is necessary to establish control over experiment variables. In this work the core variables are:

- Positive/negative electrode – Material(s), thickness, areal density, preparation method and deposition method, current collector.
- Electrolyte – Salt, solvent, molar concentration, fabrication method, quantity.
- Cell separation material.
- Cell containment materials and method.
- Temperature

There are two aspects of interest within this work, spray deposition of electrode material and the electrode composition. Spray deposition of electrode material was performed using an airbrush i.e. pneumatic atomisation. In the initial study of spray deposition, the electrode composition was kept identical to one used in Section 5.3 (which were produced by tape casting i.e. 95% Sigma PAC and 5% SBR/CMC binder). In conjunction with this, similar electrode thicknesses and areal densities were also produced alongside consistent use of 1.5M TEA⁺BF₄⁻ in dry ACN as the electrolyte and 30 μm Toyal Carbo® as the CC (current collector); this allowed for a fair comparison between electrode deposition techniques. The precise fabrication processes and techniques of spray deposition are described subsequently in Section 0.

The second aspect of interest within this work was the positive/negative electrode material composition. It has been found that the addition of CNTs (carbon nanotubes) into an electrode can reduce its electronic resistance [129, 130, 131] due to excellent electric conductivity along their length [70, 127, 128]. Further to this, CNT’s present reasonable mass specific capacitance values of between 20 to 80 F g⁻¹ [10] when combined with the electrolyte TEA⁺BF₄⁻ in ACN. Such a finding suggests that CNTs could replace carbon black, a material often used as a conductive additive in electrodes, but which is lacking in significant capacitive response due to its low surface area [292]. The specific type of CNTs used in this study will be those of the multi-walled variety (i.e. MWCNTs), due to their lower toxicity than SWCNTs (single-walled carbon nanotubes) [140, 141] and higher conductivity [293].

Attempts were made to hold constant the variables related to cell separation material and cell containment method. Cell separation was achieved with 60 μm NKK TF40-60 cellulose separator and cell containment used industry standard CR2032 coin cell cases; the precise
containment procedures to be followed are detailed in section 4.5.3. The temperature was held constant at 25°C for all experimentation, using an environmental chamber.

7.2.3 Electrochemical Analysis and Key Performance Indicators

The electrochemical analysis techniques used in the following experimentation were CCCD (constant current charge discharge) and CV (cyclic voltammetry); see section 3.4.3 for detailed understanding of these techniques. In the case of CCCD the current density (A g⁻¹) can be stated with respect to the mass of positive electrode, mass of negative electrode or total electrode mass. In the case of the experiments at hand, the mass of the positive and negative electrodes will always approach equality and thus the current density relative to the mass of a single electrode will be double that relative to the mass of both electrodes. To fully assess power capabilities, it was deemed necessary to perform CCCD at a wide range of current densities; specifically, 0.1, 0.25, 0.5, 1, 2.5 and 5 A g⁻¹ relative to the mass of both electrodes. Current densities higher than this yielded extremely rapid cycling with only a few (5 to 10) data points acquired during charge and discharge; this could have been avoided by increasing the data sampling rate from 0.2 s. To maintain good comparability with the results of section 5.3, which were tested at 280 mA g⁻¹, quantitative properties were derived at 250 mA g⁻¹. Three CCCD cycles at these current densities were conducted between voltages of 0 and 2.5 V, which ensured device performance had stabilised as the 1ˢᵗ cycle is often influenced by prior electrochemical analysis techniques.

CV analysis was conducted at a scan rates of 0.01, 0.025, 0.05, 0.1, 0.25, 0.5 and 1 mV s⁻¹ between voltages of 0 and 2.5 V. This technique allowed for definition of adverse chemical reactions at higher voltages whilst providing a qualitative view of cell performance. It should be noted that CV analysis was not used for deriving any quantitative properties, as they are difficult to derive and lack substantial definition; a min/average/max capacitance derived from CV bears little meaning in comparison to the definitive capacitance values, which can be derived from CCCD. As such, for comparative purposes it was only deemed necessary to present the extreme scan rates of 10 and 1000 mV s⁻¹.
The quantitative properties of interest (and their method of derivation) in the following experiments are:

- Mass Specific Capacitance (from CCCD at 0.25 A g⁻¹)
- Areal Resistance (from CCCD at 0.25 A g⁻¹)
- Charge Storage Efficiency (from CCCD at 0.25 A g⁻¹)
- Energy Storage Efficiency (from CCCD at 0.25 A g⁻¹)
- Mass Specific Energy Density (from CCCD at 0.25 A g⁻¹)
- Mass Specific Power Density (from CCCD at 0.25 A g⁻¹)

Using these properties, it was possible to definitively identify trends in the gathered results. It should be noted that resistance was presented relative to electrode area; while all electrodes in this work do possess an equal area, it facilitates a rapid transfer of knowledge from the research to industry where such metrics are common. Note: the capacitance is derived per total active material mass of both electrodes within the cell.

7.3 Spray Deposition of Electrode Coatings

Custom electrodes were fabricated by spray deposition, followed by electrode disk cutting. The intent of this process was to assess the production of spray deposited electrodes possessing high (>1 mg cm⁻²) areal densities. The primary electrode material composition used in experimentation was 95 m% Sigma PAC and 5 m% SBR/CMC binder. Subsequently, a series of electrode material compositions were created which contained the addition of MWCNTs (at 2 m%, 5 m%, 10 m% and 20 m%), Sigma PAC and SBR/CMC binder. The slurry solutions produced for spray deposition were small in quantity (40 ml) and significantly less viscous in comparison to slurry solutions produced in section 4.4.2 but contained a high solid content in comparison to standard spray deposition materials i.e. paint.

7.3.1 Equipment and Configuration

Weighing materials for small quantity slurries was conducted with a Denver Instruments SI 234 with a resolution of 0.1 mg. Mixing of wet slurry was conducted for small quantity slurries with a Thermo Scientific VARIOMAG® Poly 15 magnetic stirrer. Ultrasonic mixing was conducted with a Fisherbrand FB11002 ultrasonic bath.
All spray deposition was conducted inside a fume hood possessing a high efficiency particulate air (HEPA) filter. For spray deposition, an Iwata Revolution CR airbrush was used with a 0.5 mm nozzle. This airbrush is gravity fed by a 10 ml cup and features streamlined internals i.e. the ‘slurry’ is mixed with compressed gas almost at the nozzle exit, this feature reduced the chance of blockage with slurries of high solid content. Compressed nitrogen gas was supplied from the main gas supply line on site; it was not possible to deduce the exact gas pressure as there was no indicator at the gas outlet. As such, the gas valve was opened gradually while test spray depositions were conducted with water until a satisfactory level of dispersion was achieved, at this point the valve was not adjusted until spray deposition had been completed. A plastic stencil with a square pattern area of 5 by 5 cm was prepared for producing consistent spray patterns (see Appendix 15 for image). A Fisher Scientific Isotemp hotplate was used for drying wet coatings. A compact precision disk cutter (product code MSK-T-07 from MTI Corporation), with a 15 mm cutting die, was used for electrode cutting. The thickness of electrode cuttings was measured using a Mitutoyo IP65 Micrometer with a resolution of 1 μm.

7.3.2 Dilute Slurry Preparation for Spray Deposition

**PAC Based Slurry**

A PAC based slurry was produced, it comprised 95 m% Sigma PAC, 5 m% SBR/CMC binder and the total mass of DIW added was ~400% that of the Sigma PAC mass. The slurry (40 ml) contained 8 g of Sigma PAC, 2.81 g of PSBR100 (consisting of 0.42 g SBR/CMC and 2.4 g of DIW) and 29.6 g of additional DIW. A binder solution of PSBR100 and all additional DIW was prepared. This solution was magnetically stirred at 200 rpm for 30 minutes followed by 30 minutes ultrasonic mixing (in an ultrasonic bath) at room temperature.

Subsequently, the dry PAC powder was split into 4 equal batches that were added in steps using a weighing powder scoop. Each step consisted of magnetic stirring for 30 minutes at 200 rpm, it was found that powder readily dispersed without additional interference (i.e. additional stirring by spatula, see Section 4.4.2). The final slurry solution possessed a viscosity like cream.

**PAC Based Slurry with MWCNT Addition**

A variety of PAC, MWCNT and SBR/CMC compositions were produced. The Sigma PAC contents of the different slurries was 93 m%, 90 m%, 85 m% and 75 m% which corresponded to an MWCNT content of 2 m%, 5 m%, 10 m% and 20 m%, the SBR/CMC binder content was 5 m% in all samples. Shown in Table 7.1 is the precise content of Sigma
PAC, MWCNT additive and SBR/CMC binder solutions (in DIW) produced for spray deposition.

The process of fabricating a PAC based slurry with an MWCNT addition was split into three stages. The first stage was to prepare a dispersion containing the appropriate Sigma PAC and CMC/SBR content. For this, 0.67 g PSBR100 (consisting of 0.1 g SBR/CMC and 0.56 g DIW) was dispersed in 2.34 g of additional DIW, providing a total DIW content of 3g for binder/PAC dispersion. This solution was magnetically stirred at 200 rpm for 30 minutes followed by 30 minutes ultrasonic mixing (in an ultrasonic bath) at room temperature. Subsequently, the dry PAC powder was split into 4 equal batches that were added in steps using a weighing powder scoop. Each step consisted of magnetic stirring at 200 rpm for 30 minutes, it was found that powder readily dispersed without additional interference (see Section 4.4.2). The final slurry solution possessed a viscosity like runny honey (judged by eye).

The second stage was MWCNT dispersion. The MWCNTs used in the experiments were provided in an agglomerated form thus dispersion was required prior to addition with the Sigma PAC and SBR/CMC binder. This dispersion was achieved using ultrasonic mixing (in an ultrasonic bath) for 5 minutes with an MWCNT concentration of 1 m% in DIW. From Table 7.1 it can be clearly seen that the large DIW quantities required for MWCNT dispersion necessitated the use of low Sigma PAC quantities in order to maintain the appropriate material mass percent.

The third stage was combination of the two previous dispersions. The Sigma PAC and CMC/SBR dispersion was set on balance and the appropriate quantity of MWCNT dispersion was added. It was found that re-agglomeration of the MWCNT dispersion occurred after a few minutes and as such re-dispersion for 5 minutes was conducted prior to combination. Additional DIW content was added to produce solutions with comparable viscosity, the precise quantities for each slurry composition are described in Table 7.1. The slurry compositions were subsequently magnetically stirred at 200 rpm for 30 minutes followed by 30 minutes ultrasonic mixing (in an ultrasonic bath) at room temperature, after which spray deposition was conducted. The final slurry compositions possessed a viscosity like milk.
Table 7.1  Material content of slurry compositions for spray deposition using Sigma PAC, an MWCNT additive (stated by mass percent (m%) on the left) and 5 m% SBR/CMC binder. Note, the DIW content is identified by its source during slurry fabrication.

<table>
<thead>
<tr>
<th></th>
<th>Sigma PAC</th>
<th>MWCNT</th>
<th>CMC/SBR</th>
<th>DIW from binder/PAC dispersion</th>
<th>DIW from MWCNT dispersion</th>
<th>DIW additional</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 m% MWCNT</td>
<td>1.86</td>
<td>0.04</td>
<td>0.1</td>
<td>3</td>
<td>3.96</td>
<td>40</td>
</tr>
<tr>
<td>5 m% MWCNT</td>
<td>1.80</td>
<td>0.10</td>
<td>0.1</td>
<td>3</td>
<td>9.90</td>
<td>30</td>
</tr>
<tr>
<td>10 m% MWCNT</td>
<td>1.70</td>
<td>0.20</td>
<td>0.1</td>
<td>3</td>
<td>19.8</td>
<td>20</td>
</tr>
<tr>
<td>20 m% MWCNT</td>
<td>1.50</td>
<td>0.40</td>
<td>0.1</td>
<td>3</td>
<td>39.6</td>
<td>0</td>
</tr>
</tbody>
</table>

7.3.3 Spray Deposition

Upon the completion of slurry preparation, spray deposition was conducted. The desired foil CC (current collector) was cut to squares 8 by 8 cm length and placed centrally under the stencil, a stainless-steel support was used underneath the CC for facile sample transfer to the drying apparatus. Approximately 5 ml of desired slurry was transferred to the airbrush cup by pipette. Airbrushing was conducted by hand with a distance from nozzle to CC of ~20 cm; at this distance the airbrush deposited a circular coating which encompassed the entire 25 cm² stencil area.

Table 7.2  Electrode compositions fabricated by spray deposition. The composition is described in the format X/Y/Z where X is the Sigma PAC m% content, Y is the MWCNT m% content and Z is the SBR/CMC m% content.

<table>
<thead>
<tr>
<th></th>
<th>Layer 1 (base)</th>
<th>Layer 2</th>
<th>Layer 3</th>
<th>Layer 4</th>
<th>Layer 5 (top)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 m% MWCNT</td>
<td>95/0/5</td>
<td>95/0/5</td>
<td>95/0/5</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>2 m% MWCNT</td>
<td>93/2/5</td>
<td>93/2/5</td>
<td>93/2/5</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>5 m% MWCNT</td>
<td>90/5/5</td>
<td>90/5/5</td>
<td>90/5/5</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>10 m% MWCNT</td>
<td>85/10/5</td>
<td>85/10/5</td>
<td>85/10/5</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>20 m% MWCNT</td>
<td>75/20/5</td>
<td>75/20/5</td>
<td>75/20/5</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>MWCNT top-coat</td>
<td>95/0/5</td>
<td>95/0/5</td>
<td>95/0/5</td>
<td>85/10/5</td>
<td>75/20/5</td>
</tr>
<tr>
<td>MWCNT base-coat</td>
<td>75/20/5</td>
<td>85/10/5</td>
<td>95/0/5</td>
<td>95/0/5</td>
<td>95/0/5</td>
</tr>
</tbody>
</table>
Chapter 7: A study of multilayer spray deposition for composite carbon electrodes

Upon completion of the coating process, the stainless steel support (including coated CC sample and stencil) was lifted from the coating area onto the hotplate which was operated at 80 °C. Once the coating was visibly dry, subsequent coating layers could be deposited and the drying process repeated. Producing electrodes of high quality was difficult for all slurry compositions used; the initial coating layer often possessed inconsistent coverage upon drying. As such, multiple coating layers were required with coverage substantially improving at three layers. Circular electrode disks were cut out and had their thickness and mass measured in the same manner as described in Section 4.4.4; nine cuttings could be taken from a single 5 by 5 cm coating. The precise electrode compositions fabricated are described in Table 7.2.

7.3.4 Spray Deposition Method Analysis

Coating Quality

Analysis of electrode coatings produced by the spray deposition method will now be conducted. The findings of this analysis are primarily associated with coatings consisting of 95 m% Sigma PAC and 5 m% SBR/CMC binder i.e. 0 m% MWCNT, but they also include electrodes fabricated with MWCNT content. Shown in Figure 7.1 is a comparison between the areal density and averaged coating thickness for three layer coatings of Sigma PAC and SBR/CMC binder. It is clear to see that even though the number of coating layers was held constant there are substantial variations (indicated by the low R^2 fitting value) between areal coatings of the same average coating thickness.

![Figure 7.1 Scatter plot (including linear fit) relating the areal density to the average coating thickness of electrodes fabricated by spray deposition (three coating layers) and dried at 80 °C. The active material consists of Sigma PAC (95 m%) and SBR/CMC binder (5 m%) while the current collector is Toyal Carbø.](image)

Richard Fields - February 2018

265
The numerical range of thickness measurements (three for each 1.767 cm² disk sample) was calculated for each sample to assess if this was a possible source of variation; the maximum range was found to be 51 μm, the minimum range was 2 μm and the average range was 12 μm. These values represent variations in coating thickness measurement of approximately ±10%, double that of electrodes fabricated by tape casting. As accurate measurements had been conducted on previously fabricated electrodes, with an instrument resolution of 1 μm (see Section 4.4.5), it was deemed that measurement was not the source of variation. As such, SEM analysis was conducted with the core task of finding the source of this variance. Samples in this case were mounted in both cross-sectional and planar views to better assess surface uniformity.

![Cross-sectional SEM images](image)

Figure 7.2 Cross-sectional SEM image showing an electrode fabricated by spray deposition (three coating layers) and dried at 80 °C. The active material consists of 95 m% Sigma PAC and 5 m% SBR/CMC binder while the current collector is Toyal Carbo®. (a) cavernous internal void and (b) tall non-planar structure.

Shown in Figure 7.2 are cross-sectional SEM images of the same electrode fabricated by spray deposition and dried at 80 °C. Imaged in Figure 7.2 (a) was a cavernous internal void; this void dramatically increased the apparent electrode thickness by ~50 μm in comparison to the surrounding area. Notice how this void does not appear to begin at the CC base, instead it has been formed mid-coating indicating that this structure was formed during the 2nd or 3rd coating. This structure could have been produced in a similar manner to that explained in Section 4.4.5 i.e. pressurised steam producing vents-like voids. The difference in this case is that the electrodes were thinner than those in Section 4.4.5 yet still exhibited this phenomenon. As such, instead of associating this phenomenon with electrode thickness, it is more likely to be associated with water content, which was also believed to be high for electrodes produced by tape casting which exhibited this phenomenon.
Imaged in Figure 7.3 (b) was a tall non-planar structure. Such structures could have been produced by the spraying process but interestingly they were not seen in any planar images (see Figure 7.3 and Appendix (16)). As such, it is believed they are in fact results of the sample preparation process for SEM imaging, specifically the cutting of samples with a scalpel in order to produce appropriate sizes. This belief is supported by examining the left side of Figure 7.2 (b) which appears to be devoid of coating, something which is unlikely to have occurred after three consecutive coatings. As such, the predominant cause of the variation seen in Figure 7.1 is believed to be due to the phenomenon presented in Figure 7.2 (a).

![Figure 7.3 Planar SEM image showing an electrode fabricated by spray deposition (three coating layers) and dried at 80 °C. The active material consists of 95 m% Sigma PAC and 5 m% SBR/CMC binder while the current collector is Toyal Carbo®.](image)

Shown in Figure 7.3 are planar SEM images of the same electrode fabricated by spray deposition and dried at 80 °C. In Figure 7.3 (a) the coating appears on first sight to be uniform but note how the top left and bottom left regions show gaps between particles while the in bottom centre and mid right regions there is cohesion between particulated matter, this indicates an uneven surface coating with certain material types gathering together. Further to this, Figure 7.3 (b) shows significant surface defects; while not entirely circular they do appear to present a continuous outer perimeter. Also, note that these defects have central voids, possibly similar in nature to those found in tape casting (see Section 4.4.5), these could have formed through bubbling of liquid material ejected from within the electrodes surface. Interestingly, the internal areas are brighter than the external areas.
EDX analysis of the defects presented in Figure 7.3 (b) was conducted. Areas of distinct difference were selected to quantify their elemental make up, the results of EDX analysis are presented in Table 7.3 and relate to POIs indicated in Figure 7.4; their corresponding spectra can be found in Appendix 17.

Figure 7.4  SEM image of spray deposited electrode containing 95% Sigma PAC under EDX examination; POIs are elementally quantified in Table 7.3. The active material consists of 95 m% Sigma PAC and 5 m% SBR/CMC binder while the current collector is Toyal Carbo®.

POIs 1 and 2 encompass areas of coating defect, they mostly possess high carbon, oxygen and aluminium content but small percentages of silicon and sulfur are also found. At this point it is necessary to consider the chemical makeup of the electrode constituent components; Sigma PAC is believed to be almost entirely carbon, trace elements are minimal in the manufacturer specification, the SBR component of the binder is based on butadiene and styrene [294]  and the CMC component of the binder is predominantly hydrogen, carbon and oxygen based [295]. In addition, the specifications of PSBR100, the source of the SBR/CMC binder, state that the material is ‘modified’; quite what this implies is unknown but it suggests additives may be present [230].

As such, the high oxygen content of POIs 1 and 2, and the low presence of oxygen in CMC, suggest that these POIs are predominantly binder material. This is partially supported by the high carbon content, but this could have also been contributed by the Sigma PAC. The source of the sulfur and silicon could be due to the ‘modified’ nature of the binding material as they are present in very small quantities.
The presence of aluminium is intriguing; its only apparent source is from the CC as both the primary substrate and AlC$_3$ nanowhiskers. It seems unlikely that the primary substrate could have been liquidised and transported to the surface, it is more probable that the conductive nanowhiskers, the tips of which were examined in Section 4.3, could have been stripped (possibly along with the carbon particle content they were binding) and transported to the electrode surface through the ejection of internally pressurised steam. Contrary to this suggestion is the fact that coatings were conducted in layers, by the 3rd coating the base layer would have ideally already been dried and solidified thus prohibiting transportation of CC associated materials to the coating surface; but this process may not have been ideal, subsequent coatings could have re-wetted the base coating causing it to become liquid again. This is one of the issues faced when producing multiple coatings by spray deposition and is believed to have been the cause of the difficulty found in producing coatings more than three layers thick. Further support of this theory is that heating was applied from below (as it was drying on a hotplate), this could have caused the aluminium to expand thus inducing structural stress upon the AlC$_3$ nanowhisker coating, possibly leading to their delamination and diffusion into the wet slurry solution.

Table 7.3  Normalised weight % of constituent elements found through EDX analysis of NXA-513; POIs as indicated in Figure 4.5. The active material consists of 95 m% Sigma PAC and 5 m% SBR/CMC binder while the current collector is Toyal Carbon.

<table>
<thead>
<tr>
<th>POI</th>
<th>Carbon</th>
<th>Oxygen</th>
<th>Aluminium</th>
<th>Silicon</th>
<th>Sulfur</th>
<th>Chlorine</th>
<th>Potassium</th>
<th>Titanium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>1</td>
<td>74</td>
<td>15</td>
<td>8</td>
<td>2</td>
<td>1</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>2</td>
<td>74</td>
<td>15</td>
<td>8</td>
<td>2</td>
<td>1</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>3</td>
<td>85</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>n/a</td>
<td>0.87</td>
<td>n/a</td>
</tr>
<tr>
<td>4</td>
<td>86</td>
<td>7</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

POIs 3 and 4 encompass areas of standard particulated coating, they possess higher carbon content with lower oxygen and aluminium content than POIs 1 and 2. Interestingly, despite the oxygen content being lower, which suggests less CMC is present, there appears to be an abundance of added elements i.e. chlorine, potassium and even titanium. The presence of these here is surprising, it would have been expected that any potential PSBR.100 ‘modification’ additives would be found evenly distributed with binder content i.e. also in POIs 1 and 2.
Further, it appears the content of silicon and sulfur has increased at POIs 3 and 4, despite the decrease in oxygen content.

The findings above could mean one of several things; errors in the EDX analysis (as was found in Section 4.2.1 when examining material NXA 513), where the additional elemental content is not associated with the CMC component of the binder or the additional element is not associated with the binder content at all. For the first suggestion, a literature survey was conducted but no known elemental mis-identifications were found for these elements. The third suggestion could represent the possibility that the coating was contaminated but the EDX findings presented here are corroborated by findings from other sites (provided in Appendix 17). As such, the second suggestion appears the most likely. This could potentially imply that the binding material has disassociated into its constituent parts, with CMC being transported to some locations and SBR to others while ‘modification’ additives appearing to be associated with the SBR content.

The primary findings on these defects thus far are that they possess a continuous perimeter which is almost circular in shape, they have voids at their centre which are possibly associated with vents for high pressure moisture, the perimeter material has a high oxygen content suggesting they are strongly composed of CMC, the perimeter material also has high aluminium content suggesting material from the CC coating has been transported to the surface and does not appear to be associated with the SBR component of the binder.

A theory which fits with these findings is that the high water content of spray deposited slurries did indeed strip away the CC conductive coating; this coating material subsequently combined with the wet slurry material which was heated, causing it to vent to the cooler surface plane (which is not heated). At this point, a bubble was rapidly formed at the surface; it is widely known that high liquid surface tension can allow bubbles to endure higher pressures [296]. This high liquid surface tension could have been attained through the presence of CMC, which is a thickening agent [230]. As the pressure built behind the bubble it would be caused to pop thus leaving the continuous perimeter (which almost circular in shape), defects in this shape could have been formed by the presence of bubbles with a common wall.

This analysis shows that the coating process used in this case was less than ideal. It is possible that a different drying mechanism, i.e. oven drying, would have produced different results and possibly produced coatings with the same quality as those achieved by tape casting. Regardless,
determination of the electrochemical performance of such coatings was desirable as they may prove a useful performance benchmark for future work.

7.4 Multi-layer Spray Deposition of PAC Electrodes

7.4.1 Cell Configurations

This section presents the results of basic EDLC devices which can be used to assess the basic properties of electrodes fabricated by spray deposition. Five sample cells were created to ascertain mean values and relative standard deviation (RSD%) of their electrochemical properties.

Table 7.4 Cell configurations of spray deposited electrodes containing 95% Sigma PAC and 5% CMC/SBR binder. Note that areal density and mass values refer to the active material alone.

<table>
<thead>
<tr>
<th>0% MWCNT</th>
<th>Areal Density (+/-)</th>
<th>Single Electrode Mass (+/-)</th>
<th>Mass Ratio m(+ : -)</th>
<th>Combined Mass</th>
<th>Average Electrode Thickness (+/-)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg cm^{-2}</td>
<td>mg</td>
<td></td>
<td>mg</td>
<td>μm</td>
</tr>
<tr>
<td>Sample A</td>
<td>4.99 / 5.20</td>
<td>8.82 / 9.19</td>
<td>1 : 1.04</td>
<td>18.02</td>
<td>148 / 150</td>
</tr>
<tr>
<td>Sample B</td>
<td>6.75 / 6.78</td>
<td>11.93 / 11.97</td>
<td>1 : 1</td>
<td>23.91</td>
<td>178 / 188</td>
</tr>
<tr>
<td>Sample C</td>
<td>6.07 / 6.05</td>
<td>10.72 / 10.69</td>
<td>1 : 1</td>
<td>21.42</td>
<td>199 / 204</td>
</tr>
<tr>
<td>Sample D</td>
<td>6.15 / 5.96</td>
<td>10.86 / 10.53</td>
<td>1 : 0.97</td>
<td>21.40</td>
<td>195 / 186</td>
</tr>
<tr>
<td>Sample E</td>
<td>4.90 / 4.96</td>
<td>8.65 / 8.76</td>
<td>1 : 1.01</td>
<td>17.42</td>
<td>175 / 167</td>
</tr>
</tbody>
</table>

Shown in Table 7.4 are the cell configurations for spray deposited electrodes containing Sigma PAC and SBR/CMC binder, there was no MWCNT content. The areal density and mass values refer to the active material alone i.e. not including other cell components such as current collector. The precise electrode mass and associated thickness could not be effectively controlled during the spray deposition process (see Section 7.3.4). As such, the single electrode mass has an RSD% of 12.46% and ranges by ± 3.32 mg; such variance is also demonstrated in terms of average electrode thickness. Although this demonstrates a lack of control in some aspects, it does provide the opportunity to assess if electrode mass and average thickness impact electrode performance.

The mass ratio of samples tends towards m(1:1) but is not always ideal; this again was due to difficulty in producing electrodes with absolutely identical mass. In addition to this, almost all samples meet the desired thickness range set in research aim 5 i.e. electrode coatings should possess thicknesses between 100 and 200 μm. Samples A and E do not meet the desired single
electrode mass i.e. being greater than 10 mg, it was of interest to see if this caused the results of electrochemical analysis to differ significantly.

7.4.2 Results and Analysis

The results of CCCD testing at 100 mA g\(^{-1}\) and 2,500 mA g\(^{-1}\) are shown in Figure 7.5 (A) and Figure 7.5 (B), respectively; the top right insets show the transition between charge and discharge phases. Note: a full suite of CCCD testing results (at all currents) can be found in supplement B. It can be clearly seen that cells containing electrodes fabricated by spray deposition and based upon Sigma PAC demonstrate generally consistent performance. The deviation present may possibly be explained by the variance in electrode mass or average electrode thickness; such a possibility will be considered further upon quantification of cell properties (at 250 mA g\(^{-1}\)).

![Figure 7.5 Results of CCCD testing at (A) 100 mA g\(^{-1}\) (3rd run) and (B) 2,500 mA g\(^{-1}\) (3rd run) for EDLC cells containing electrodes fabricated by spray deposition.](image)

The results of CV testing at 10 mV s\(^{-1}\) and 1,000 mV s\(^{-1}\) are shown in Figure 7.6 (A) and Figure 7.6 (B), respectively. Again, cells containing electrodes fabricated by spray deposition and

![Figure 7.6 Mass specific capacitance-voltage plots derived from CV testing at (A) 10 mV s\(^{-1}\) (3rd cycle) and (B) 1,000 mV s\(^{-1}\) (3rd cycle) for EDLC cells containing electrodes fabricated by spray deposition.](image)
based upon Sigma PAC generally demonstrate consistent performance. Qualitative assessment of Figure 7.6 (A) suggests that sample C possesses a capacitance which is lower than other samples of the same type. This finding is based upon mass specific values and as such the contribution of mass differences should be negated, especially since sample C does not possess an abnormal total electrode mass and a well-balanced electrode mass. Instead, it was noticed that this sample did contain the thickest electrodes, albeit by a minimal difference with other samples; this would increase the areal resistance of such an electrode.

Another interesting find from this figure is that the mass specific capacitance starts to linearly increase above 1 V and does not present a redox peak above 2.25 V. This runs counter to the findings presented in Figure 5.3 (a) (section 5.3.2), albeit the scan rate in that experiment was half of that used in Figure 7.6 (A). As the electrode compositions were identical in both cases, the source of this variance is brought into question. Although it is possible that different deposition methods may give rise to differing electrode structure, which potentially affect electronic contact, it was not thought possible by the author for the deposition method to change fundamental material properties such as capacitance. Alternative explanations for such a phenomenon may be the use of refined fabrication techniques developed throughout previous sections, particularly relating to electrode drying and electrolyte preparation.

Qualitative assessment of Figure 7.6 (B) suggests that sample E possesses a higher resistance than other samples, this is indicated by the narrower CV window. Such resistance could be due to a variation in the density of electrodes used in its fabrication; sample E has the lowest combined electrode mass but significantly thicker electrodes than sample A (which has comparable electrode mass). This indicates that AC particles are not tightly packed, which possibly increases the contact resistance, thus causing the narrow CV window. This issue clearly exemplifies the inconsistent electrode fabrication by spray deposition experienced in this study.

Shown in Table 7.5 are the KPIs (key performance indicators) for EDLC cells containing electrodes fabricated by spray deposition, they are derived purely from CCCD analysis at 250 mA g⁻¹. All samples are included in the calculation of mean and RSD% (relative standard deviation). These values are comparable with those also calculated by CCCD analysis in Table 5.3 (see section 5.3.2); both sets of KPIs are associated with cells containing 95 % Sigma PAC and 5 % SBR/CMC binder. The only major difference between this and previous work is the deposition method i.e. tape casting versus spray deposition. One minor difference in the derivation of these results is the current density at which values were calculated; in the case of
previous work (section 5.3.2) a current density of 280 mA g⁻¹ was used while in this work 250 mA g⁻¹ was used.

Table 7.5 KPIs for EDLC cells containing electrodes fabricated by spray deposition, they contain 95 % Sigma PAC and 5 % SBR/CMC binder.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F g⁻¹</td>
<td>Ω cm²</td>
<td>%</td>
<td>%</td>
<td>W h kg⁻¹</td>
<td>kW kg⁻¹</td>
</tr>
<tr>
<td>Sample A</td>
<td>14.2</td>
<td>3.49</td>
<td>98</td>
<td>91</td>
<td>11.9</td>
<td>43.9</td>
</tr>
<tr>
<td>Sample B</td>
<td>13.6</td>
<td>3.37</td>
<td>98</td>
<td>90</td>
<td>11.3</td>
<td>34.3</td>
</tr>
<tr>
<td>Sample C</td>
<td>13.0</td>
<td>5.10</td>
<td>100</td>
<td>92</td>
<td>10.8</td>
<td>25.3</td>
</tr>
<tr>
<td>Sample D</td>
<td>14.4</td>
<td>2.62</td>
<td>99</td>
<td>91</td>
<td>11.9</td>
<td>49.3</td>
</tr>
<tr>
<td>Sample E</td>
<td>14.2</td>
<td>5.50</td>
<td>100</td>
<td>92</td>
<td>11.8</td>
<td>28.8</td>
</tr>
<tr>
<td>Mean</td>
<td>13.9</td>
<td>4.02</td>
<td>99</td>
<td>91</td>
<td>11.5</td>
<td>36.3</td>
</tr>
<tr>
<td>Relative Standard Deviation</td>
<td>±4.15 %</td>
<td>±30.6 %</td>
<td>±1.01 %</td>
<td>±0.84 %</td>
<td>±4.18 %</td>
<td>±27.8 %</td>
</tr>
</tbody>
</table>

a At 250 mA g⁻¹ relative to mass of both electrodes
b Under matched load condition with a peak voltage of 2.5 V

Previous experiments have been conducted using the electrode composition (95 % Sigma PAC and 5 % SBR/CMC) and the tape casting fabrication method (see section 5.3.2); in that work it was found by CCCD analysis that the average mass specific capacitance was 15.1 F g⁻¹ with a RSD% of ±2.91. In this work (i.e. same composition fabricated by spray deposition) it was found that the average mass specific capacitance was 13.9 F g⁻¹ with a RSD% of ±4.15%; this indicates that mass specific capacitance is 8% lower and more variable than that achieved when fabricating electrodes by tape casting. A slightly different view could be taken by excluding samples C and E which presents obvious differences in CV analysis; this would result in an average mass specific capacitance of 14.1 F g⁻¹ with a RSD% of ±2.96 %, a slight improvement over previous analysis but still indicating that spray deposition provides a lower mass specific capacitance.

In terms of average areal resistance, tape casting and spray deposition gave 4.62 and 4.02 Ω cm², respectively. This result is interesting because it appears spray deposition provides a reduction in electrode resistance; in fact, the exclusion of samples C and E reduces the average
areal resistance to 3.16 Ω cm². Such a finding is highly intriguing as it was previously thought by the author that spray deposition may lead to electrodes with less ‘compact’ coatings, thus increasing resistance. One aspect which is very similar between fabrication methods appears to be the RSD% of areal resistance (±31.4 % for tape casting and ±30.6 % for spray deposition). This could indicate (as previously suggested throughout Section 5) that resistance is not purely associated with the cell but also its connection method to the testing apparatus.

Mass specific power density is dependent upon areal resistance. In the case of cells containing spray deposited electrodes, the decrease in areal resistance (compared to tape casted electrodes) provides a 4% improvement in power capability. In conjunction with this; the RSD% also decreases from ±39.86 % to ±27.8 % for tape casted and spray deposited electrodes, respectively. This improvement signifies that not only are spray deposited electrodes more powerful but they are also more consistent; such a finding contrasts the inconsistent electrode coatings observed during fabrication. As such, the author proposes that these improvements may also be related to the refinement of cell fabrication techniques.

With regards to efficiency: the charge storage efficiency is almost ideal (100 %) and is also comparable to values achieved in previous experiments using tape casting. The energy storage efficiency is slightly improved over values achieved previously (91 % by spray deposition and 88 % by tape casting); this is certainly due to the decrease in areal resistance exhibited by electrodes fabricated with spray deposition.

The mass specific energy density of EDLC cells fabricated using tape casted electrodes was found to be 12.37 W h kg⁻¹ with a RSD% of ±1.59 %. In this work, electrodes fabricated by spray deposition presented a lower value of 11.5 W h kg⁻¹ with a RSD% of ±4.18 %; this level of deviation agrees with that of mass specific capacitance (±4.15 %). As such, it is believed the primary contributor to lower mass specific energy density is the decrease in mass specific capacitance (which is not outweighed by the increase in energy storage efficiency).

Overall, the KPIs presented in Table 7.5 provide one perspective (with regards to current density) of cell performance. An additional perspective can be obtained by viewing the electrochemical response of spray deposited EDLC electrodes with varying current density. Such an approach has been taken throughout Figure 7.7 and Figure 7.8; these figures present data acquired by CCCD analysis at current densities of 0.1, 0.25, 0.5, 1, 2.5 and 5 A g⁻¹.
From Figure 7.7 (A) it is possible to see that there is a non-linear decrease in mass specific capacitance which occurs as the current density is increased. Such a graph seems to imply that if the current density were to be decreased below 0.1 A g⁻¹ the capacitance may yet increase further, but this is not a complete picture. Consider Figure 7.7 (B) in which charge and energy efficiency are compared to CCCD current density, notice how at 0.1 A g⁻¹ the efficiency is not maximal. This reduction in charge and energy efficiency at low current density is associated with the occurrence of chemical reactions; such reactions may be irreversible but it is also entirely possible that some are reversible (such as ion intercalation/de-intercalation). Consequently, the mass specific capacitance at 0.1 A g⁻¹ may be above the value which represents the true operational value; it is partially for this reason that KPIs in Table 7.5 were taken at 0.25 A g⁻¹, a current density which offers both high charge and energy efficiency. The link between current density and the presence of chemical reactions is rather complex; consider that as current density is increased the cell spends less time above voltages which may induce chemical reaction. A subtler influence of this result may be the lack of a dwell period (i.e. a period of ‘rest’ between charge and discharge phases) in CCCD testing. At high current density, there may be insufficient time for a full EDL (electric double layer) to form thus reducing the quantity of charge stored at the EDL; such a change would negatively impact the mass specific capacitance.

![Graph A](image1.png)  ![Graph B](image2.png)

Figure 7.7 Cells containing spray deposited electrodes based upon 95 % Sigma AC and 5 % SBR/CMC binder. (A) Mass specific capacitance with respect to current density during CCCD analysis. (B) Charge and energy efficiency with respect to current density during CCCD analysis. Indicated current densities are 0.1, 0.25, 0.5, 1, 2.5 and 5 A g⁻¹.

A further aspect of interest is energy storage efficiency (Figure 7.7 (B)). At the lowest current density of 0.1 A g⁻¹ this efficiency is ~85 % at 0.1 A g⁻¹, increases to ~92 % between 0.25 and 0.5 A g⁻¹, then steadily decreases to ~70 % as the current density is increased to 5 A g⁻¹. The
low efficiency at low current density can be associated with the loss of charge due to chemical reactions while the decrease in efficiency at high current density can be associated with ohmic losses i.e. energy loss due to resistive heating (see Equation (2.4)). Another trend of this data relates to the standard deviation; this is large at both low and high current densities while minimal at current densities between 0.25 and 0.5 A g\(^{-1}\). It appears to a certain degree that as the current density is increased, so too is the variability of energy efficiency.

Shown in Figure 7.8 (A) is mass specific energy density with respect to current density. It is firstly noticeable that the mass specific energy density decreases as the current density increases; this is not unsurprising given similar trend in mass specific capacitance which is directly proportional to energy density. Again, as this trend is dependent upon the quantity of charge stored at the EDL, it may be that the lack of CCCD dwell time negatively impacts energy density; such a trend has been previously noted by Andrew Burke in [38].

![Figure 7.8 Cells containing spray deposited electrodes based upon 95 % Sigma AC and 5 % SBR/CMC binder. (A) Mass specific energy density with respect to current density during CCCD analysis. (B) Areal resistance and mass specific power with respect to current density during CCCD analysis. Indicated current densities are 0.1, 0.25, 0.5, 1, 2.5 and 5 A g\(^{-1}\).](image)

The areal resistance and mass specific power with respect to current density are presented comparably in Figure 7.8 (B). It appears that as the current density increases the areal resistance decreases, such a phenomenon implies resistance is comprised of different attributing factors such as electronic and ionic resistance (including its diffusion through a tortuous electrode structure).

Figure 7.8 (B) possibly shows a link between areal resistance and mass specific power (i.e. as resistance decreases, power increases), but with substantial uncertainty between different samples. Whilst this link could be taken at face value, the suggestion that resistance decreases as current density increases is intriguing. Such a situation may imply that fundamental changes to
the electrode structure and possibly the electrolyte system are taking place. In fact, the decreasing resistance in this case is a phenomenon of the analysis technique utilised. Recall that resistance has been calculated from the voltage drop upon the initiation of discharge during CCCD testing; immediately prior to this point the cell has been subjected to a voltage of 2.5 V. At, or close to, 2.5 V these cells are known to experience adverse chemical reactions due to their capacitance symmetric nature (see Section 5.4 with regards to the impact of capacitance symmetry). Thus, the voltage drop (from which resistance was inferred) experienced not only a drop due to resistance but also due to the consumption of charge by chemical reactions. At high current densities, these reactions have insufficient reaction time to significantly impact the reported resistance value. From this understanding it may be considered appropriate to take the areal resistance as its lowest recorded value i.e. \( \sim 1.2 \ \Omega \ \text{cm}^2 \). Ultimately, the uncertainty between samples is significant; the trends Figure 7.8 (B) purportedly shows are not clearly defined.

7.4.3 Conclusion

The aim of this section was to assess the general performance of EDLC type EC devices using spray deposited electrodes. This was achieved through the directed atomisation (by airbrush) of dilute electrode slurry to fabricate electrodes containing 95 % Sigma PAC and 5 % SBR/CMC. Such an electrode composition was also used in previous work which involved fabricating electrodes by tape casting (see section 5.3.2); a direct comparison between fabrication techniques was thus appropriate. Cells were tested using both CCCD and CV techniques but quantitative data was acquired only from CCCD analysis.

Previous work (see section 5.3.2) showed that electrodes containing 95 % Sigma PAC and 5 % SBR/CMC fabricated by tape casting exhibited an average mass specific capacitance of 15.1 F g\(^{-1}\) with a RSD% of \( \pm 2.91 \). In this work, it was found that electrodes of the same composition, but fabricated by spray deposition, exhibited a reduced average mass specific capacitance of 13.9 F g\(^{-1}\) with a RSD% of \( \pm 4.15 \) %. Thus, electrodes fabricated by spray deposition present an average mass specific capacitance 8% lower than electrodes fabricated by tape casting.

It appears that spray deposition of electrodes also results in decreased areal resistance when compared to electrodes fabricated by tape casting. Including all data, the areal resistance is 4.02 \( \Omega \ \text{cm}^2 \) whilst excluding cells which exhibit abnormal behaviour drops this to 3.16 \( \Omega \ \text{cm}^2 \). Such a finding may be associated with intrinsic electrode structures formed during spray deposition.
Chapter 7: A study of multilayer spray deposition for composite carbon electrodes

The reduced resistance has an apparently positive impact upon the power capability and energy storage efficiency of devices containing spray deposited electrodes. The maximum mass specific power density value achieved was 49.3 kW kg\(^{-1}\) whilst the average energy storage efficiency was 91 %. Unfortunately, such improvements did not translate to an improvement in mass specific energy density when compared to electrodes fabricated by tape casting; the average mass specific energy density was 11.5 W h kg\(^{-1}\), a drop of 7 % from tape cast electrodes. This drop is primarily associated with the decrease in mass specific capacitance.

7.5 Multi-layer Spray Deposition of Composite PAC/MWCNT Electrodes

7.5.1 Cell Configurations

In the previous section the basic properties of electrodes fabricated by spray deposition were assessed and compared with same electrodes fabricated by tape casting. The focus of this section was to combine MWCNTs (multi-walled carbon nanotubes) with previously tested electrode materials (i.e. Sigma PAC and SBR/CMC binder). This was to assess if MWCNTs exhibit high-quality dispersion during spray deposition and, if so, what effect this has upon electrode resistance.

Four electrode compositions, containing 2, 5, 10 and 20 % MWCNT content alongside 5 % SBR/CMC binder with the remainder being Sigma PAC, were tested. Four samples of each composition were produced, this allowed for the calculation of mean KPI values and relative standard deviation (RSD%) of their electrochemical properties.

Shown in Table 7.6 through to Table 7.9 are the cell configurations for spray deposited electrodes containing Sigma PAC and SBR/CMC binder and MWCNT content of 2, 5, 10 and 20 % MWCNT, respectively. The areal density and mass values refer to the active material alone i.e. not including other cell components such as current collector. As with previous uses of spray deposition, the effective electrode mass and associated thickness could not be precisely controlled; as such, the single electrode mass has an RSD% of 24.29 % and ranges by 4.63 mg. The mass ratio of samples tends towards m(1:1) but is not always ideal; this again was due to difficulty in producing electrodes with absolutely identical mass.
Table 7.6  Cell configurations of spray deposited electrodes containing 2 % MWCNT, 93 % Sigma PAC and 5 % CMC/SBR binder. Note that areal density and mass values refer to the active material alone.

<table>
<thead>
<tr>
<th>Sample</th>
<th>2% MWCNT</th>
<th>Areal Density (+ / -)</th>
<th>Single Electrode Mass (+ / -)</th>
<th>Mass Ratio m(+ : -)</th>
<th>Combined Mass</th>
<th>Average Electrode Thickness (+ / -)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>2.42 / 2.34</td>
<td>4.28 / 4.13</td>
<td>1 : 0.96</td>
<td>8.42</td>
<td>138 / 117</td>
<td></td>
</tr>
<tr>
<td>Sample B</td>
<td>2.80 / 2.84</td>
<td>4.94 / 5.02</td>
<td>1 : 1.02</td>
<td>9.97</td>
<td>146 / 141</td>
<td></td>
</tr>
<tr>
<td>Sample C</td>
<td>2.56 / 2.65</td>
<td>4.52 / 4.68</td>
<td>1 : 1.04</td>
<td>9.21</td>
<td>140 / 142</td>
<td></td>
</tr>
<tr>
<td>Sample D</td>
<td>2.27 / 2.40</td>
<td>4.01 / 4.23</td>
<td>1 : 1.05</td>
<td>8.25</td>
<td>141 / 131</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.7  Cell configurations of spray deposited electrodes containing 5 % MWCNT, 90 % Sigma PAC and 5 % CMC/SBR binder. Note that areal density and mass values refer to the active material alone.

<table>
<thead>
<tr>
<th>Sample</th>
<th>5% MWCNT</th>
<th>Areal Density (+ / -)</th>
<th>Single Electrode Mass (+ / -)</th>
<th>Mass Ratio m(+ : -)</th>
<th>Combined Mass</th>
<th>Average Electrode Thickness (+ / -)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>2.85 / 2.77</td>
<td>5.03 / 4.90</td>
<td>1 : 0.97</td>
<td>9.94</td>
<td>164 / 176</td>
<td></td>
</tr>
<tr>
<td>Sample B</td>
<td>3.61 / 3.69</td>
<td>6.38 / 6.51</td>
<td>1 : 1.02</td>
<td>12.90</td>
<td>189 / 183</td>
<td></td>
</tr>
<tr>
<td>Sample C</td>
<td>3.53 / 3.62</td>
<td>6.23 / 6.40</td>
<td>1 : 1.03</td>
<td>12.64</td>
<td>178 / 184</td>
<td></td>
</tr>
<tr>
<td>Sample D</td>
<td>2.72 / 2.72</td>
<td>4.81 / 4.80</td>
<td>1 : 1.00</td>
<td>9.62</td>
<td>163 / 164</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.8  Cell configurations of spray deposited electrodes containing 10 % MWCNT, 85 % Sigma PAC and 5 % CMC/SBR binder. Note that areal density and mass values refer to the active material alone.

<table>
<thead>
<tr>
<th>Sample</th>
<th>10% MWCNT</th>
<th>Areal Density (+ / -)</th>
<th>Single Electrode Mass (+ / -)</th>
<th>Mass Ratio m(+ : -)</th>
<th>Combined Mass</th>
<th>Average Electrode Thickness (+ / -)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>4.18 / 4.29</td>
<td>7.39 / 7.58</td>
<td>1 : 1.03</td>
<td>14.98</td>
<td>202 / 4.29</td>
<td></td>
</tr>
<tr>
<td>Sample B</td>
<td>3.67 / 3.48</td>
<td>6.49 / 6.15</td>
<td>1 : 0.95</td>
<td>12.65</td>
<td>175 / 3.48</td>
<td></td>
</tr>
<tr>
<td>Sample C</td>
<td>2.88 / 3.07</td>
<td>5.09 / 5.43</td>
<td>1 : 1.07</td>
<td>10.53</td>
<td>151 / 3.07</td>
<td></td>
</tr>
<tr>
<td>Sample D</td>
<td>4.62 / 4.42</td>
<td>8.17 / 7.80</td>
<td>1 : 0.95</td>
<td>15.98</td>
<td>227 / 4.42</td>
<td></td>
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</tbody>
</table>
Table 7.9  Cell configurations of spray deposited electrodes containing 20 % MWCNT, 75 % Sigma PAC and 5 % CMC/SBR binder. Note that areal density and mass values refer to the active material alone.

<table>
<thead>
<tr>
<th>20% MWCNT</th>
<th>Areal Density (+ / -)</th>
<th>Single Electrode Mass (+ / -)</th>
<th>Mass Ratio m(+ : -)</th>
<th>Combined Mass</th>
<th>Average Electrode Thickness (+ / -)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg cm²</td>
<td>mg</td>
<td></td>
<td>mg</td>
<td>μm</td>
</tr>
<tr>
<td>Sample A</td>
<td>2.27 / 2.16</td>
<td>4.01 / 3.82</td>
<td>1 : 0.95</td>
<td>7.84</td>
<td>152 / 141</td>
</tr>
<tr>
<td>Sample B</td>
<td>2.12 / 2.00</td>
<td>3.74 / 3.54</td>
<td>1 : 0.95</td>
<td>7.29</td>
<td>148 / 134</td>
</tr>
<tr>
<td>Sample C</td>
<td>2.51 / 2.51</td>
<td>4.43 / 4.44</td>
<td>1 : 1.00</td>
<td>8.88</td>
<td>160 / 153</td>
</tr>
<tr>
<td>Sample D</td>
<td>2.56 / 2.49</td>
<td>4.52 / 4.39</td>
<td>1 : 0.97</td>
<td>8.92</td>
<td>157 / 154</td>
</tr>
</tbody>
</table>

7.5.2 SEM Analysis of MWCNT Dispersion in Spray Deposited Electrodes

MWCNTs were added to the electrode composition with the belief they would increase electronic conductivity. This belief was based upon the concept that MWCNTs can form interparticle conductive pathways i.e. areas where MWCNT bridge between particles; these pathways possibly provide additional contact area for electronic charge transfer thus reducing electronic resistance. An additional bonus to reducing electronic resistance, which could otherwise be achieved through the addition of carbon black, is the capacitive response of MWCNTs [10]. Compositions of electrodes containing 2, 5, 10 and 20 % MWCNT content alongside a Sigma PAC based electrode containing 5 % SBR/CMC were fabricated. This section details analysis of the dispersion and whether interparticle conductive pathways were indeed formed and if so, to what extent.

![SEM images of an electrode fabricated by spray deposition containing 2% MWCNT, 93% Sigma PAC, and 5% SBR/CMC binder; (a) shows an area sparsely covered and (b) shows an area of agglomeration.](image)
Figure 7.9 (a) and (b) show electrode material coatings which consist of 2% MWCNT (by weight); it can be clearly seen that this value is in fact an idealised global value. At the local scale, it appears dispersion is non-ideal; Figure 7.9 (a) demonstrates an area with minimal MWCNT content while Figure 7.9 (b) demonstrates an area of MWCNT agglomeration. It should be noted that no substantial (> 1 μm in length) interparticle conductive pathways were found in this examination.

![Figure 7.9](image)

Figure 7.10 SEM images of an electrode fabricated by spray deposition containing 5% MWCNT, 90% Sigma PAC, and 5% SBR/CMC binder; (a) shows MWCNTs bridging between particles and (b) shows particle covering by MWCNTs.

![Figure 7.10](image)

Figure 7.11 SEM images of an electrode fabricated by spray deposition containing 10% MWCNT, 85% Sigma PAC, and 5% SBR/CMC binder; (a) shows multiple MWCNT interparticle bridges and (b) shows an extremely long bridge.

![Figure 7.11](image)
Figure 7.12 SEM images of an electrode fabricated by spray deposition containing 20% MWCNT, 75% Sigma PAC, and 5% SBR/CMC binder. (a) shows MWCNTs bridging between particles and (b) shows particle smoothing by MWCNTs.

Figure 7.10 (a) and (b) show electrode material coatings which consist of 5% MWCNT (by weight). This was the lowest MWCNT concentration at which substantial interparticle conductive pathways were found, as shown in Figure 7.10 (a). It was clear that coverage of Sigma PAC by MWCNTs was substantially improved, relatively uniform particle covering is shown in Figure 7.10 (b).

Figure 7.11 (a) and (b) show electrode material coatings which consist of 10% MWCNT (by weight); this concentration appeared to present optimal coverage across all areas examined. Multiple interparticle conductive pathways, exemplified by Figure 7.11 (a), were found throughout the coating. This electrode composition also presented extensive interparticle conductive pathways, some upwards of 18 μm in length as shown in Figure 7.11 (b).

Figure 7.12 (a) and (b) show electrode material coatings which consist of 20% MWCNT (by weight); this coating presented substantial covering, verging on smoothing in some areas, of the AC materials by MWCNT. While some areas presented well-formed interparticle conductive pathways were formed, as shown in Figure 7.12 (a), other areas presented active material smoothing, as shown in Figure 7.12 (b). Smoothing of the active materials may be detrimental to their performance, it can lead to reduced ionic conductivity (as they must pass through a tortuous layer of tangled MWCNTs). One plausible reason behind its occurrence is MWCNTs agglomerating with binding materials during dispersion (by either physical stirring or ultrasonic mixing).
7.5.3 Electrochemical Results and Analysis

Figure 7.13 shows the results of CCCD testing at 0.1 A g⁻¹ (left plots) and 2.5 A g⁻¹ (right plots) for EDLC cells containing electrodes fabricated by spray deposition and with varying percentages of MWCNT content. It should be noted that samples C and D of 5% MWCNT were improperly fabricated (lacking two spacers) and could not be used for testing. Also note: a full suite of CCCD testing results (at all currents) can be found in supplement B. It appears samples are generally in good agreement with one another; sample D of 20% MWCNT at 2.5 A g⁻¹ is quite clearly an outlier with excessive resistance and will be excluded from data analysis. Figure 7.13 generally shows that at low current densities (0.1 A g⁻¹) the time taken for one complete cycle reduces as the MWCNT content increases. At high current densities (2.5 A g⁻¹) this trend is not clearly reproduced, only cells containing 20% MWCNT content show a clear reduction in time for one cycle to complete.

Figure 7.14 shows the results of CV testing at 10 mV s⁻¹ (left plots) and 1000 mV s⁻¹ (right plots). With regards to individual cell configurations it appears samples are in good agreement. Sample D of 20% MWCNT again presents deviation from is sample group and as such will certainly be excluded from analysis but other samples, such as C from 2% MWCNT and D from 10% MWCNT, also present deviations. These samples will not be excluded as KPIs (key performance indicators) are derived from CCCD analysis in which these samples appear to be in good agreement with their peers.

One aspect of interest which Figure 7.14 presents is the apparent reduction in chemical reactions as the MWCNT content is increased. This is visible when testing at 0.1 A g⁻¹, such reactions typically result in an increase in ‘capacitance’ above 2 V. This could indicate that the addition of MWCNT expands the stable voltage window but it is also possible that these nanotubes are themselves more stable and as such react at voltages above those tested. One further aspect, which is in fact believed the most likely contributor, is the mass ratio of these samples. Although efforts were made to select electrodes with equivalent mass ratios it appears samples of 20% MWCNT generally possess more mass at their positive electrode compared to their negative electrode; such a configuration is known to reduce the occurrence of chemical reactions (see Section 5.4).
Figure 7.13 Results of CCCD testing at (left plots) 100 mA g\(^{-1}\) (3\(^{rd}\) run), (right plots) 2,500 mA g\(^{-1}\) (5\(^{th}\) run) for EDLC cells containing electrodes fabricated by spray deposition. All electrodes contain 5% SBR/CMC alongside (A) and (B) 2% MWCNT, (C) and (D) 5% MWCNT, (E) and (F) 10% MWCNT, (G) and (H) 20% MWCNT with the remaining electrode material content being Sigma PAC.
Figure 7.14 Mass specific capacitance–voltage plots derived from CV testing at (left plots) 10 mV s\(^{-1}\) (3\(^{rd}\) run) and (right plots) 1,000 mV s\(^{-1}\) (5\(^{th}\) run) for EDLC cells containing electrodes fabricated by spray deposition. All electrodes contain 5% SBR/CMC alongside (A) and (B) 2% MWCNT, (C) and (D) 5% MWCNT, (E) and (F) 10% MWCNT, (G) and (H) 20% MWCNT with the remaining electrode material content being Sigma PAC.
Chapter 7: A study of multilayer spray deposition for composite carbon electrodes

The KPIs for EDLC cells containing electrodes fabricated by spray deposition are shown in Table 7.10, Table 7.11, Table 7.12 and Table 7.13 which correspond respectively to samples containing 2, 5, 10 and 20 % MWCNT content; these values are derived purely from CCCD analysis at 0.25 A g⁻¹. While the KPIs are interesting, the trends they present are not inherently obvious; as such, it was decided that these findings should also be presented in a graphical format to allow for an effective assessment of the impacts MWCNT content has on EDLC type EC devices. Such plots are presented subsequently in Figure 7.14 to Figure 7.18.

Cells containing 2 % MWCNT content are the closest in design to those containing 0 % MWCNT (previously analysed in Section 7.4.2). As such, it is important to compare these cell configurations to assess the impact of minimal MWCNT addition to EDLC type EC devices. The mean mass specific capacitance of cells containing 0% MWCNT was 13.9 F g⁻¹ with an RSD of 4.15%, in the case of cells containing 2 % MWCNT this value dropped by over 10 % to 12.5 F g⁻¹ with an RSD of 2.53%. This is confusing as the MWCNT content is believed to be capacitive and its addition should ideally present a decrease in capacitance between 0 and 2 %, far below that exhibited by these results.

The obvious difference appears to be material quantity, the electrodes containing 2 % MWCNT are roughly half as massive as those containing 0 % MWCNT but as the capacitance is calculated relative to the quantity of material the KPIs should remain approximately the same. Another difference is the apparent electrode density; cells containing 0 % MWCNT have an average combined mass of 20.4 mg with an average thickness of 179 μm resulting in an apparent density of 0.114 mg μm⁻¹; in contrast, cells containing 2 % MWCNT have an average combined mass of 8.96 mg with an average thickness of 137 μm resulting in an apparent density of 0.0654 mg μm⁻¹ (note, the area covered by each electrode was constant throughout). Such a reduction in electrode density could have increased the likelihood that some particles do not have adequate electronic contact, thus resulting in a loss of capacitance while maintaining mass. The reason for this decrease in electrode ‘compaction’ is not exactly clear but does indicate that the desired webbing of MWCNT content between particles (i.e. to produce interparticle conductive pathways) may also prohibit particles from settling into a more compact form during drying. Equally, this argument could be countered by suggesting the thickness measurements are not fully representative of the spray deposited electrodes used in this study due to the presence of coating anomalies such as internal voids (see Section 7.3.4).
Beyond these findings, a marginal reduction in areal resistance was found when 2% MWCNT is added, but this does not consider the reduced electrode mass; the mass specific power density best represents this and indicates the effective power capability of these electrodes has almost tripled from 36.3 kW kg\(^{-1}\) to 94.3 kW kg\(^{-1}\). Such a result suggests spray deposition is a viable method for achieving adequate MWCNT dispersion throughout an AC based electrode. This is a significant finding which may possibly translate across electrochemical devices in general.

With regards to charge storage efficiency the cells perform similarly but there is a slight reduction when 2% MWCNT is added. Additionally, the energy storage efficiency is reduced despite the improvement in power capability thus probably because of decreased charge storage efficiency. The mass specific energy density has also decreased but this is certainly due to the reduction in mass specific capacitance.

Table 7.10 KPIs for EDLC cells containing electrodes fabricated by spray deposition, they contain 2 % MWCNTs, 93 % Sigma PAC and 5 % SBR/CMC binder.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass Specific Capacitance (^{a}) (CCCD)</th>
<th>Areal Resistance (^{a}) (CCCD)</th>
<th>Charge storage efficiency (%) (CCCD)</th>
<th>Energy storage efficiency (%) (CCCD)</th>
<th>Mass Specific Energy Density (%) (CCCD)</th>
<th>Mass Specific Power Density (^{ab}) (CCCD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>12.7</td>
<td>2.31</td>
<td>99</td>
<td>93</td>
<td>10.7</td>
<td>141</td>
</tr>
<tr>
<td>Sample B</td>
<td>12.1</td>
<td>3.17</td>
<td>96</td>
<td>84</td>
<td>10.0</td>
<td>86.7</td>
</tr>
<tr>
<td>Sample C</td>
<td>12.8</td>
<td>6.50</td>
<td>96</td>
<td>87</td>
<td>10.6</td>
<td>45.5</td>
</tr>
<tr>
<td>Sample D</td>
<td>12.4</td>
<td>3.20</td>
<td>97</td>
<td>88</td>
<td>10.4</td>
<td>104</td>
</tr>
<tr>
<td>Mean</td>
<td>12.5</td>
<td>3.80</td>
<td>97</td>
<td>88</td>
<td>10.4</td>
<td>94.3</td>
</tr>
</tbody>
</table>

Relative Standard Deviation

- 2.53 %
- 48.7 %
- 1.46 %
- 4.25 %
- 3.00 %
- 42.0 %

\(^{a}\) At 250 mA g\(^{-1}\) relative to mass of both electrodes
\(^{b}\) Under matched load condition with a peak voltage of 2.5 V
Table 7.11 KPIs for EDLC cells containing electrodes fabricated by spray deposition, they contain 5 % MWCNTs, 90 % Sigma PAC and 5 % SBR/CMC binder.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>F g⁻¹</td>
<td>Ω cm²</td>
<td>%</td>
<td>%</td>
<td>Wh kg⁻¹</td>
<td>kW kg⁻¹</td>
<td></td>
</tr>
<tr>
<td>Sample A</td>
<td>12.3</td>
<td>2.28</td>
<td>97</td>
<td>90</td>
<td>10.4</td>
<td>122</td>
</tr>
<tr>
<td>Sample B</td>
<td>12.4</td>
<td>2.75</td>
<td>97</td>
<td>91</td>
<td>10.5</td>
<td>77</td>
</tr>
<tr>
<td>Mean</td>
<td>12.35</td>
<td>2.52</td>
<td>97</td>
<td>90.5</td>
<td>10.5</td>
<td>99.5</td>
</tr>
<tr>
<td>Relative Standard Deviation</td>
<td>0.57 %</td>
<td>13.2 %</td>
<td>0 %</td>
<td>0.78 %</td>
<td>0.68 %</td>
<td>32 %</td>
</tr>
</tbody>
</table>

a At 250 mA g⁻¹ relative to mass of both electrodes
b Under matched load condition with a peak voltage of 2.5 V

Table 7.12 KPIs for EDLC cells containing electrodes fabricated by spray deposition, they contain 10 % MWCNTs, 85 % Sigma PAC and 5 % SBR/CMC binder.

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>F g⁻¹</td>
<td>Ω cm²</td>
<td>%</td>
<td>%</td>
<td>Wh kg⁻¹</td>
<td>kW kg⁻¹</td>
<td></td>
</tr>
<tr>
<td>Sample A</td>
<td>12.6</td>
<td>2.09</td>
<td>97</td>
<td>90</td>
<td>10.6</td>
<td>88</td>
</tr>
<tr>
<td>Sample B</td>
<td>12.3</td>
<td>2.40</td>
<td>97</td>
<td>90</td>
<td>10.4</td>
<td>90</td>
</tr>
<tr>
<td>Sample C</td>
<td>12.3</td>
<td>3.42</td>
<td>99</td>
<td>92</td>
<td>10.5</td>
<td>76</td>
</tr>
<tr>
<td>Sample D</td>
<td>12.5</td>
<td>2.96</td>
<td>97</td>
<td>90</td>
<td>10.6</td>
<td>58</td>
</tr>
<tr>
<td>Mean</td>
<td>12.4</td>
<td>2.71</td>
<td>97.5</td>
<td>90.5</td>
<td>10.5</td>
<td>78</td>
</tr>
<tr>
<td>Relative Standard Deviation</td>
<td>1.21 %</td>
<td>21.7 %</td>
<td>1.03 %</td>
<td>1.10 %</td>
<td>0.91 %</td>
<td>18.84 %</td>
</tr>
</tbody>
</table>

a At 250 mA g⁻¹ relative to mass of both electrodes
b Under matched load condition with a peak voltage of 2.5 V
Table 7.13  KPIs for EDLC cells containing electrodes fabricated by spray deposition, they contain 20 % MWCNTs, 75 % Sigma PAC and 5 % SBR/CMC binder.

<table>
<thead>
<tr>
<th></th>
<th>Mass Specific Capacitance a (CCCD)</th>
<th>Areal Resistance a (CCCD)</th>
<th>Charge storage efficiency (CCCD)</th>
<th>Energy storage efficiency (CCCD)</th>
<th>Mass Specific Energy Density (CCCD)</th>
<th>Mass Specific Power Density a,b (CCCD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F g⁻¹</td>
<td>Ω cm²</td>
<td>%</td>
<td>%</td>
<td>Wh kg⁻¹</td>
<td>kW kg⁻¹</td>
</tr>
<tr>
<td>Sample A</td>
<td>10.2</td>
<td>3.16</td>
<td>99</td>
<td>92</td>
<td>8.65</td>
<td>111</td>
</tr>
<tr>
<td>Sample B</td>
<td>10.2</td>
<td>3.90</td>
<td>99</td>
<td>92</td>
<td>8.64</td>
<td>96.8</td>
</tr>
<tr>
<td>Sample C</td>
<td>10.7</td>
<td>2.57</td>
<td>99</td>
<td>94</td>
<td>9.13</td>
<td>121</td>
</tr>
<tr>
<td>Sample D</td>
<td>10.7</td>
<td>11.1</td>
<td>99</td>
<td>91</td>
<td>8.94</td>
<td>27.3</td>
</tr>
<tr>
<td>Mean e</td>
<td>10.4</td>
<td>3.21</td>
<td>99</td>
<td>93.6</td>
<td>8.84</td>
<td>109.6</td>
</tr>
<tr>
<td>Relative Standard Deviation e</td>
<td>2.78 %</td>
<td>20.76</td>
<td>0 %</td>
<td>1.25 %</td>
<td>3.18 %</td>
<td>11.1 %</td>
</tr>
</tbody>
</table>

a At 250 mA g⁻¹ relative to mass of both electrodes
b Under matched load condition with a peak voltage of 2.5 V
c Excluding sample D due to significant differences shown in Figures 7.15 and 7.16.

While the KPIs of interest, the trends they present are not inherently obvious; as such, it was decided that these findings should also be presented in a graphical format. This allowed for an effective assessment of MWCNT content. Shown below in Figure 7.15 is the relationship between mass specific capacitance and MWCNT content within spray deposited electrodes. The initial drop between 0 % and 2 % has previously been discussed. Between 2 % and 10 % MWCNT content the mass specific capacitance remains relatively constant at low current densities (left); at high current densities (right) there is a slight increase in performance. This finding mildly reflects that of cells containing carbon black as a conductive additive [32]; when this standard material is used the performance increase at high current is significantly more pronounced (27 % increase in mass specific capacitance at high current) and occurs predominantly when an electrode contains 5 % carbon black. The addition of 20 % MWCNT content reduces the mass specific capacitance by approximately 18 % from electrodes containing 2 % MWCNT and significantly more from electrodes containing 0 % MWCNT.
Figure 7.15 Mass specific capacitance of cells containing spray deposited electrodes with varying degrees of MWCNT content. (left) 100 mA g$^{-1}$ (3$^{rd}$ run), (right) 2,500 mA g$^{-1}$ (5$^{th}$ run).

Figure 7.16 shows the relationship between MWCNT content and related KPIs i.e. charge storage efficiency and energy storage efficiency; these values have been calculated at low current density (left plot) and high current density (right plot). At low current density (0.1 A g$^{-1}$) charge storage efficiency drops upon the minimal addition of MWCNT content but slightly increases upon further addition of MWCNT content. It is quite apparent that the trend experienced in charge storage efficiency also translates to energy storage efficiency, this suggests that the latter is dependent upon the former.

Figure 7.16 Charge and energy storage efficiency of cells containing spray deposited electrodes with varying degrees of MWCNT content. (left) 100 mA g$^{-1}$ (3$^{rd}$ run), (right) 2,500 mA g$^{-1}$ (5$^{th}$ run).

At high current density (2.5 A g$^{-1}$) the charge storage efficiency approaches ideality up to 10 % MWCNT content but decreases slightly with 20 % MWCNT content, this could suggest that the MWCNTs are more reactive than standard Sigma PAC. In addition to this, a significant improvement in energy storage efficiency occurs apparently upon the addition of MWCNT
content, but such a finding does not consider the impact of areal loading and electrode thickness; Figure 7.17 exemplifies why this is important.

![Graph showing areal resistance and mass specific power vs. MWCNT content](image)

**Figure 7.17** Areal resistance and mass specific power of cells containing spray deposited electrodes with varying degrees of MWCNT content. (left) 100 mA g⁻¹ (3rd run), (right) 2,500 mA g⁻¹ (5th run).

One possible reason for an improvement in energy efficiency is a reduction in areal resistance, this would reduce the energy loss due to ohmic resistance. Figure 7.17 (left) shows the relationship between electrode MWCNT content of spray deposited electrodes versus the areal resistance and mass specific power when tested at low current densities. It is quite apparent that although the areal resistance increases at 2% MWCNT loading, the mass specific power also increases; this runs contrary to the understanding that higher resistance leads to a lower power capability, as per (3.3, Section 3.4.3). The actual source of the increase in mass specific power is believed due to the fact that samples containing MWCNTs were approximately half the mass of samples without MWCNTs, as the power capability is evaluated as a mass specific value it thus results in a doubling of the power.

At high current density (2.5 A g⁻¹) there appears to be more of a trend in decreasing resistance with increasing MWCNT content, it may be that at low currents these trends are masked by excessive chemical reactions. Again though, this trend does not translate directly to the mass specific power. After the initial increase from 25 kW kg⁻¹ at 0 % MWCNT to 125 kW kg⁻¹ at 2 % MWCNT there appears to be a decrease in power related performance until 20 % MWCNT is added at which point the power capability returns to ~125 kW kg⁻¹. Interestingly, this trend appears to coincide with trends in the combined mass of each sample; of all electrode containing MWCNT content samples with 5 and 10 % MWCNT were notably more massive than samples containing 2 and 20 % MWCNT. Again, this could certainly be related to the
variations in electrode thickness (caused by the spray deposition method) which presumably also causes the large margins of error associated with mass specific power values.

![Graph](image1.png)

**Figure 7.18** Mass specific energy density of cells containing spray deposited electrodes with varying degrees of MWCNT content. (left) 100 mA g⁻¹ (3rd run), (right) 2,500 mA g⁻¹ (5th run).

Figure 7.18 shows the relationship between MWCNT content of spray deposited electrodes and mass specific energy density at current densities of 0.1 A g⁻¹ (left) and 2.5 mA g⁻¹ (right). At 0.1 A g⁻¹ there is a trend of decreasing energy storage capability, this is expected due to the decreasing content of high capacitance material. At 2.5 A g⁻¹ there is an apparent increase in energy storage capability, this is believed to be related to the improvement in energy efficiency rather than an overall increase in energy storage.

![Graph](image2.png)

**Figure 7.19** Comparative Ragone plot of cells containing spray deposited electrodes with varying degrees of MWCNT content. Test current densities were (right to left) 0.1, 0.25, 0.5, 1, 2.5 and 5 A g⁻¹.

Figure 7.19 shows a comparative Ragone plot of cell containing spray deposited electrodes with either no (0%) MWCNT content or the inclusion of 2, 5, 10 and 20 % MWCNT (by
weight). It is quite clear that the results are not ideally comparable with the main difference being in terms of power density; this is certainly associated with the fact that electrodes containing MWCNT content were thinner and lighter than those with no MWCNT content but detailed attention has been paid to this previously.

One aspect of interest is the variability in results exhibited by samples containing MWCNT content; in some cases, there are mid-plot peaks which have not been found in previous research. Advanced data analysis using the analysis standards laid out in IEC 62576 (see Section 3.4.3) has been conducted. Specifically, it states that a cell can be analysed using CCCD at multiple current densities; what should arise is a linear response between $\Delta I$ and $\Delta V$ of which the gradient is $R_{ESR}$ as per Ohm’s law. Ideally, the electronic resistance of a purely capacitive system is not dependent upon current density thus giving rise to a linear response.

It has been found that some samples created for this experiment exhibited non-linear responses when increasing current was applied. A clear example of this was found between samples of 20% MWCNT, it has been presented in Figure 7.20 where (A) is sample A and (B) is sample D. Notice that sample A presents a variable response which depends upon discharge current while sample D presents an ideally linear response across all currents tested.

![Graphs](image_url)

**Figure 7.20** Relationship between change in discharge current and resulting drop in voltage during CCCD analysis as per IEC 62576. Both plots relate to cells containing electrodes with 20% MWCNT content (by mass), (A) is sample A and (B) is sample D.

The above example is an extreme representative example of a widespread issue: issues were also found in samples A and B of 2% MWCNT, A of 5% MWCNT, A and B of 10% MWCNT and A, B and C of 20% MWCNT (see Appendix 18).

It is not entirely certain why these variations occur, it certainly must be a current density related issue but the transferral of charge should not directly impact resistance. One method in
which an impact on resistance could arise is through a change in temperature, such a change would occur over repeated cycling due to ohmic heating in previous cycles (see Equation (2.4)). There are two reasons it is thought this is not the cause of variance: firstly, samples were placed in an environmentally controlled chamber during testing and secondly, low currents were used in previous tests thus heat output would have been minimal.

Another possible method for which variations could arise is through structural changes in the electrode. Some MWCNT may not be bound tight to the underlying electrode material (Sigma PAC) and could be moved with sufficient force. It is possible that as electrodes are charged/discharged the movement of ions also causes a slight shift in MWCNT positioning, particularly relating to contact positions. To check the validity of this occurring, samples containing 0% MWCNT were analysed (see Appendix 18); samples A, B, C and D exhibited perfectly linear responses but sample E presented significant deviation above current densities of 0.5 A g⁻¹. This could suggest that the phenomenon is not associated purely with the addition of MWCNT content.

A final method could be like the above but associated more with the method of electrode fabrication (i.e. spray deposition). It could be that as the electrode is cycled certain voids or poorly connected areas either attach or detach and thus change the local (and thus global) electrode resistance. Judging by the lack of electrode uniformity (see Section 7.3.4) the author believes this final method to be the most likely source of error. As such, it was deemed appropriate to produce a second Ragone plot which excludes any sample data with erratic voltage/current relationships (by IEC 62576 standard), this can be found in Figure 7.21.

![Figure 7.21 Comparative Ragone plot of cells containing spray deposited electrodes with varying degrees of MWCNT content, samples with erratic voltage/current relationships have been removed (see text). Test current densities were (right to left) 0.1, 0.25, 0.5, 1, 2.5 and 5 A g⁻¹.](image-url)
From Figure 7.21 it is possible to see that the exclusion of erratic samples does not eliminate the peculiar Ragone plot behaviour, but it is noticeably reduced. The general impact of this data exclusion is a reduction in power density across all sample types containing MWCNT content. Whilst this approach may be suitable, it does reduce the amount of data upon which conclusions could be drawn (particularly in the case of 5% MWCNT which now only has one usable sample).

Tentatively, the results indicate that the performance of electrodes with 2% MWCNT content is superior in terms of power capability. This is followed by electrodes containing 5% and 10% MWCNT content, but while maintaining energy capability there is a marked reduction in power capability at high current density. Lastly, samples containing 20% MWCNT attain significantly reduced energy density but achieve power capabilities approaching those achieved using 2%. Ultimately, the author believes it is suitable to say that the addition of MWCNT content may improve power capabilities of EDLC electrodes fabricated by spray deposition, but further testing is required before this can be asserted as fact.

7.5.4 Conclusion

The focus of this section was to combine MWCNTs (multi-walled carbon nanotubes) with previously tested electrode materials (i.e. Sigma PAC and SBR/CMC binder). This was to assess if MWCNTs exhibit high-quality dispersion during spray deposition and, if so, what effect this has upon an electrodes resistance. To achieve this, electrodes were created by spray deposition and contained 2, 5, 10 and 20% MWCNT content (by weight) alongside 5% SBR/CMC binder with the remaining weight percent being Sigma PAC. One issue with the coatings produced was the lack of consistent total mass; samples with 2, 5, 10 and 20% MWCNT possessed average combined electrode masses of 8.96, 11.3, 13.5 and 8.36 mg cm$^{-2}$, respectively.

The dispersion of MWCNTs within electrodes of each type was assessed by SEM analysis. As expected, MWCNT coverage increased as their weight percentage increased. At 2% the dispersion was non-ideal, some areas had good coverage while others did not; it was also noticed that few inter-particle conductive pathways were formed. With 5% MWCNT content electrodes demonstrated substantial inter-particle conductive pathways alongside uniform electrode coverage. At 10% MWCNT content it was believed optimal coverage was obtained and extensive inter-particle conductive pathways were formed. With 20% MWCNT coating samples were essentially smothered by MWCNTs, something which was thought to be
detrimental to electrode performance due to reduced ionic conductivity (as ions must pass through a tortuous layer of tangled MWCNTs to reach the underlying AC structure).

Electrochemical analysis of electrode configurations containing MWCNT content was conducted by CCCD (0.1 A g\(^{-1}\) to 5 A g\(^{-1}\)) and CV (10 mV s\(^{-1}\) to 1000 mV s\(^{-1}\)) techniques. Analysis of the results was conducted and found to indicate trends in performance, such as a decrease in mass specific capacitance and an increase in power capability as MWCNT content increased. The validity of these trends is dampened by the fact that areal density was not held constant between samples containing MWCNT; indeed, trends in mass specific power appeared to also correlate with the areal density of samples tested. As such, a strong conclusion cannot be drawn but results may indicate improvements in power capability as MWCNT content is increased.

Additionally, on the surface samples appeared to have consistent properties (within respective sample types), but consistency was found to be an issue upon in-depth analysis using the IEC 62576 resistance analysis technique. This technique specifically related to CCCD analysis and showed that samples were behaving erratically as the current density was increased; the result of which lead to some samples be excluded from the final Ragone plot. The source of this erratic behaviour is not known with certainty, but it is believed that the movement of MWCNT content during testing may be the cause.

7.6 Targeted MWCNT deposition in Multi-layer Spray Deposition of Composite PAC/MWCNT Electrodes

7.6.1 Cell Configurations

Up until now electrodes fabricated by spray deposition have consisted of a singular slurry composition i.e. the electrode consisted of an ideally homogeneous material distribution. In the culmination of this work, attempts were made to create electrodes with inhomogeneous material distributions. Specifically, it was of interest to study whether the targeted (by layer) deposition of MWCNT content could improve electrode performance while minimising the utilisation of conductive additives (MWCNTs). If this is found to be so it could potentially maximise gravimetric performance by allowing for thicker electrodes whilst minimising the replacement of activated carbon, the primary capacitive (and thus energy storage) material.
It was deemed appropriate to study the addition of MWCNTs to key areas in an electrode, the top-coating and the base-coating. Targeted deposition of MWCNTs at these locations may provide beneficial inter-particle conductivity, but it is not yet certain at which location their deposition would be most beneficial. A schematic of the proposed electrode structures has been provided in Figure 7.22; each electrode should consist of equivalent material content with the sole change being the exact location of that material content.

![Figure 7.22 Schematic of the electrode structures fabricated by targeted spray deposition. The SBR/CMC binder was held constant at 5% in all samples with the remaining electrode material content being Sigma PAC.](image)

As shown in Figure 7.22, electrodes will always contain three coating layers without MWCNTs (i.e. purely Sigma PAC and SBR/CMC based); one coating will also contain 5% MWCNT and one coating will contain 20% MWCNT content. This is roughly based upon the learnings from Section 7.5 in which it was found that electrode coatings containing 20% MWCNT content provide the highest power capability. A layer containing 5% MWCNT coating was also included to provide a transition layer between those with MWCNT content and those without. The three layers of 0% MWCNT provide the possibility of comparing results with those of Section 7.4 in which no MWCNT content was included.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Areal Density (± / -)</th>
<th>Single Electrode Mass (± / -)</th>
<th>Mass Ratio m(+ : -)</th>
<th>Combined Mass</th>
<th>Average Electrode Thickness (± / -)</th>
<th>MWCNT top-coat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg cm⁻²</td>
<td>mg</td>
<td>pg</td>
<td></td>
<td>pg µm</td>
<td></td>
</tr>
<tr>
<td>Sample A</td>
<td>7.96 / 7.71</td>
<td>14.1 / 13.6</td>
<td>1 : 0.97</td>
<td>27.7</td>
<td>241 / 259</td>
<td></td>
</tr>
<tr>
<td>Sample B</td>
<td>8.51 / 8.69</td>
<td>15.0 / 15.4</td>
<td>1 : 1.02</td>
<td>30.4</td>
<td>265 / 278</td>
<td></td>
</tr>
<tr>
<td>Sample C</td>
<td>8.21 / 8.23</td>
<td>14.5 / 14.5</td>
<td>1 : 1</td>
<td>29.0</td>
<td>262 / 291</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.14 Cell configurations of spray deposited electrodes containing a top-coating of MWCNTs. Note that areal density and mass values refer to the active material alone.
Table 7.15  Cell configurations of spray deposited electrodes containing a base-coating of MWCNTs. Note that areal density and mass values refer to the active material alone.

<table>
<thead>
<tr>
<th>MWCNT base-coat</th>
<th>Areal Density (+/-) mg cm(^{-2})</th>
<th>Single Electrode Mass (+/-) mg</th>
<th>Mass Ratio m(+/ -)</th>
<th>Combined Mass mg</th>
<th>Average Electrode Thickness (+/-) (\mu)m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>6.49 / 6.38</td>
<td>11.5 / 11.3</td>
<td>1 : 0.98</td>
<td>22.7</td>
<td>215 / 225</td>
</tr>
<tr>
<td>Sample B</td>
<td>8.31 / 8.76</td>
<td>14.7 / 15.5</td>
<td>1 : 1.05</td>
<td>30.1</td>
<td>274 / 287</td>
</tr>
<tr>
<td>Sample C</td>
<td>7.60 / 7.43</td>
<td>13.4 / 13.1</td>
<td>1 : 0.98</td>
<td>26.5</td>
<td>269 / 247</td>
</tr>
<tr>
<td>Sample D</td>
<td>6.93 / 7.12</td>
<td>12.2 / 12.6</td>
<td>1 : 1.03</td>
<td>24.8</td>
<td>237 / 232</td>
</tr>
</tbody>
</table>

Table 7.14 shows cell configurations for electrodes fabricated with a top-coating with MWCNTs; it should be noted that originally four samples were fabricated but sample D proved non-functional, as such it has been excluded from analysis. This leaves three samples with an average areal density of 8.53 mg cm\(^{-2}\), an average electrode mass of 15.1 mg and an average combined mass of 30.1 mg. All cells have mass ratios approaching mass symmetry.

Table 7.15 shows cell configurations for electrodes fabricated with a bottom-coating with MWCNTs. Four functional samples were produced with an average areal density of 7.38 mg cm\(^{-2}\), an average electrode mass of 13.0 mg and an average combined mass of 26.0 mg. These values were not identical to those of a cell containing top coating, on average there was a 14% reduction in electrode mass; in order to provide a fully informed analysis this will have to be taken into consideration as electrode mass (and consequent thickness) can affect power capabilities.

Ultimately, this study is aligned with the research aims 3 and 4 i.e. electrode coatings are to be produced where the material composition of individual layers may differ through the inclusion of conductive additives by spray deposition of electrode materials (see Section 2.8). The average electrode thickness was above that laid out in research aim 5 i.e. to be between 100 and 200 \(\mu\)m but the active material mass of a single electrode was certainly greater than 10 mg in all samples. Also, through considerate experimental design research aim 6 was also met, i.e. electrode configurations and containment reflect industry standards.
7.6.2 SEM Analysis of Targeted MWCNT Deposition in Spray Deposited Electrodes

The fabrication of electrodes containing targeted (by layer) MWCNT deposition was studied in this work; essentially, either a base or top coating of MWCNTs was provided to an otherwise standard (activated carbon) based electrode. The exact composition of these electrodes has been detailed previously in Table 7.14 and Table 7.15. The author proposes that such targeted deposition may bring the benefits of reduced electrode resistance without excessive use of MWCNTs.

Figure 7.23 exemplifies the findings of SEM analysis for a base layer with high (20 %) MWCNT content (shown in Figure 7.23 (a)), a middle layer of low (5 %) MWCNT content (shown in Figure 7.23 (b)) and a top coating of no (0 %) MWCNT content Figure 7.23 (c). It was found that this electrode composition exhibited similar issues to those found in the previous composition; bald AC particles i.e. those with no attached MWCNT content, were found in the base/middle layers which ideally contained significant MWCNT content; a clear example of this can be found in Figure 7.23 (c) where an AC particle smothered in MWCNT is near a bald AC particle. It is believed a similar phenomenon as described above, i.e. the re-wetting of base layers, was the cause of this. The result of this will be a reduction in ‘conductive netting’ across the electrode base, thus deviating the experimental setup away from its ideal composition. Again, it is believed that a significant quantity of the MWCNT material continued to reside within the base/middle layers, thus enabling a reasonable comparison with other targeted deposition type electrodes.

![SEM images](image)

Figure 7.23  SEM images of a base-coated electrode fabricated by spray deposition containing (a) a single top layer coating of 20% MWCNT, 75% Sigma PAC, and 5% SBR/CMC binder, (b) a single middle layer coating of 5% MWCNT, 90% Sigma PAC, and 5% SBR/CMC binder and (c) a triple base layer coating of 0% MWCNT, 95% Sigma PAC, and 5% SBR/CMC binder.

Figure 7.24 exemplifies the findings of SEM analysis for a base layer with no (0 %) MWCNT content (shown in Figure 7.24 (a)), a middle layer of low (5 %) MWCNT content
Chapter 7: A study of multilayer spray deposition for composite carbon electrodes

It shows that MWCNT content could be found in all targeted layers, including those which were supposed to contain no MWCNT content. This finding suggests that MWCNT content has been transported from the top/middle layers down to the base layers. This was almost certainly caused by the re-wetting of previously dry layers upon the application of further coatings; such a process potentially enabled loosely bound MWCNTs to drift from the top/middle layers down to the base layer. An implication of this is that neither the top nor middle layers contain the exact MWCNT percentage defined by their slurry composition, as some has been transferred to the base layers which ideally should possess no MWCNT content. This will reduce the extent of ‘conductive netting’ across the electrode top surface, thus deviating the experimental setup away from its ideal composition. Regardless, it is believed that a significant quantity of the MWCNT material continued to reside within the top/middle layers, thus enabling a reasonable comparison with other targeted deposition type electrodes.

7.6.3 Electrochemical Results and Analysis

Figure 7.25 shows the results of CCCD (constant current charge-discharge) testing at 100 mA g⁻¹ (left plots) and 2,500 mA g⁻¹ (right plots) for EDLC cells containing electrodes fabricated by targeted spray deposition. Note: a full suite of CCCD testing results (at all currents) can be found in supplement B. Specifically, Figure 7.25 (A) and (B) show the results of electrodes with a top coating of MWCNTs while Figure 7.25 (C) and (D) show the results of electrodes with a base coating of MWCNTs. The results of all samples are very consistent with their comparative
samples, although at high current there appears to be slightly more variability. The source of this variability could be related to the deposition method which has been shown to produce defects in the electrode surface (see Section 7.3.4). Qualitative analysis of the CCCD plots presented in Figure 7.25 was conducted, the resulting KPI (key performance indicators) are presented later in Table 7.16.

Figure 7.26 shows the results of CV (cyclic voltammetry) testing at 10 mV s\(^{-1}\) (left plots) and 1,000 mV s\(^{-1}\) (right plots) for EDLC cells containing electrodes fabricated by targeted spray deposition. Specifically, Figure 7.26 (A) and (B) show the results of electrodes with a top coating of MWCNTs while Figure 7.26 (C) and (D) show the results of electrodes with a base coating of MWCNTs. The results of samples tested at low scan rate are in precise agreement with one another with minimal to no difference between samples containing top or base coatings. At high a scan rate there is more variability, this includes both differences in mass specific capacitance and the overall CV shape. Regardless, it does appear the overall performance is qualitatively similar in samples of both varieties.

![Graphs](image)

Figure 7.25 Results of CCCD testing at (left plots) 100 mA g\(^{-1}\) (3\(^{rd}\) run), (right plots) 2,500 mA g\(^{-1}\) (5\(^{th}\) run) for EDLC cells containing electrodes fabricated by targeted spray deposition. Plots (A) and (B) relate to cells with a top-coating of MWCNTs while plots (C) and (D) relate cells with a base-coating of MWCNTs.
Chapter 7: A study of multilayer spray deposition for composite carbon electrodes

![Image of plots](image)

Figure 7.26 Results of CV testing at (left plots) 10 mV s\(^{-1}\) (3\(^{rd}\) run), (right plots) 1,000 mV s\(^{-1}\) (5\(^{th}\) run) for EDLC cells containing electrodes fabricated by targeted spray deposition. Plots (A) and (B) relate to cells with a top-coating of MWCNTs while plots (C) and (D) relate cells with a base-coating of MWCNTs.

KPIs have been derived from CCCD testing at 250 mA g\(^{-1}\), they are presented in Table 7.16 and Table 7.17 and associate with top-coated and base-coated electrode configurations, respectively. It is important to note that these samples are comparable, while non-ideally, to samples presented in Section 7.4.2 i.e. three-layer spray deposited Sigma PAC; to aid comparison, the mean and RSD\% (relative standard deviation) of cells with 0\% MWCNT have been presented in Table 7.17.

From these KPI it can be see that there is a negligible difference between mass specific capacitance (13.7 F g\(^{-1}\)), charge storage efficiency (99\%) and mass specific energy density (11.4 W h kg\(^{-1}\)). This is also true for the RSD\% of each value which is consistently below 2\%, these shows that the fundamental electrochemical performance of each material is unchanged. When compared to cells containing 0\% MWCNT content (see Section 7.4.2) it becomes apparent there has been a slight decrease in mass specific capacitance (1\%), this could relate to the replacement of some mass by MWCNTs which are known to have a lower mass specific capacitance value (see Section 2.4.1). The impact of this decrease has possibly been exhibited in by mass specific energy density, which has also slightly decreased upon the addition of MWCNTs in this work. Charge storage efficiency has remained constant throughout and the
RSD% has been reduced in samples in this study, this is not due to improvements in experimental setup as all samples were produced at the same time.

Areal resistance has been reduced by between 35 % (top coating) and 21 % (base coating) despite being significantly thicker (~35 %) than samples containing 0% MWCNT. The resulting power capability remains equivalent despite thicker electrode coatings. Such a finding bodes well for improving the gravimetric and volumetric performance of a fully contained device; for the same quantity of active material less current collector material is required while maintaining equivalent power capabilities. An additional benefit of the decrease in areal resistance is an increase in energy storage efficiency by between 1.4 % (top coating) and 1.9 % (base coating).

Table 7.16  KPIs for EDLC cells containing electrodes fabricated by spray deposition including a targeted MWCNT top-coating.

<table>
<thead>
<tr>
<th>MWCNT top-coat</th>
<th>Mass Specific Capacitance $^a$ (CCCD)</th>
<th>Areal Resistance $^a$ (CCCD)</th>
<th>Charge storage efficiency (CCCD)</th>
<th>Energy storage efficiency (CCCD)</th>
<th>Mass Specific Energy Density (CCCD)</th>
<th>Mass Specific Power Density $^{a,b}$ (CCCD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F g$^{-1}$</td>
<td>Ω cm$^2$</td>
<td>%</td>
<td>%</td>
<td>W h kg$^{-1}$</td>
<td>kW kg$^{-1}$</td>
</tr>
<tr>
<td>Sample A</td>
<td>13.5</td>
<td>2.86</td>
<td>99</td>
<td>92</td>
<td>11.2</td>
<td>34.8</td>
</tr>
<tr>
<td>Sample B</td>
<td>13.9</td>
<td>2.97</td>
<td>99</td>
<td>92</td>
<td>11.6</td>
<td>30.6</td>
</tr>
<tr>
<td>Sample C</td>
<td>13.6</td>
<td>2.11</td>
<td>99</td>
<td>93</td>
<td>11.4</td>
<td>45.2</td>
</tr>
<tr>
<td>Mean</td>
<td>13.7</td>
<td>2.65</td>
<td>99</td>
<td>92.3</td>
<td>11.4</td>
<td>36.9</td>
</tr>
<tr>
<td>Relative Standard Deviation</td>
<td>1.52 %</td>
<td>16.7 %</td>
<td>0 %</td>
<td>0.63 %</td>
<td>1.75 %</td>
<td>20.4 %</td>
</tr>
</tbody>
</table>

$^a$ At 250 mA g$^{-1}$ relative to mass of both electrodes
$^b$ Under matched load condition with a peak voltage of 2.5 V
Table 7.17 KPIs for EDLC cells containing electrodes fabricated by spray deposition including a targeted MWCNT top-coating.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>13.3</td>
<td>2.66</td>
<td>99</td>
<td>93</td>
<td>11.2</td>
<td>45.7</td>
</tr>
<tr>
<td>Sample B</td>
<td>13.8</td>
<td>3.69</td>
<td>99</td>
<td>93</td>
<td>11.5</td>
<td>24.8</td>
</tr>
<tr>
<td>Sample C</td>
<td>13.7</td>
<td>3.40</td>
<td>99</td>
<td>93</td>
<td>11.4</td>
<td>30.0</td>
</tr>
<tr>
<td>Sample D</td>
<td>13.8</td>
<td>3.07</td>
<td>99</td>
<td>92</td>
<td>11.6</td>
<td>35.6</td>
</tr>
<tr>
<td>Mean</td>
<td>13.7</td>
<td>3.20</td>
<td>99</td>
<td>92.7</td>
<td>11.4</td>
<td>34.0</td>
</tr>
<tr>
<td>Relative Standard Deviation</td>
<td>1.74 %</td>
<td>13.8 %</td>
<td>0 %</td>
<td>0.54 %</td>
<td>1.49 %</td>
<td>26.3 %</td>
</tr>
</tbody>
</table>

$^a$ At 250 mA g$^{-1}$ relative to mass of both electrodes  
$^b$ Under matched load condition with a peak voltage of 2.5 V

The cause of decreased areal resistance is certainly due to the presence of MWCNTs, the results of Section 7.5 attest to this. Of most interest is the role MWCNT location (within an electrode) plays in reducing areal resistance; it appears a top coating of MWCNTs is preferable to a base-coating.

To understand why this may be, it is necessary to review the SEM analysis presented in Section 7.6.2. It was found that when a base coating of MWCNTs was applied these stayed very much within the target location; in contrast to this, MWCNTs applied as a top coating were found to disperse down throughout the lower electrode layers. This presumably occurred due to the rewetting of lower layers allowing some MWCNTs to disperse away from their targeted location; note that most MWCNTs were still found close to the top layer. As such, it is believed the top MWCNT coating formed a sort of covering ‘net’ which significantly improved the conductive pathways to particles which may otherwise have been poorly connected (as on the top side they are exposed without further contact points). Such a ‘net’ is not as beneficial in the base layers due to AC particles being surrounded and possibly compacted by the layers above.

To appreciate the results above from a different perspective it was necessary to plot KPI derived from CCCD as a function of current density; unfortunately, comparison in this manner to prior work (see Section 5.3.2) was not possible due to analysis being conducted at single
current densities. In the following plots samples with an MWCNT top-coat are left and with an MWCNT base-coat are right.

![MWCNT Top-coat](image1.png) ![MWCNT Bottom-Coat](image2.png)

**Figure 7.27** Mass specific capacitance as a function of current density for cells containing spray deposited electrodes with MWCNT deposition targeted at either the top layers (left) or base layers (right).

Figure 7.27 shows the relationship between mass specific capacitance and CCCD current density. The difference is minimal; both demonstrate a mass specific capacitance approaching 14 F g$^{-1}$ at 0.1 mA g$^{-1}$ which decreases to 12 F g$^{-1}$ at 5 A g$^{-1}$. A slight difference can be seen in the variability of samples, indicated by the error bars, with an MWCNT top-coat appearing to be more variable in its performance.

It is not until reviewing Figure 7.28, which presents areal resistance as a function of current density, that significant differences in performance can be seen. It appears the addition of an MWCNT top-coat significantly reduces the areal resistance at all current densities of a cell when compared to cells with an MWCNT base coat, this corroborates with previous KPI analysis. It is also important to consider this finding in light that samples with an MWCNT top-coat were on average 11 % more massive and 7 % thicker than samples with an MWCNT base-coat, thus the reduction in areal resistance of top-coated electrodes is even more impressive.
Figure 7.28 Areal resistance as a function of current density for cells containing spray deposited electrodes with MWCNT deposition targeted at either the top layers (left) or base layers (right).

An effect of this improvement can be seen in Figure 7.29 which presents charge and energy storage efficiency as a function of current density. Whilst charge storage efficiency remains close to 100% in both top and base coated samples, there is a noticeable difference (9%) in energy storage efficiency at a current density of 5 A g⁻¹. This improvement is certainly related to the reduction in areal resistance as it is this which leads to ohmic heating, a form of energy loss during energy storage. At lower current density, the energy storage efficiency is roughly the same between coating types.

Figure 7.29 Charge and energy storage efficiency as a function of current density for cells containing spray deposited electrodes with MWCNT deposition targeted at either the top layers (left) or base layers (right).
A further effect of the reduced areal resistance exhibited by MWCNT top-coated samples can be found in Figure 7.30, it shows that mass specific power capability is around 8% higher than base-coated samples when current densities greater than 1 A are applied. This is further clarification of the fact that providing a top-coating of MWCNTs is more beneficial than providing a base-coating.

![Figure 7.30](image1.png)

Figure 7.30 Mass specific power density as a function of current density for cells containing spray deposited electrodes with MWCNT deposition targeted at either the top layers (left) or base layers (right).

It can be seen from Figure 7.31 that changes in areal resistance (and consequent power capability) do not significantly affect mass specific energy density. In both cases the peak energy density remains close to 12 W h kg\(^{-1}\) at low current density and drops to approximately 7 W h kg\(^{-1}\) at high current density. Such a finding was roughly expected due to similar trends in mass specific capacitance (Figure 7.27) while the increase in energy storage efficiency at 5 A g\(^{-1}\) does indeed improve energy density at this current density.

![Figure 7.31](image2.png)

Figure 7.31 Mass specific energy density as a function of current density for cells containing spray deposited electrodes with MWCNT deposition targeted at either the top layers (left) or base layers (right).
Chapter 7: A study of multilayer spray deposition for composite carbon electrodes

7.6.4 Conclusion

The aim of this section was to test the hypothesis that targeted (by layer) deposition of MWCNT content could improve electrode performance while minimising the utilisation of conductive additives (MWCNTs); this was tentatively found to be true.

Electrodes were created by spray deposition of electrode content onto an aluminium carbide current collector. It was selected to add a coating of electrode material containing 20% MWCNT, 75% Sigma PAC and 5% SBR/CMC as either the top or base coating; at the opposing side of this coating were three layers containing no MWCNT content. A layer containing 5% MWCNT coated was also included to provide a transition layer between those with MWCNT content and those without.

Figure 7.32 Comparative Ragone Plot of cells containing spray deposited electrodes with either no MWCNT content, an MWCNT top-coat or an MWCNT base-coat. Test current densities were (right to left) 0.1, 0.25, 0.5, 1, 2.5 and 5 A g⁻¹ and the average electrode thickness is stated in the legend.

A Ragone plot comparing the performance between samples with no MWCNT coating and those with top and base coats of MWCNTs is presented in Figure 7.32: the average electrode thickness was also stated in the legend. Such a plot clearly shows the benefits of targeted MWCNT addition to predominantly AC coatings; the thickest electrodes, which would traditionally have had lower power capabilities, are shown to perform equally as well with thinner electrodes when MWCNT content is added at both the top and base layers. Ultimately, it appears an MWCNT top-coating provides the most benefit, presumably due to the identified MWCNT dispersion throughout the lower layers (as found during SEM analysis).
SEM analysis of such electrode structures was conducted. It was found that when a base coating of MWCNT content was applied, MWCNTs could only be found in said base coating. In contrast, when a top coating of MWCNT content was applied, MWCNTs could be found throughout the entire electrode structure. The source of this was certainly caused by the re-wetting of previously dry layers upon the application of further coatings; such a process enabled loosely bound MWCNTs to drift from higher layers to the lower layers.

The consequence of these respective electrode structures was demonstrated by electrochemical analysis, particularly relating to areal resistance and power related performance. It was found the addition of a top-coating of MWCNTs reduced areal resistance by approximately 15 % despite this type of electrode being 11 % more massive, and 7 % thicker, than the alternative base-coated electrodes. Such an improvement in power performance did not negatively impact mass specific capacitance which remained roughly equal in both types of electrode. A consequence of the decreased areal resistance was increased power capability energy density with samples reaching up to 40 Wh kg⁻¹, and increased energy storage efficiency at high current densities.

Ultimately, it appears an MWCNT top-coating provides the most benefit, presumably due to the identified MWCNT dispersion throughout the lower layers (as found during SEM analysis). This was clearly demonstrated in the form of a Ragone plot.

7.7 Summary and Outlook

The aim of this chapter was to investigate the hypothesis that introducing MWCNTs at specific locations within an otherwise standard PAC based electrodes (e.g. at the base or top layer) may in fact bring the benefit of reduced electrode resistance without excessive use of MWCNTs. For this purpose it was decided that spray deposition of electrode coatings must be utilised in order to provide the flexibility of altering layer composition at specific locations.

As such, multi-layer spray deposition of electrode coatings containing 95 % Sigma PAC and 5 % SBR/CMC was attempted. While the approach proved to be relatively simple the results were substandard, often the coatings had defects in the form of voids (identified by SEM analysis). These voids were later associated with the use of a hot plate for drying during electrode fabrication; it is thought that using a different drying mechanism (e.g. oven drying) would have produced coatings with the same quality as those achieved by tape casting.
Chapter 7: A study of multilayer spray deposition for composite carbon electrodes

These electrodes fabricated by spray deposition (and containing 95 % Sigma PAC and 5 % SBR/CMC) were electrochemically analysed, they were compared with electrodes of the same composition but fabricated by tape casting (see Chapter 5). It was found that the mass specific capacitance of spray deposited electrodes was 13.9 F g⁻¹, a decrease of 8 % when compared to tape casted electrodes. In contrast, the areal resistance decreased when using spray deposition and some electrodes thus achieved astounding power densities of 49.3 kW kg⁻¹. The corresponding average energy density of these samples was 11.5 W h kg⁻¹, a drop of 7 % compared to tape casted electrodes; this drop is primarily associated with the decrease in mass specific capacitance.

Subsequently, multi-layer electrodes containing MWCNT content were fabricated by spray deposition. Four electrode compositions, containing 2, 5, 10 and 20 % MWCNT content alongside 5 % SBR/CMC binder with the remainder being Sigma PAC, were tested in mass symmetric configurations. Analysis by SEM revealed an improvement in MWCNT coating dispersion as MWCNT content was increased from 2 to 10 % but at 20 % samples were found to be smothered by MWCNTs. Analysis of the results was conducted and found to indicate trends in performance, such as a decrease in mass specific capacitance and an increase in power capability as MWCNT content increased.

An issue with these trends was identified. The coatings produced lacked consistent total mass; samples with 2, 5, 10 and 20 % MWCNT possessed average combined electrode masses of 8.96, 11.3, 13.5 and 8.36 mg cm⁻², respectively. It was noticed that trends in mass specific power appeared to also correlate with the areal density of samples tested. As such, a strong conclusion cannot be drawn but results may indicate improvements in power capability as MWCNT content is increased.

Ultimately, multi-layer electrodes with either a base- or top-coating of MWCNT content were fabricated by spray deposition. This was done to test the hypothesis that targeted (by layer) deposition of MWCNT content could improve electrode performance while minimising the utilisation of conductive additives (MWCNTs). The results of testing showed such a hypothesis to be tentatively true. The potential impact of this on future energy storage devices could be an increase in electrode thickness, thus minimising the use of current collector material and consequently improving gravimetric energy and power performance. Note the use of the general term energy storage devices; it is certainly possible that the effects found here could translate across both EC and battery type electrodes.
Prior to this, improvement must be made to the spray deposition technique implemented; electrode quality was deemed mediocre by SEM analysis, samples still exhibited the structural voids found in homogeneous electrodes (see Section 7.3.4). This could possibly be alleviated by using oven drying at lower temperatures (around 40 °C instead of the 80 °C used in this study). Additionally, it is believed that the use of electrostatic forces during spray deposition could improve coating homogeneity; a high quality description of this process, and its implementation in fabricating battery electrodes, can be found in [300].
8 GENERAL DISCUSSION

Three novel areas of research have been explored throughout this thesis; they included potential methods for improving cell lifespan, improving cell energy density and improving cell power density. As such, a general discussion is required to critically examine the findings of this research; this will be done within the context of current work in this field and thus assess if the improvements above have been achieved.

Before this, a review of the experimental techniques used throughout the research entailed in this thesis will be conducted. The focus of this to identify, through hindsight, where such experimental techniques might be improved.

8.1 Experimental Techniques and Characterisation – A Review

Nitrogen sorption measurement and analysis (see Section 3.4.1) was considered a success. Use of a Belsorp Max (kindly provided by Giuliano Laudone at the University of Plymouth), was essential for evaluating microporous (> 2 nm) AC (activated carbon) materials; such an instrument can produce accurate isotherms between $P/P_0$ values of $1 \times 10^8$ and 0.997. For mesoporous (2 – 50 nm) material analysis was Belsorp Mini II was used, this instrument proved capable in this role. The use of GCMC (grand canonical monte carlo) isotherm analysis provided a theoretically sound basis for material properties such as SSA (specific surface area), SPV (specific porous volume) and PSD (pore size distribution). Regardless, it is important that these derivations are purely interpretations of an isotherm, the only ‘real’ aspect of sorption analysis. The author believes advances in this technique (particularly relating to PSDs) could be made if conclusion were drawn from analysis using multiple sorption gases (krypton or low surface area, carbon dioxide for ultramicropores (> 1 nm); it may be possible to correlate isothermal phenomena of different gases in a similar approach to that used in GCMC analysis.

Scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analysis (see Section 3.4.2) were found to be effective methods for assessing materials and electrode compositions. They proved particularly useful in identifying defects, and their cause, within electrodes fabricated by spray deposition (see Section 7.3.4). With regards to SEM, the author believed improvements could be made, particularly in the post-processing of an image. It would
be useful to have the capability of identifying the major-axis lengths of particles across an electrode surface (possibly using machine intelligence related techniques). Additionally, it would also be desirable for single MWCNTs to be identifiable when in agglomerated bundles (possibly through image deconvolution techniques). Advances in the above could aid the derivation of quantitative data from what is mostly a qualitative technique.

Electrode fabrication by tape casting was found to be an adequate method for active material deposition. It can produce coatings with a reasonable consistency, particularly at thicknesses between 100 to 250 μm. While there is some degree of variability between samples of this thickness, this variability could be accounted for in electrochemical experimentation by appropriately selecting compatible electrodes to fabricate EC cells with. Coatings with thicknesses approaching 310 μm appear to possess defects in the form of vents; as such, electrodes which were thought to exhibit this defect were not included in experimentation. The author believes this technique is sufficiently mature.

Electrode fabrication by spray deposition (see Section 7.3) proved challenging, it was found that coatings were less than ideal. From the author’s perspective, the drying method (hot plate) was not appropriate. It is quite probably that a different drying mechanism, i.e. oven drying, would have produced different results and possibly produced coatings with the same quality as those achieved by tape casting. Regardless, the electrodes produced proved sufficient for drawing tentative conclusions about potential applications of electrode spray deposition. Additionally, the use of an airbrush should be deeply considered prior to future work; while accessible, the device appears to be tailored for spraying paint rather than particulate suspensions.

Coin cell fabrication (see Section 4.5.3) has been considered a partial success; samples with same electrode compositions were found to give highly agreeable capacitance and energy related values but deviated significantly in terms of resistance and power capability. As the electrodes were often from the same coating it is believed the issues of variable resistance, and thus power capability, are intrinsic to either the containment method or connection method (with a multi-stat instrument). Specifically, it was found essential to add two spacers rather than the single typically recommended, but it was not possible to identify the exact electrode stack pressure. Additionally, a manual CR2032 crimping machine was used, this introduced an element of variability. Ideally, an automatic crimping machine should be used to minimise cell variation.

One highly beneficial technique was the incorporation of a silver quasi-reference electrode within coin cell devices (see Section 4.5.3). Such technique provided informative insight into
the operating potential of each electrode, even while the system was being tested as a two-electrode device. It is believed that the approach used was simple and effective, but the author believes advanced methods (such as coating the silver tip in relatable electrode materials) may provide information for rapid cell optimisation.

Electrochemical analysis should be considered as a three-stepped approach: data gathering, data analysis and data presentation. The gathering aspect was facilitated by an 8 channel Solartron 1480 potentiostat/galvanostat and a Solartron 1255B frequency response analyser; the author believes that operating with 8 channels is essential for rapidly assessing a broad range of samples. Such a device also enabled concurrent cell and QRE operation using individual channels (one for driving the electrochemical process and one for sensing changes in potential between electrodes and the QRE device); such an approach may be more cumbersome on a single channel device. Interestingly, one unforeseen consequence of the above benefit was significantly larger data sets for experimental setups. As such, the author strongly recommends that a semi-automated approach (excel is sufficient) is taken when deriving cell KPIs (key performance indicators).

8.2 Impact of Electrode Capacitance Ratio on Asymmetric ACC/PAC EDLC Electrochemical Capacitors using Organic Electrolytes

It was identified from a literature survey that capacitance balancing of EC electrodes is required to optimally utilise the available ESPW (electrochemical stable potential window) of an EDLC type EC device. The state-of-the-art method for achieving balance was to alter the mass of each electrode while keeping the material the same; in turn, this alters the extrinsic capacitance of each electrode and consequentially altered the extrinsic change in voltage experienced upon adding/removing an explicit amount of charge (see Section 2.4.3). This was found to be true in electrodes using AC materials and soaked in the industry standard electrolyte TEA⁺BF₄⁻ in ACN (acetonitrile), an electrode mass ratio of 1:0.54 (positive:negative) was found to be optimal [168].

A novel approach to this was hypothesised; proper capacitance balancing could also be achieved using material asymmetry i.e. by using different materials for each electrode. It was believed by that selecting two suitable materials with a specific capacitance ratio between them, capacitance balancing could also be achieved. In this case, the mass of each electrode could thus be held constant. On its own, such a possibility may not seem advantageous.
It was through advanced consideration of an additional phenomenon by which potential benefits of having a material asymmetric EC device were found. Research by Chmiola et. al. indicated that as the pore size of an electrode material approaches the size of an un-solvated ion, mass specific capacitance of the electrode/electrolyte system would increase [160] (see Section 2.4.2). This was also found to be true in electrodes using AC materials and soaked in the industry standard electrolyte TEA‘BF₄ in ACN [160]. From this, it was plausible to state that a capacitance optimal EDLC cell using AC type materials necessitates distinct PSDs at each electrode (due to corresponding ions also having distinct sizes (see Section 2.2.3).

From this a distinct advantage of the hypothesised approach was found; cells can be fabricated from materials with PSDs suitable for optimising capacitance, while facile (mass symmetric) capacitance balancing enables maximal use of an electrodes ESPW. The result of this would be an improvement in energy density (due to its dependency on capacitance), maximisation of cell cycle life at high voltage, and improvements in power capability due to said high voltage.

As such, a group of experiments were conducted to test this hypothesis, these are detailed throughout Chapter 5. Initial experiments assessed the basic performance of two potential materials, Sigma PAC (powdered activated carbon) and Kynol ACC (activated carbon cloth), with the former achieving a mass specific capacitance of 60 F g⁻¹ and the latter achieving 116 F g⁻¹. The use of Kynol ACC as a positive electrode and Sigma PAC as a negative electrode, in a mass symmetric system, translates into an electrode capacitance ratio of 1:0.52. Such a value is very close to that of the optimal mass ratio (1:0.54) found by Cericola et. al. in [168]. An assumption was made at this point, mass ratio can be directly translated to capacitance ratio; per further work shown in [168] this appears to be valid.

Sigma PAC and Kynol ACC were also assessed by nitrogen sorption and GCMC (grand canonical monte carlo) analysis; their PSDs were found to be non-conducive towards the beneficial configuration (optimal capacitance) described previously. The reasoning for this is similarity in their structures, it was found that both have bimodal PSDs with peaks at ~0.7 nm and ~1.35 nm with the only major difference being in terms of magnitude (i.e. quantity of pores). Interestingly, the microporous SSA (specific surface are) of each material was found to have a ratio of 1:0.52 (Kynol ACC : Sigma PAC), a value identical to the capacitance ratio. This finding is significant as is further bolsters the suggestion that a materials SSA and mass specific capacitance are directly related (see Section 2.4.2).
Chapter 8: General Discussion

A further part of the experimental group detailed in Chapter 5 was the validation of the previous work found in [168] i.e. capacitance balancing can be achieved by altering the mass ratio between material symmetric AC based electrodes (see Section 5.4). This validation was a success, samples containing Sigma PAC at electrode mass ratios of ‘1:0.5:4’ survived significantly longer under potentiostatic (constant voltage) ageing compared to samples of ‘1:1’ and ‘1:2’.

Ultimately, the hypothesis at hand was tested. This was done in two parts; the first part (see Section 5.5) involved directly assessing the hypothesis by producing cells in which positive and negative electrodes were based on Kynol ACC and Sigma PAC, respectively; this configuration was achieved with a mass ratio approaching ‘1:1’. It was found that such a configuration did exhibit the same longevity as the mass balanced samples fabricated in Section 5.4 i.e. the hypothesis is false. This was believed to be due to differences in the microporous surface textures, heteroatom content of the AC materials and possible moisture contamination. Specifically, it was identified that the micro-texture of activated carbon plays a significant role in its chemical stability at high voltages. On the one hand, it is believed Kynol ACC possesses a higher content of ‘sharp’ nanotexture (edges/tips/points) which in turn increase its susceptibility to chemical reaction; on the other hand, Sigma PAC is believed to possess a smoother surface texture (possibly indicated by its lower SSA or mesoporous content) and is thus less susceptible to chemical reaction.

A second set of experiments was thus conducted in which a wide variety of mass ratios (with the same asymmetric material configuration) were investigated. The aim of this was to produce something akin to Figure 1 in [168] in which the optimal mass ratio for maximising cell longevity and usable ESPO was identified. To aid analysis, a novel silver based QRE (quasi-reference electrode) was developed and incorporated into some sample devices, a review of this QRE device has been conducted previously (see Section 8.1). While such a device aided sample pre-ageing analysis, the results of potentiostatic ageing were inconclusive i.e. an optimal mass ratio was not clearly identified. This was almost certainly due to moisture contamination of the organic electrolyte.

8.3 Investigation of using a Silicon Based Negative Electrode in Lithium Ion Capacitors

To significantly improve energy density in EC devices it was identified that an alternative cell configuration, compared to standard EDLC type configurations, is required. A comprehensive overview of potential EC cell configurations was found in [85] (see Section 2.3);
it was found that alternative cell configurations typically possess at least one electrode at which redox (reduction/oxidation) reactions occur. From these potential configurations one was singled out as a matter of interest: a hybrid EDLC-Intercalation capacitor. Such a capacitor possesses one EDLC type electrode (at which no redox reactions occur) and one intercalation type electrode (at which ion intercalation occurs).

While many possible devices of this nature exist [86, 90], it was the lithium ion capacitor (LIC) which, in the authors eyes, presents a viable ‘high energy’ alternative to standard EDLC type EC devices. The viability of such a device, both in terms of research and utility, was supported by the fact that commercial examples already exist [32]. Such devices are solely based upon cell configurations in which the positive and negative electrode materials are AC and GC (graphitic carbon), respectively; this configuration was deemed state-of-the-art. This configuration is combined with a lithium containing electrolyte (such as Li+PF6 in EC/DEC); lithium is intercalated within the GC electrode while PF6 is electrostatically adsorbed on the AC electrode. The use of such configuration is prominently mentioned in the seminal paper by Khomenko et. al. titled “High-energy density graphite/AC capacitor in organic electrolyte”, published in 2007 [91]. In this work, it was identified by experiment that LIC devices may offer up to 104 W h kg⁻¹ (of total electrode mass); this compares favourably with traditional EDLC type EC devices (in organic electrolyte) which are known to have an upper limit of 28.5 W h kg⁻¹ (of total electrode mass, see Section 2.4.1). Additionally, the power capability of LIC devices was shown to be over 10 kW kg⁻¹ (of total electrode mass), the same order of magnitude as comparable EDLC type devices (which achieved 32 kW kg⁻¹). One item of note with such devices is the requirement for pre-lithiation of the negative electrode; this is required in order to overcome initial cell resistance at low (>20 %) SoC (state-of-charge).

Two important concepts were taken from [91]. First was the concept that matching the charge capacity of each electrode (such that they are fully utilised) does not necessarily present the optimal configuration. Instead, it is suggested that the intercalative negative electrode should be underutilised; it was found that as the mass ratio was decreased (i.e. less GC was utilised) the power capability increased at the cost of energy storage. This was attributed to the lower GC utilisation, which is known to have less power capability than AC due to slow Li⁺ diffusion throughout its lattice structure [36]. The second was the concept that pre-lithiation can be readily achieved using formation cycling, in essence, the cell is repeatedly charge to a high voltage i.e. a high lithiation state, followed by long periods of self-discharge. In principle, this
should shift the potential of GC to lower potentials i.e. a lithiated state, and in practice appears successful.

At this point a novel approach to these devices was identified. GC is not the only material in which lithium intercalation can occur, silicon (Si) is also a viable alternative [173, 175]; from literature, it was found that little work had been conducted in making LIC devices with silicon based negative electrodes. An initial study was conducted by the author into the potential of such material (see Section 2.5), it was found that a silicon based negative electrode may be underutilised in a similar manner to the GC underutilisation used in [91]. In theory, it was shown that an underutilised silicon electrode may enable an LIC device to possess energy density comparable to one with fully utilised electrodes, something which a GC based LIC could not [91].

As such, a novel silicon based negative electrode material was sourced from a high-performance silicon electrode manufacturer. This electrode material was designated NXA-513 and came pre-coated on battery grade copper foil. In-depth analysis of this material was conducted using SEM, EDX and N₂ sorption analysis techniques; it was found to possess a mixture of materials with silicon and MWCNTs additives being predominant, the binder was identified as PVDF and thought to account for 10% the total electrode mass. The mass specific surface area and porous volume were found to be comparable to GC.

A group of experiments were thus conducted to compare this novel silicon based negative electrode to current state-of-the-art GC electrodes. GC electrodes were fabricated by tape casting and combined with Sigma PAC electrodes to form LIC devices (see Section 6.3), the GC electrode was theoretically estimated to be 50% utilised. When combined with 1 M Li+PF₆ in EC/DEC 50/50 (V/V), the maximum energy density was found to be 50.33 Wh kg⁻¹ (per two electrode mass) when operating between 3 and 4.5 V; this is comparable to the results of Khomenko et al. [91]. Power capability of these devices was found to be 3 kW kg⁻¹, lower than that found in [91]; this was attributed to possible issues in electrode slurry preparation (see Section 4.4.2). An issue with the results of this experiment was the limited number of samples; three were intended but two did not function, leaving only one sample for device characterisation. As such, future silicon based LIC devices were compared with both this work and the experimental results of [91].

Further experiments involved the fabrication of LIC devices using silicon (NXA-513) based negative electrodes. Sigma PAC and Kynol ACC were used as the positive electrode materials;
in the case of Kynol ACC only one mass could be selected (due to its cloth like nature) but for Sigma PAC a multitude of masses were used. Unfortunately, the maximum charge capacity of these positive electrode materials (exhibited by Kynol ACC) was only enough to achieve a theoretical Si utilisation of 4.7 %, far below that of LICs with GC based negative electrodes. Regardless, from the initial study in Section 2.5 it was theoretically identified that a high-energy density (112 W h kg⁻¹) should still be achievable. One unassessed benefit of this would have been negligible volumetric expansion of the Si based electrode, a potential issue previously identified in [173].

Initial tests in this investigation did not involve formation cycling. The highest performing device utilised Kynol ACC as the positive electrode, it achieved an energy density of 97 W h kg⁻¹ during charge from 0 to 4.1 V and 68 W h kg⁻¹ during discharge from 4.6 to 0 V; the charge–discharge processes were conducted at a theoretical C-rate of 2. It was found that cells operated under this charge-discharge regime exhibited poor power capability (3.5 kW kg⁻¹), this was associated with the method of calculation (from the voltage drop during CCCD testing) and the fact that adverse chemical reactions at high voltage can influence its calculation. It was identified that chemical reactions certainly occur above 4.3 V and possible above 4.1 V.

A preliminary type of formation cycling was used in further experiments and the maximum voltage was limited to 4.3 V; the result of this was a significant improvement in power capability with sample containing Kynol ACC achieving 23.4 kW kg⁻¹, this was combined with improvements in charge and energy storage efficiency. Unfortunately, the use of formation cycling appears to also reduce the mass specific energy density to 46 W h kg⁻¹ during charge up to 4.1 V and 51 W h kg⁻¹ during discharge from 4.3 to 0 V. Upon detailed analysis, it was noted that charge efficiency was sub-optimal, indicating that cells were operating outside their stable voltage window. This was later confirmed when subsequent testing found cells had degraded significantly compared to fresh samples.

An advanced type of formation cycling was subsequently developed and the final samples of each device type were tested. It was found that the baseline operating voltage (i.e. the voltage at which charge storage starts to significantly occur) was increased, charge retention during open circuit (self-discharge) conditions was also improved across all samples.

Silver QRE devices were incorporated into the final samples of each device type. It was found that the positive AC based electrode is the primary source of voltage loss during self-discharge. This loss could be minimised by using materials with high intrinsic capacitance (and
thus high charge capacity) as the positive electrode, such as Kynol ACC. Subsequent analysis using the QRE device showed that the charge phase of the silicon based negative electrode occurs at a constant voltage, during discharge its voltage is dependent upon the SoC of the electrode. This phenomenon was associated with the silicon content of NXA-513.

A comparison between silicon and graphite based electrodes has been presented, this included the results of this work and that presented in [91]. It was shown that while the energy density of cells created in this study did not approach those presented in [91], there was a significant improvement in power capability (up from 10 to 17 kW kg\(^{-1}\)). A more accurate comparison can be made if comparisons are confined to the results of cells fabricated in this work only; it was found that the silicon based NXA-513 can achieve comparable energy density comparable with graphite whilst providing an improvement of almost 1000 % in power density.

### 8.4 Study of Multilayer Spray Deposition for Composite Carbon Electrodes

Numerous techniques and methods for fabricating electrode coatings were identified and reviewed in Section 2.6.3. Of these, only tape casting and spray deposition were deemed suitable for large scale electrode fabrication (e.g. during commercialisation). Each approach has its own merits: tape casting is a simple process suitable for accurately producing electrodes of a specific thickness, typically between 25 µm to 1 mm. Spray deposition does not involve direct contact with the substrate and electrode coatings can be applied to irregular surfaces, it can also be used to produce coatings with multiple layers. It is this last aspect which caught the authors interest, such an advantage cannot readily be achieved by tape casting.

While reviewing electrode materials (see Section 2.4.1), it was found that MWCNTs (multi-walled carbon nanotubes) may produce a capacitance up to 80 F g\(^{-1}\) when used with TEA‘BF\(_4\) solvated in ACN [10]. It was also found that MWCNTs are highly conductive along their length [70, 127, 128] which has been found to make them ideal additives for improving electrode conductivity for AC–CNT composites [129, 130, 131]. As such, the author noticed that MWCNTs can provide the optimal conductive additive for EC electrodes. Specifically, a traditional conductive additive material in EC electrodes is carbon black, such a material does present a capacitive response due to its low surface area; thus, MWCNTs can offer the benefit of improved power capability while minimising the ‘lost capacitance’ due to adding non-capacitive additives.
As such, the author proposed that the benefits of MWCNT additives may be combined with spray deposition in a novel fashion: the introduction of highly conductive MWCNT materials at specific locations in a layered coating i.e. the base layer or the top layer, may bring benefits to an electrodes power performance whilst minimising MWCNT usage. The minimisation of MWCNT usage is beneficial from both a cost and health perspective; long term exposure to CNTs in general has been proven undesirable [142].

A group of experiments were thus devised to test the above hypothesis. Firstly, it was necessary to confirm the spray deposition technique can indeed produce electrodes comparable to those made by tape casting (see Section 7.4). This was achieved using the same material composition as used in Section 5.3 i.e. 95 % Sigma PAC and 5 % SBR/CMC. The performance was found to be similar on average but with slight differences; mass specific capacitance was 8% lower but mass specific power was 4 % higher in spray deposited electrodes.

At this point, an initial assessment of the spray deposition technique was conducted. Under SEM analysis it was found that the surface texture is not uniform with localised voids appearing; these voids were later associated by EDX analysis with bubbling of the slurry dispersion medium (water). The cause of this was certainly the drying method utilised i.e. a hot plate, future implementations of this method should strive to use oven drying methods. Regardless, determination of the electrochemical performance of such coatings was desirable as they proved a useful performance benchmark.

Having shown that spray deposition is a viable electrode fabrication technique, it was necessary to assess how the inclusion of MWCNTs within the electrode composition would affect performance (see Section 7.5). The composition was thus varied by adding 2, 5 ,10 and 20 % MWCNT (by weight) and keeping 5 % SBR/CMC constant, the remaining content was Sigma PAC. It was found that dispersion varied with MWCNT content, at 10 % MWCNT content there appeared to be an even dispersion under qualitative SEM analysis. Electrochemical properties were more indicative than conclusive as to the effect of MWCNT addition; it was found that all MWCNT containing samples were more powerful (due to lower resistance) than those without, but it was also noted that a trend could be made between electrode mass, which was not constant between samples, and device power capability.

Since previous results indicated that additional MWCNT content within an electrode may be beneficial for power performance, it was deemed appropriate to test the authors hypothesis. To do this, it was elected to add a coating of electrode material containing 20 % MWCNT, 75
% Sigma PAC and 5 % SBR/CMC as either the top or base coating; at the opposing side of this coating were three layers containing no MWCNT content. A layer containing 5 % MWCNT coated was also included to provide a transition layer between those with MWCNT content and those without. A clear representation of this can be found in Section 7.6.

It was found the addition of a top-coating of MWCNTs reduced areal resistance by approximately 15 % despite this type of electrode being 11 % more massive, and 7 % thicker, than the alternative base-coated electrodes. Such an improvement in power performance did not negatively impact mass specific capacitance which remained roughly equal in both types of electrode. A consequence of the decreased areal resistance was increased power capability energy density with samples reaching up to 40 W h kg⁻¹, and increased energy storage efficiency at high current densities.

Ultimately, it appears an MWCNT top-coating provides the most benefit, presumably due to the identified MWCNT dispersion throughout the lower layers (as found during SEM analysis). This was clearly demonstrated in the form of a Ragone plot. The potential impact of this on future energy storage devices could be an increase in electrode thickness, thus minimising the use of current collector material and consequently improving gravimetric energy and power performance. Note the use of the general term energy storage devices; it is certainly possible that the effects found here could translate across both EC and battery type electrodes.

Prior to this, improvement must be made to the spray deposition technique implemented; electrode quality was deemed mediocre by SEM analysis, samples still exhibited the structural voids found in homogeneous electrodes (see Section 7.3.4). This could possibly be alleviated by using oven drying at lower temperatures (around 40 °C instead of the 80 °C used in this study). Additionally, it is believed that the use of electrostatic forces during spray deposition could improve coating homogeneity; a high-quality description of this process, and its implementation in fabricating battery electrodes, can be found in [300].
9 CONCLUSIONS AND FUTURE WORK

9.1 Conclusions

The research entailed in this thesis has focused on advancing EC (electrochemical capacitor) technology. These advances were aimed towards filling the performance gap between batteries (high energy, low power) and traditional ECs (low energy, high power). Such a gap can be clearly seen in Figure 9.1 while novel chemistries can be seen filling said gap. At present, most EC applications relate to providing rapid bursts of energy to perform emergency tasks [14] or providing short power boosts to augment other power provision systems [15]. Instead, improved ECs could possibly provide adequate device runtime alongside a shorter recharge time, possibly refining the operation dynamics of many systems; the potential benefits of improvements in EC technology must not be underestimated.

![Gravimetric energy and power capabilities of electrochemical and capacitor devices. Dashed lines indicate RC time constant; red and green areas indicate batteries. From ref [6].](image)

Figure 9.1 Gravimetric energy and power capabilities of electrochemical and capacitor devices. Dashed lines indicate RC time constant; red and green areas indicate batteries. From ref [6].
Chapter 9: Conclusions and future work

It was noticed from the onset that three metrics define the applicability of ECs and EcESDs (electrochemical energy storage devices) in general. These are: cycle life i.e. the number of cycles until significant performance loss, energy density i.e. the quantity of energy they can store in a certain weight (or volume) and power density i.e. the power they can provide in a certain weight (or volume). As such, three key aims (KAs) were identified for this work:

1. Improve the cycle life performance of EC devices.
2. Improve the mass specific energy density of EC devices.
3. Improve the mass specific power density of EC devices.

The author believes that routes toward meeting these aims have been identified and experimentally verified throughout this thesis. Balancing electrode capacitance and capacity can optimise a cell for extended cycle life and higher operating voltages, significantly increasing the maximum stable energy storage capability. The simplest route to balancement is altering the mass of materials at each electrode. Attempts to achieve balancement by selectively matching materials, and keeping the mass equal, did not produce the desired capacitance balancing effect. This is believed to be due to the differing microporous surface texture of different AC materials. From this, and broader considerations of the literature, the author believes a complex relationship between electrode and electrolyte system influences the maximum stable voltage of such system. It is quite possible that significant improvements in EC device performance can be achieved by appropriately balancing the capacitance/capacity of their electrodes. This is believed by the author to be appropriately true for all types of EC devices.

A novel LIC (lithium ion capacitor) type EC device has been developed; it forgoes the traditional GC (graphitic carbon) based negative electrode and instead uses a novel silicon based negative electrode. It was found that such an electrode, which also contained MWCNTs (multi-walled carbon nanotubes), can significantly improve the mass specific power density of LIC type EC devices (by 570 % compared to similar GC based devices). It must be stated that this did also come at a 20 % loss of mass specific energy density compared to GC based devices. Such a compromise may be considered appropriate as the maximum energy density should still exceed traditional EDLC type EC devices. The author believes some variety LIC device will play a significant role in future energy storage systems, primarily due to its high operating voltage (estimated between 3 and 4 V) and consequential high energy density.

Spray deposition of electrode coatings (by airbrush) has been investigated albeit with inconsistent quality. The source of these inconsistencies was found to be associated with
rewetting of previously deposited layers and the use of a hotplate for drying. The novelty of this work was the targeted deposition of conductive additives (MWCNTs); base or top coatings of MWCNTs were added to electrodes to assess if they could provide additional performance whilst minimising their usage. It was tentatively found that providing a top coating of MWCNTs can improve electrode power capability, thus enabling thicker electrodes to be produced than plain activated carbon (AC) electrodes. The author believes such an approach could be used to increase electrode thickness and reduce the quantity of current collector required in a device, thus improving gravimetric and volumetric performance.

A silver quasi-reference electrode (QRE) has been incorporated into coin cells with great success. The addition of this QRE allowed for accurate determination of the change in voltage experienced by both positive and negative electrodes during operation. The author believes that the full potential of such a device has yet to be realised, it may be possible to effectively optimise and design future cell configurations based upon only two or even one sample type.

Overall, the results of the work included in this thesis provide indication as to viable techniques, materials and processes for advancing EC type energy storage devices. It is appreciated that this work has been detailed in great depth. The author believes the depth provided should enable others to fully appreciate the extent of thought required when designing and fabricating advanced EC devices, it is not a trivial task.

9.2 Future Work

The author envisions that extensive future work is still required to produce not only a market leading energy storage device, but one which could transform societies interaction with energy storage devices. Techniques and procedures around capacitance and capacity balancing must be improved and conveyed; the author found no conclusive and decisive guide towards achieving an appropriately balanced device. Such techniques and procedures are invaluable for ensuring the maximum desired capability of an electrochemical configuration (of which there are many) can be achieved. An example of such techniques or procedures could be in depth description of QRE devices or general knowledge such as acceptable sample transfer times between dry environments.

The use of sodium ion associated technology should be promoted and pursued [301, 302], it offers a next generation alternative to lithium ion technology. It should be noted that the energy density of devices associated with sodium technology is typically lower than that of
lithium technology; sodium is the fith most abundant element in the earth's crust while lithium is not even in the top 100 [303]. Such technology could be used to produce sodium ion capacitors (SICs), an alternative to the LICs investigated in this work.

Spray deposition of electrode materials could be an invaluable manufacturing technique. It can allow for the fabrication of base electrode materials and the targeted deposition of conductive additives. Future work in this area could pursue the alteration of electrode materials between consecutive deposition layers, appropriate binder selection could prohibit the removal of previous layers (due to possible insolubility of the current layer solvent). Further, the dispersion of additives directly into a primary sprayed medium should be pursued. This could take the approach of having a secondary spray (containing the desired additives) being focused onto the primary spray, to achieve uniformity the secondary spray could be either all encompassing of the primary or rotated around the primary.

Further afield to this, the study of electrolytes should be vigorously pursued as a potential route to achieving a significant advancement in energy storage technology. One recent (2017) advance in this area may provide a direction for future research; a glass like electrolyte has been fabricated by Goodenough et al. [304] (a co-inventor of the original lithium ion battery). It is believed this technology may enable low temperature operation of lithium ion batteries while providing a significant improvement in energy and power capability.
10 References


Chapter 9: Conclusions and future work


Chapter 9: Conclusions and future work


Capacitive Energy Storage: Filling the gap


Chapter 9: Conclusions and future work


Chapter 9: Conclusions and future work


Capacitive Energy Storage:
Filling the gap


Chapter 9: Conclusions and future work


Capacitive Energy Storage: Filling the gap


340 Richard Fields - February 2018
Chapter 9: Conclusions and future work


Capacitive Energy Storage: 
Filling the gap


Chapter 9: Conclusions and future work


Chapter 9: Conclusions and future work


Appendices

Appendix 1 – Derivation of Energy Stored in Capacitor.

The voltage $V$ (V) between two points is a measure of work done $dW$ (J) when a unit of charge $dq$ (C) flows from one point to the other. As such:

$$dW = Vdq$$

Capacitance $C$ (F) is described as the ratio between charge transferred $q$ (C) and subsequent voltage between electrodes. As such:

$$V = \frac{q}{C}$$

Thus:

$$dW = \frac{q}{C}dq$$

The total work done $W$ (J) can be found by integrating the above equation with respect to the total charge $Q$ (C) transferred:

$$W(q) = \int_0^Q \frac{q}{C}dq = \left[ \frac{1}{2} \frac{q^2}{C} \right]_0^Q = \frac{1}{2} \frac{Q^2}{C}$$

By rearranging and reintroducing capacitance, the total work done can be described as:

$$W = \frac{1}{2} \frac{Q^2}{C} = \frac{1}{2} CV^2$$

The total work done in charging a capacitor is equal to the total energy $E$ (J) stored by it. Thus:

$$E = \frac{1}{2} CV^2$$
Appendix 2 – Review of pseudocapacitive materials.

Polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh), poly [3-methylthiophene] (PMTH) and poly [3,4-ethylenedioxythiophene] (PEDOT) are electronically conducting polymers (ECPs). They exhibit a pseudocapacitive response, based upon the underpotential deposition mechanism [297]; in which ions from the electrolyte transfer onto the polymer backbone during charge. Used on their own, ECPs often experience excessive swelling, breakage and shrinkage which causes degradation of power capability. As such, it has been deemed necessary to integrate CNTs into ECP electrodes for improving SSA values and mechanical stability [21].

Impressive material symmetric two-electrode capacitance values have been achieved with MWCNT/PPy and MWCNT/PANI achieving 190 F g⁻¹ and 360 F g⁻¹, respectively. The primary issue with purely ECP ECs is their extremely low ESPWs which cannot exceed 0.6 to 0.8 V, this may be overcome through implementation in a hybrid cell but will still be intrinsically limited to low (> 2 V) voltages. Coupled with the high cost of production it is considered they will find only limited practical application [21].

Ruthenium dioxide (RuO₂) is a classic transition metal oxide (TMO) EC material which uses an aqueous electrolyte; in its purest form it exhibits a capacitance of 720 F g⁻¹ and good electronic conductivity of 10⁴ S cm⁻¹. However, it is a rare material with high cost and toxicity, make this material rather undesirable for use in large-scale applications. Manganese dioxide (MnO₂), which also uses an aqueous electrolyte; has also been tested but has shown a rather mediocre gravimetric capacitance of 200 to 250 F g⁻¹ when used in thick films under three-electrode testing; coupled with its low electronic conductivity of 10⁷ to 10³ S cm⁻¹ this material also seems rather undesirable [79]. The charge storage mechanism in both of these cases is intrinsic redox pseudocapacitance.

Another approach in the use of TMOs is to incorporate a non-aqueous electrolyte, commonly ones which possess lithium or sodium ions. Due to their non-aqueous nature they can sustain ESPWs of up to 4 V, a substantial improvement on the aqueous variety. One popular material is vanadium pentoxide (V₂O₅) which, in a high SSA amorphous or nanocrystalline form; presents pseudocapacitance, as such; it is considered extrinsically pseudocapacitive by nature [79]. While it has been found to exhibit a high gravimetric capacitance of up to 1300 F g⁻¹ under three-electrode testing, it is also a poor conductor of electricity which significantly hinders power capability, it has been suggested that this may be overcome through the
incorporation of conductive additives [298, 79]. Other examples of non-aqueous TMO EC materials are titanium dioxide (TiO₂) and niobium pentoxide (Nb₂O₅) which exhibit ESPWs less than 3 V [299, 89].

An interesting tactic in the production of pseudocapacitive electrodes has been the doping of AC with oxygen or nitrogen heteroatoms. This produces a form of hybrid electrode which utilises both EDLC and pseudocapacitive charge storage mechanisms. Heteroatom functionalities may be introduced either through the activation of a heteroatom rich carbon or through post activation treatment in a heteroatom rich atmosphere. Nitrogen appears to be the most common functionality with only few examples of oxygen functionalisation [21]. Significant gravimetric capacitance values were produced from nitrogen functionalised TCs and graphene which achieved 340 F g⁻¹ and 280 F g⁻¹, respectively [300, 301]. While not all examples of heteroatom enriched ECs were used with aqueous electrolytes, the beneficial pseudocapacitive properties were not exhibited when used with non-aqueous electrolytes [21].
Appendix 3 – Gravimetric coulomb capacity for a carbon electrode using the intercalative (lithium) charge storage mechanism.

Free lithium ions can be intercalated inside a carbon negative electrode, forming the lithiation state LiC₆. This means that 6 carbon atoms have the potential to store 1 lithium ion.

A mole of carbon contains $6.022 \times 10^{23}$ atoms (Avogadro’s number). As the ratio of carbon atoms to lithium atoms is 6:1, one mole of carbon can store $1.003 \times 10^{23}$ lithium ions.

The excess charge possessed by one lithium ion is equal to the elementary charge $1.60 \times 10^{-19}$ coulomb (C). One coulomb is equal to $6.24 \times 10^{18}$ elementary charges. Thus, one coulomb is equal to the total excess charge of $6.24 \times 10^{18}$ lithium ions.

As such, the total excess charge which can be stored by one mole of carbon is:

$$\frac{1.003 \times 10^{23}}{6.24 \times 10^{18}} = 16,070 \text{ C mol}^{-1}$$

The quantity of charge transferred by a current of 1 amp (A) over 1 hour (h) is equal to 3600 C. As such:

$$3.6 \text{ C} = 1 \text{ mAh}$$

Thus:

$$\frac{16,071 \text{ C mol}^{-1}}{3.6} = 4,464 \text{ mAh mol}^{-1}$$

The atomic mass of carbon is 12.01 g mol⁻¹. As such, the gravimetric coulomb capacity is:

$$\frac{4,464 \text{ mAh mol}^{-1}}{12.01 \text{ g mol}^{-1}} = 371.7 \text{ mAh g}^{-1}$$

Appendix 4 – Gravimetric energy density for an LIC based on an activated carbon positive electrode and graphitic carbon negative electrode

Primary assumptions for this calculation are:

- Activated carbon (AC⁺) presents mass specific capacitance of 100 F g⁻¹.
Graphitic carbon (GC) presents gravimetric coulomb capacity of 372 mAh g\(^{-1}\).
The coulometric capacity of both electrodes is equal and 100% utilised.
Graphitic carbon experiences intercalation at a constant 2.95 V.
The full cell voltage is charged from 3 V to 4.3 V, i.e. the AC positive electrode is charged from 0 to 1.3 V.

The mass specific energy \( E \) (Wh kg\(^{-1}\)) stored by both electrodes must now be calculated. First, the mass specific energy \( E \) (J kg\(^{-1}\)) stored by the AC\(^{+}\) electrode, with \( C \) taken as the mass specific capacitance (100 F g\(^{-1}\) or \( \times 10^5 \) F kg\(^{-1}\)), charged from 0 to 1.3 V can be calculated by:

\[
E \text{ J kg}^{-1} = \frac{1}{2} \cdot C \cdot V^2 = \frac{1}{2} \times 10^5 \times 1.3^2 = 85,000 \text{ J kg}^{-1}
\]

Thus, the mass specific energy \( E \) (J kg\(^{-1}\)) of the AC\(^{+}\) electrode can be converted to mass specific energy \( E \) (Wh kg\(^{-1}\)) as per:

\[
\frac{85,000 \text{ J kg}^{-1}}{3,600} = 23.6 \text{ Wh kg}^{-1}
\]

A simpler approach can be taken for the GC\(^{-}\) electrode as lithiation occurs at constant 2.95 V. The mass specific energy \( E \) (Wh kg\(^{-1}\)) stored by the GC\(^{-}\) electrode, taking gravimetric coulomb capacity \( Q \) to be 372 Ah kg\(^{-1}\), charged at 3V can be calculated by:

\[
E \text{ Wh kg}^{-1} = Q \cdot V = 372 \times 2.95 = 1,097 \text{ Wh kg}^{-1}
\]

Now, the mass ratio of the AC\(^{+}\) to GC\(^{-}\) (at equal coulometric capacity) must be calculated. The gravimetric coulomb capacity of an AC\(^{+}\) electrode (of 100 F g\(^{-1}\)) charged from 0 to 1.3 V will be:

\[
\frac{100 \text{ F g}^{-1} \times 1.3 \text{ V}}{3.6} = 36.1 \text{ mAh g}^{-1}
\]

Thus, in order to achieve an equal coulometric capacity of both electrodes, the mass of the AC\(^{+}\) must be 10.3 times greater than GC\(^{-}\) as per:

\[
\frac{372 \text{ mAh g}^{-1}}{36.1 \text{ mAh g}^{-1}} = 10.3
\]
At this point, it can be seen that if a hypothetical LIC were to be created which used 1 kg GC\(^{-}\) as its negative electrode, it would also necessitate 10.3 kg AC\(^{+}\) as its positive electrode. Thus, the energy stored by the GC\(^{-}\) negative electrode would be 1,097 Wh and the energy stored by the AC\(^{+}\) positive electrode would be 243 Wh.

As such, the total mass of both electrodes would be 11.3 kg while the total energy stored by both electrodes would be 1,340 Wh. Thus, the gravimetric energy density of an LIC using the configuration and assumptions described above can be calculated as:

\[
\frac{1,340 \text{ Wh}}{11.3 \text{ kg}} = 118.6 \text{ Wh kg}^{-1}
\]
Appendix 5 – Gravimetric coulomb capacity for a silicon electrode using the intercalative (lithium) charge storage mechanism.

Free lithium ions can be intercalated inside a silicon electrode, forming the lithiation state Li₂S₃. This means that 5 silicon atoms have the potential to store 22 lithium ions.

A mole of silicon contains $6.022 \times 10^{23}$ atoms, as per Avogadro’s number. As the ratio of silicon atoms to lithium atoms is 5:22, one mole of silicon can store $2.65 \times 10^{24}$ lithium ions.

The excess charge possessed by one lithium ion is equal to the elementary charge $1.60 \times 10^{-19}$ coulomb (C). One coulomb is equal to $6.24 \times 10^{18}$ elementary charges. Thus, one coulomb is equal to the total excess charge of $6.24 \times 10^{18}$ lithium ions.

As such, the total excess charge which can be stored by one mole of silicon is:

$$\frac{2.65 \times 10^{24}}{6.24 \times 10^{18}} = 424,500 \text{ C mol}^{-1}$$

The quantity of charge transferred by a current of 1 amp (A) over 1 hour (h) is equal to 3600 C. As such:

$$3.6 \text{ C} = 1 \text{ mAh}$$

Thus:

$$\frac{424,500 \text{ C mol}^{-1}}{3.6} = 118,000 \text{ mAh mol}^{-1}$$

The atomic mass of carbon is 28.09 g mol⁻¹. As such, the gravimetric coulomb capacity is:

$$\frac{118,000 \text{ mAh mol}^{-1}}{28.09 \text{ g mol}^{-1}} = 4,200 \text{ mAh g}^{-1}$$
Chapter 0: Appendices

Appendix 6 – Gravimetric energy density for an LIC based on an activated carbon positive electrode and silicon negative electrode

Primary assumptions for this calculation are:

- Activated carbon (AC⁺) presents mass specific capacitance of 100 F g⁻¹.
- Silicon (Si) presents gravimetric coulomb capacity of 4,200 mAh g⁻¹.
- The coulometric capacity of both electrodes is equal and 100% utilised.
- Silicon experiences intercalation at a constant 2.6 V.
- The full cell voltage is charged from 2.6 V to 3.9 V, i.e. the AC positive electrode is charged from 0 to 1.3 V.

The mass specific energy \( E \) (Wh kg⁻¹) stored by both electrodes must now be calculated. First, the mass specific energy \( E \) (J kg⁻¹) stored by the AC⁺ electrode, with \( C \) taken as the mass specific capacitance (100 F g⁻¹ or \( 10^5 \) F kg⁻¹), charged from 0 to 1.3 V can be calculated by:

\[
E \text{ J kg}^{-1} = \frac{1}{2} CV^2 = \frac{1}{2} \times 10^5 \times 1.3^2 = 85,000 \text{ J kg}^{-1}
\]

Thus, the mass specific energy \( E \) (J kg⁻¹) of the AC⁺ electrode can be converted to mass specific energy \( E \) (Wh kg⁻¹) as per:

\[
\frac{85,000 \text{ J kg}^{-1}}{3,600} = 23.6 \text{ Wh kg}^{-1}
\]

A simpler approach can be taken for the Si electrode as lithiation occurs at constant 2.6 V. The mass specific energy \( E \) (Wh kg⁻¹) stored by the Si electrode, taking gravimetric coulomb capacity \( Q \) to be 4,200 Ah kg⁻¹, charged at 2.6 V can be calculated by:

\[
E \text{ Wh kg}^{-1} = QV = 4,200 \times 2.6 = 10,920 \text{ Wh kg}^{-1}
\]

Now, the mass ratio of the AC⁺ to Si (at equal coulometric capacity) must be calculated. The gravimetric coulomb capacity of an AC⁺ electrode (of 100 F g⁻¹) charged from 0 to 1.3 V will be:

\[
\frac{100 \text{ F g}^{-1} \times 1.3 \text{ V}}{3.6} = 36.1 \text{ mAh g}^{-1}
\]
Thus, in order to achieve an equal coulometric capacity of both electrodes, the mass of the AC⁺ must be 116 times greater than Si as per:

\[
\frac{4,200 \text{ mAh g}^{-1}}{36.1 \text{ mAh g}^{-1}} = 116
\]

At this point, it can be seen that if a hypothetical LIC were to be created which used 1 kg Si as its negative electrode, it would also necessitate 116 kg AC⁺ as its positive electrode. Thus, the energy stored by the Si negative electrode would be 10,920 Wh and the energy stored by the AC⁺ positive electrode would be 2,740 Wh.

As such, the total mass of both electrodes would be 117 kg while the total energy stored by both electrodes would be 13,660 Wh. Thus, the gravimetric energy density of an LIC using the configuration and assumptions described above can be calculated as:

\[
\frac{13,660 \text{ Wh}}{117 \text{ kg}} = 117 \text{ Wh kg}^{-1}
\]

Appendix 7 – Gravimetric energy density for an LIC based on an activated carbon positive electrode and an underutilised negative electrode.

The method presented in this appendix is based around the methods exemplified in appendices 4 and 6. This method introduces a negative electrode utilisation factor \( \eta \) this is taken as the utilisation of the negative electrode theoretical gravimetric coulomb capacity. In both prior examples \( \eta = 1 \) (100% utilisation) and as such this method was not necessitated. Essentially, \( \eta \) should be applied to the gravimetric coulomb capacity such that:

\[
\text{Underutilised gravimetric coulomb capacity} = \eta Q
\]

Where \( \eta < 1 \) and \( Q \) is the theoretical maximum of gravimetric coulomb capacity. An example of this is to say that a graphitic carbon (GC) negative electrode experiencing 50% utilisation (\( \eta = 0.5 \)) has a gravimetric coulomb capacity of 186 Ah kg⁻¹.

Using this approach, it is possible to vary the extent of utilisation and find the effect on gravimetric energy density. Let us continue using the example for an LIC based on a GC⁻ negative electrode, all assumptions are the same as those in appendix 4 except the GC⁻ electrode experiences 50% utilisation.
Mass specific energy \( E \) (Wh kg\(^{-1}\)) stored by the GC electrode:

\[
E \text{ Wh kg}^{-1} = \eta Q V = 0.5 \times 372 \times 2.95 = 548 \text{ Wh kg}^{-1}
\]

In order to achieve an equal coulometric capacity of both electrodes, the mass of the activated carbon (AC\(^+\)) (100 F g\(^{-1}\)) positive electrode must be 5.2 times greater than GC\(^-\) as per:

\[
\frac{0.5 \times 372 \text{ mAh g}^{-1}}{36.1 \text{ mAh g}^{-1}} = 5.2
\]

As such, a hypothetical LIC which used 1 kg GC\(^-\) (50% utilised) as its negative electrode, would also necessitate 5.2 kg AC\(^+\) as its positive electrode. Thus, the total energy stored by the GC\(^-\) negative electrode would be 548 Wh and the energy stored by the AC\(^+\) positive electrode would be 123 Wh.

Thus, the total mass of both electrodes would be 6.2 kg while the total energy stored by both electrodes would be 671 Wh. As such, the gravimetric energy density of an LIC, using an underutilised (\( \eta = 0.5 \) or 50%) GC\(^-\) electrode while retaining the general configuration and assumptions stated in appendix 6, can be calculated as:

\[
\frac{671 \text{ Wh}}{6.2 \text{ kg}} = 109 \text{ Wh kg}^{-1}
\]

Inputting a broad range of \( \eta \) values allows for an assessment of how the gravimetric energy density would vary at those \( \eta \) values. This will now be applied to LIC devices based upon GC\(^-\) and silicon (Si) based negative electrodes.
For an LIC based on AC⁺ (100 F g⁻¹ & 36.1 mAh g⁻¹) and GC⁻ (372 mAh g⁻¹)

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For an LIC based on AC⁺ (100 F g⁻¹ & 36.1 mAh g⁻¹) and Si⁻ (4,200 mAh g⁻¹)

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Appendix 8 – Inference of specific surface area (SSA) from a pore size distribution (PSD) with the underlying assumption of slit shaped pores.

While isotherm analysis using GCMC methods in BELMaster (version 2.3.1) readily produces PSD data, it does not provide SSA and SPV data. It was found in [243] that it is possible to calculate this manually (from PSD data) if a simple pore geometry (slit or cylinder) has been assumed during isotherm analysis. The following analysis approach is specific to the slit-pore assumption; an example of such a geometry has been provided below where $W$ is the pore width, $T$ is the pore thickness and $L$ is the pore length. Note: a slit in this case consists of two parallel surfaces which are not in contact around its periphery edges.

\[
SSA = \sum_{i=1}^{n} 2 \frac{V_i}{W_i}
\]

Essentially, PSD data is often presented as the relationship between pore width (nm) versus the mass specific internal porous volume (cm$^3$ g$^{-1}$) associated with said pore width. Due to the slit-like assumption, the mass specific volume associated with a pore width can be thought of as a cuboidal volume i.e. one defined by width, thickness and length. As the mass specific volume is known, it is thus possible calculate the frontal area ($T \times L$) of the slit surface by dividing the volume by pore width e.g. a pore with a width of 2 nm and a porous volume of 0.01 cm$^3$ g$^{-1}$ will have a frontal area of 5 m$^2$ g$^{-1}$. With the knowledge that the slit geometry consists of two planar surfaces it is possible to state that the pore in the above example will have mass specific surface area of 10 m$^2$ g$^{-1}$.

The process above can be conducted at each discrete pore width data point captured by isotherm analysis; summation of mass specific surface areas associated with all pore widths can thus define the total mass specific surface area for the entire porous structure. Such a process can be described mathematically as:

Where $n$ is the number of pore width data points, $V_i$ is the porous volume of a single data point and $W_i$ is the pore width associated with a single data point.
Appendix 9 – SEM Images of Activated Carbon Materials

Kynol 507-15 Activated Carbon Cloth
Sigma C9157 Powdered Activated Carbon
Appendix 10 – EDX Analysis of NXA-513

Normalised Wt. %

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</table>
Corresponding Spectra for POI 1

Corresponding Spectra for POI 2

Corresponding Spectra for POI 3
Corresponding Spectra for POI 4

Corresponding Spectra for POI 5

Corresponding Spectra for POI 6
Appendix 11 – Variance in reference point for a silver quasi-reference electrode (QRE) incorporated into a coin cell device.

It was found that when a QRE is implemented in coin cells the electrode potential relative to that QRE was not the same in all cells e.g. if the total cell voltage was 0 V the potential of the positive and negative electrodes relative to a QRE could differ by up to 0.5 V between cells. An example of this variance is presented below.

Appendix 12 – Calculating the quantity of lithium atoms in 1 g 1M LiPF₆ EC/DEC 50/50 electrolyte.

It was deemed necessary to calculate the number of lithium ions available in the electrolyte and compare this to the quantity of carbon atoms available in the GC electrode. The process towards the calculation was to break the electrolyte down into its atomic content and then calculate the mass percent of each atomic component, this can be achieved because the atomic weight of each atomic component is known.

As such, it is possible to state that Li accounts for 4.57 % the mass of the salt LiPF₆. Using the molar mass of the individual electrolyte components it is possible to state that the mass contribution of each component in the electrolyte 1M LiPF₆ EC/DEC 50/50 will be 151.9 g LiPF₆, 660 g EC (density 1.32 g cm⁻³) and 487 g DEC (density 0.975 g cm⁻³) which can be interpreted as 1298.9 g per one litre of electrolyte. As the mass of LiPF₆ relative to the total mass of one litre 1M LiPF₆ EC/DEC 50/50 has been calculated, it is possible to state infer that lithium accounts for 0.534 % of the total electrolyte weight.
Chapter 0: Appendices

Elemental breakdown of 1M LiPF₆ EC/DEC 50/50 electrolyte.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Element</th>
<th>Atomic weight</th>
<th>No. Atoms</th>
<th>Mass percent</th>
<th>Molar Mass</th>
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</thead>
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<td>Li</td>
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<td>151.9 g/mol</td>
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<td>30.97</td>
<td>1</td>
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<td></td>
<td>F</td>
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<td>75.04%</td>
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<td>40.92%</td>
<td>88.06 g/mol</td>
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<td>O</td>
<td>16.00</td>
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</table>

With knowledge that the atomic weight of Li is 6.941 it is possible to calculate the molarity of Li in 1 g 1M LiPF₆ EC/DEC 50/50 electrolyte as 0.534 % of 6.941, i.e. there is 0.000769 mol of Li in 1 g electrolyte. Multiplying this by Avogadro’s number (6.02 x 10²³ mol⁻¹) gives the quantity of lithium ions in 1 g electrolyte to be 4.63 x 10²⁰.

Appendix 13 – Constant current charge-discharge (CCCD) of sample A of a lithium ion capacitor (LIC) with a graphite based negative electrode.

Sample A of an LIC with a graphite based negative electrode presented poor performance throughout all testing; the plot below exemplifies the large voltage drop exhibited by this sample upon discharge. Such a drop is strongly associated with high electronic resistance.
Capacitive Energy Storage:
Filling the gap

CCCD testing at 0.1 A g⁻¹ (3rd cycle) of a single LIC type EC device using Sigma PAC as the positive electrode and graphitic carbon as the negative electrode combined with a LiPF₆ EC/DEC 50/50 (v/v).

Appendix 14 – Constant current charge-discharge (CCCD) plots of silicon based LIC devices (3rd sample only) with increasing current density

Test current and associated current density relative to the total mass of Silicon and NXA-513 present at the negative electrode.

<table>
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<th>Test Current</th>
<th>Current Density Silicon Only</th>
<th>Current Density NXA-513</th>
</tr>
</thead>
<tbody>
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<td>mA</td>
<td>mA g⁻¹</td>
<td>mA g⁻¹</td>
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<tr>
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</table>
Sample B – Si based LIC

200 mA g\(^{-1}\)  

550 mA g\(^{-1}\)  

1,100 mA g\(^{-1}\)  

2,150 mA g\(^{-1}\)  

5,500 mA g\(^{-1}\)  

Combined
Sample C – Si based LIC

200 mA g\(^{-1}\)  

550 mA g\(^{-1}\)  

1,100 mA g\(^{-1}\)  

2,150 mA g\(^{-1}\)  

5,500 mA g\(^{-1}\)  

Combined
Sample D – Si based LIC

200 mA g\(^{-1}\)  

550 mA g\(^{-1}\)  

1,100 mA g\(^{-1}\)  

2,150 mA g\(^{-1}\)  

5,500 mA g\(^{-1}\)  

Combined
Sample E-Si based LIC

200 mA g\(^{-1}\)

550 mA g\(^{-1}\)

1,100 mA g\(^{-1}\)

2,150 mA g\(^{-1}\)

5,500 mA g\(^{-1}\)

Combined
Appendix 15 – Plastic stencil used for spray deposition

A plastic stencil with a square pattern area of 5 by 5 cm was prepared for producing consistent spray patterns. Note, the inner edges were chamfered to improve coating quality near the edges.
Appendix 16 – Planar SEM images of spray deposited electrodes.

Planar images of spray deposited electrodes. Note: the circular white spots are associated with moisture vents during drying. Structures significantly protruding from the surface would be visible either due a lack of focus or through shadowing of other areas.
Appendix 17 – EDX analysis of defects present in spray deposited electrodes

Electrode Site A

![Image of EDX analysis]

Normalised Wt. %

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<th>POI</th>
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<th>O-K</th>
<th>Al-K</th>
<th>Si-K</th>
<th>S-K</th>
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Atom %

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Corresponding Spectra for POI 1

Corresponding Spectra for POI 2

Corresponding Spectra for POI 3
Chapter 0: Appendices

Corresponding Spectra for POI 4

Electrode Site B

Normalised Wt. %

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Capacitive Energy Storage: Filling the gap

Atom %

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Corresponding Spectra for POI 1
Chapter 0: Appendices

Corresponding Spectra for POI 2

Corresponding Spectra for POI 3

Corresponding Spectra for POI 4
Corresponding Spectra for POI 5

Corresponding Spectra for POI 6

Corresponding Spectra for POI 7
Chapter 0: Appendices

Corresponding Spectra for POI 8

![Graph of Corresponding Spectra for POI 8](image)

Corresponding Spectra for POI 9

![Graph of Corresponding Spectra for POI 9](image)
Appendix 18 – Analysis of spray deposited samples using IEC 62576 standards

0 % MWCNT – Sample A

0 % MWCNT – Sample B

0 % MWCNT – Sample C

0 % MWCNT – Sample D

0 % MWCNT – Sample E
Chapter 0: Appendices

2 % MWCNT – Sample A

\[ y = 1.069x + 0.0013 \]

2 % MWCNT – Sample B

\[ y = 0.9256x + 0.0078 \]

2 % MWCNT – Sample C

\[ y = 2.924x + 0.004 \]

2 % MWCNT – Sample D

\[ y = 1.0978x + 0.0054 \]

5 % MWCNT – Sample A

\[ y = 0.9999x + 0.006 \]

5 % MWCNT – Sample B

\[ y = 1.2342x + 0.0063 \]
Chapter 0: Appendices

20% MWCNT – Sample A

\[ y = 0.8853x + 0.0088 \]

20% MWCNT – Sample B

\[ y = 1.3429x + 0.0008 \]

20% MWCNT – Sample C

\[ y = 6.4954x + 0.0007 \]

\( R^2 = 0.9997 \)

20% MWCNT – Sample D

Richard Fields - February 2018 383
LIST OF TABLES

Table 2.1 Comparison of typical classical capacitor, battery and EC characteristics.............................. 35
Table 4.1 Normalised weight % of constituent elements found through EDX analysis of NXA-513; POIs as indicated in Figure 4.5......................................................................................................................... 103
Table 4.2 Specific surface area (SSA) values acquired from nitrogen adsorption isotherm analysis by BET, BJH and GCMC methods. Values are presented as either total SSA values or pore related SSA values. ........................................................................................................................................................................... 107
Table 4.3 Specific pore volume (SPV) values acquired from nitrogen adsorption isotherm analysis by BET, BJH and GCMC methods. Values are presented as either total SPV values or pore related SPV values. Porous particle density (PPD) is interpreted taking the particle density of graphite to be 2.2 g cm\(^{-3}\). ........................................................................................................................................................................................................................................... 108
Table 4.4 Normalised weight % of constituent elements found through EDX analysis of Toyol Carbo®; POIs as indicated in Figure 4.13. ......................................................................................................................................................................................................................................................... 113
Table 5.1 Cell configurations for material and mass symmetric samples containing Sigma PAC. Note that areal density and mass values refer to the active material alone......................................................................................................................... 138
Table 5.2 Cell configurations for material and mass symmetric samples containing Kynol ACC. Note that areal density and mass values refer to the active material alone.............................................................................................................. 138
Table 5.3 KPIs for material and mass symmetric cells containing Sigma PAC...................................................... 145
Table 5.4 KPIs for material and mass symmetric cells containing Kynol ACC................................................... 147
Table 5.5 Cell configurations for material asymmetric but mass symmetric samples containing Sigma PAC; the target mass ratio is defined above sample name. Note that areal density and mass values refer to the active material alone. ......................................................................................................................................................................................................................................................... 151
Table 5.6 Theoretical mass specific capacitance for cells based on Sigma PAC at both electrodes and electrode mass ratios M(1:1), M(1:2) and M(1:0.54)......................................................................................................................... 152
Table 5.7 KPIs for material symmetric (Sigma PAC) cells with mass ratios of M(1:1), M(1:2) and M(1:0.54); target mass ratio is defined above sample name......................................................................................................................... 156
Table 5.8 Cell configurations for material asymmetric samples utilizing Sigma PAC as the negative electrode and Kynol ACC as the positive electrode, descriptive mass ratio is defined above sample name. Note that areal density and mass values refer to the active material alone ......................................................................................................................................................................................................................................................... 164
Table 5.9 Theoretical mass specific capacitance for material asymmetric (‘ACC:PAC’) cells with mass ratios of M(1:0.93) and M(0.51)......................................................................................................................... 165
Table 5.10 KPIs for material asymmetric (‘ACC:PAC’) cells with mass ratios of M(1:0.93) and M(0.51), descriptive mass ratio is defined above sample name ......................................................................................................................................................................................................................................................... 168
Chapter 0: List of Tables

Table 5.11 Cell configurations for material and mass asymmetric samples utilizing Sigma PAC as the negative electrode and Kynol ACC as the positive electrode; descriptive mass ratio is defined above sample name. Note that areal density and mass values refer to the active material alone. ........................................ 176

Table 5.12 Theoretical mass specific capacitance and electrode specific capacitance and voltage values for material and mass asymmetric (‘ACC:PAC’) cells with a range of mass ratios. Note that electrode specific voltage values are calculated by assuming an EDLC cell is charged from 0 to 2.5 V. ........................................ 177

Table 5.13 KPIs for material and mass asymmetric (‘ACC:PAC’) cells with a range of mass ratios, descriptive mass ratio is defined above sample name. .................................................. 186

Table 6.1 Theoretical energy density of an LIC device which contains Sigma PAC as the positive electrode and graphitic carbon as the negative electrode. The negative electrode charge capacity utilization has been defined as 50%. The peak cell voltage has been taken as 4.5 V. .................................................. 211

Table 6.2 Theoretical energy density of an LIC device which contains Sigma PAC as the positive electrode and graphitic carbon as the negative electrode. The electrode mass ratio is pre-defined by the results presented in Table 6.1. The peak cell voltage has been taken as 4 V. .................................................. 212

Table 6.3 Cell configurations and sample identification for LIC devices using a graphite based negative electrode and a Sigma PAC based positive electrode. Note that areal density and mass values refer to the active material alone. ........................................................................ 213

Table 6.4 Charge transfer during CCCD testing at 0.1 A g⁻¹ (3rd cycle) at differing CCCD voltage windows. Input refers to the charging process while output refers to the discharging process. .......................................................... 217

Table 6.5 KPIs derived from CCCD testing at 0.1 A g⁻¹ (3rd cycle) at differing CCCD voltage windows. All values correspond to the discharge phase unless explicitly stated otherwise. .......................................................... 218

Table 6.6 Theoretical properties of an LIC device which contains Sigma PAC as the positive electrode and silicon based NXA-513 as the negative electrode. The peak cell voltage has been taken as 4.1 V. .... 224

Table 6.7 Theoretical properties of an LIC device which contains Kynol ACC as the positive electrode and silicon based NXA 513 as the negative electrode. The peak cell voltage has been taken as 4.1 V. ... 225

Table 6.8 Cell configurations and sample identification for LIC devices using a silicon based negative electrode (NXA-513) and either Sigma PAC or Kynol ACC based positive electrode. Note that areal density and mass values refer to the active material alone. In the case of NXA-513 the areal density and mass represents only the silicon content. ........................................................................ 227

Table 6.9 Theoretical maximum charge capacity and associated 1 C-rate current for LIC devices using a silicon based negative electrode (NXA-513) and either Sigma PAC or Kynol ACC based positive electrode. ........................................................................ 229

Table 6.10 KPIs derived from CCCD testing at 2 C-rate theoretical charge capacity (5th cycle) from 0 to 4.6 V of differing LIC type EC devices using either Sigma PAC or Kynol ACC as the positive electrode and silicon based NXA-513 as the negative electrode combined with a LiPF₆ EC/DEC 50/50 (v/v). All values correspond to the discharge phase unless explicitly stated otherwise. .......................................................... 231

Table 6.11 KPIs derived from CCCD testing at 0.5 C-rate theoretical charge capacity (5th cycle) from 0 to 4.3 V of silicon based LIC type EC devices with varying silicon utilization, post formation cycling. All values correspond to the discharge phase unless explicitly stated otherwise. .......................................................... 238

Richard Fields - February 2018

385
TABLE 6.12 Effects on charge storage efficiency by formation cycling, calculated from CV plots presented in Figure 6.13. Pre- , mid- and post- formation associate with 1st, 2nd and 3rd CV plots.

TABLE 6.13 Test current and associated current density relative to the total mass of Silicon and NXA-513 present at the negative electrode.

TABLE 6.14 KPIs derived from CCCD testing 200 mA g⁻¹ (relative to total Si content) (3rd cycle) from 1.5 to 4 V of differing LIC type EC devices with varying silicon utilization. All values correspond to the discharge phase unless explicitly stated otherwise.

TABLE 6.15 Comparison of Si and GC based LIC devices fabricated and tested during this investigation alongside a GC based LIC devices fabricated in literature [91].

TABLE 7.1 Material content of slurry compositions for spray deposition using Sigma PAC, an MWCNT additive (stated by mass percent (m%) on the left) and 5 m% SBR/CMC binder. Note, the DIW content is identified by its source during slurry fabrication.

TABLE 7.2 Electrode compositions fabricated by spray deposition. The composition is described in the format X/Y/Z where X is the Sigma PAC m% content, Y is the MWCNT m% content and Z is the SBR/CMC m% content.

TABLE 7.3 Normalised weight % of constituent elements found through EDX analysis of NXA-513; POIs as indicated in Figure 4.5. The active material consists of 95 m% Sigma PAC and 5 m% SBR/CMC binder while the current collector is Toyal Corbo®.

TABLE 7.4 Cell configurations of spray deposited electrodes containing 95 % Sigma PAC and 5 % CMC/SBR binder. Note that areal density and mass values refer to the active material alone.

TABLE 7.5 KPIs for EDLC cells containing electrodes fabricated by spray deposition, they contain 95 % Sigma PAC and 5 % SBR/CMC binder.

TABLE 7.6 Cell configurations of spray deposited electrodes containing 2 % MWCNT, 93 % Sigma PAC and 5 % CMC/SBR binder. Note that areal density and mass values refer to the active material alone.

TABLE 7.7 Cell configurations of spray deposited electrodes containing 5 % MWCNT, 90 % Sigma PAC and 5 % CMC/SBR binder. Note that areal density and mass values refer to the active material alone.

TABLE 7.8 Cell configurations of spray deposited electrodes containing 10 % MWCNT, 85 % Sigma PAC and 5 % CMC/SBR binder. Note that areal density and mass values refer to the active material alone.

TABLE 7.9 Cell configurations of spray deposited electrodes containing 20 % MWCNT, 75 % Sigma PAC and 5 % CMC/SBR binder. Note that areal density and mass values refer to the active material alone.

TABLE 7.10 KPIs for EDLC cells containing electrodes fabricated by spray deposition, they contain 2 % MWCNT’s, 93 % Sigma PAC and 5 % SBR/CMC binder.

TABLE 7.11 KPIs for EDLC cells containing electrodes fabricated by spray deposition, they contain 5 % MWCNT’s, 90 % Sigma PAC and 5 % SBR/CMC binder.
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<td>KPIs for EDLC cells containing electrodes fabricated by spray deposition, they contain 10% MWCNTs, 85% Sigma PAC and 5% SBR/CMC binder.</td>
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<td>Table 7.13</td>
<td>KPIs for EDLC cells containing electrodes fabricated by spray deposition, they contain 20% MWCNTs, 75% Sigma PAC and 5% SBR/CMC binder.</td>
</tr>
<tr>
<td>Table 7.14</td>
<td>Cell configurations of spray deposited electrodes containing a top-coating of MWCNTs. Note that areal density and mass values refer to the active material alone.</td>
</tr>
<tr>
<td>Table 7.15</td>
<td>Cell configurations of spray deposited electrodes containing a base-coating of MWCNTs. Note that areal density and mass values refer to the active material alone.</td>
</tr>
<tr>
<td>Table 7.17</td>
<td>KPIs for EDLC cells containing electrodes fabricated by spray deposition including a targeted MWCNT top-coating.</td>
</tr>
<tr>
<td>Table 7.18</td>
<td>KPIs for EDLC cells containing electrodes fabricated by spray deposition including a targeted MWCNT top-coating.</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

FIGURE 1.1 GRAVIMETRIC ENERGY AND POWER CAPABILITIES OF COMMERCIALLY AVAILABLE ELECTROCHEMICAL AND CAPACITOR DEVICES. DASHED LINES INDICATE RC TIME CONSTANT; RED AND GREEN AREAS INDICATE BATTERIES. FROM REF [6]................................................................................................. 2

FIGURE 2.1 ILLUSTRATION OF DIFFERENT ELECTRODE SETUPS WHERE (A) IS A THREE ELECTRODE SETUP AND (B) IS A TWO ELECTRODE SETUP. ......................................................................................................................... 11

FIGURE 2.2 SCHEMATIC REPRESENTING RELATIONSHIP BETWEEN CHARGE AND VOLTAGE FOR AN IDEAL BATTERY AND FOR A CAPACITOR UNDER CONSTANT CURRENT CHARGE/DISCHARGE. TOC: TOP OF CHARGE, EOD: END OF DISCHARGE. ADAPTED FROM REF [10]........................................................................................................... 14

FIGURE 2.3 SCHEMATIC OF CHARGE-DISCHARGE PROCESSES IN A TMO+/GRAPHITE LITHIUM ION BATTERY. DURING CHARGE AND DISCHARGE, LITHIUM IONS TRANSFER TO THE NEGATIVE AND POSITIVE ELECTRODES, RESPECTIVELY. 15

FIGURE 2.4 SCHEMATIC OF CHARGE-DISCHARGE PROCESSES IN A COMMON ELECTROSTATIC CAPACITOR. IN A CHARGED STATE THE PRESENCE OF AN ELECTROSTATIC FIELD, DENOTED BY FIELD LINES, IS WHAT LEADS TO STORED ELECTRICAL ENERGY. ................................................................................................................................. 17

FIGURE 2.5 SCHEMATIC OF ION SOLVATION SHELLS FORMED OF DIPOLE SOLVENTS. NOTE, SOME IONS HAVE ONLY ONE SOLVATION SHELL. ADAPTED FROM [54]........................................................................................................ 21

FIGURE 2.6 IONIC BALL-AND-STICK MODELS FOR (A) TEA+ AND (B) BF4− WITH THEIR CORRESPONDING ELECTROSTATIC POTENTIAL MAPS, (C) TEA+ AND (D) BF4−; AREAS SHARED RED AND BLUE REPRESENT LOWEST AND HIGHEST ELECTROSTATIC POTENTIAL ENERGY RESPECTIVELY. REPRODUCED WITH PERMISSION OF ANDREW DUNNE. 23

FIGURE 2.7 (A) HELMHOLTZ EDLC MODEL AND (B) STRUCTURE OF STERN EDLC MODEL FOR AN ELECTRIC DOUBLE-LAYER AT A POSITIVE ELECTRODE WHERE \( \Phi_0 \) IS ELECTRODE POTENTIAL. NOTE, THE TERM DOUBLE LAYER REFERS TO THE MODEL PRESENTED IN (A) AND NOT TO THE STERN AND DIFFUSE LAYERS PRESENTED IN (B). .................................................. 24

FIGURE 2.8 SCHEMATICS OF PSEUDOCAPACITIVE PHENOMENA; (A) UNDERPOTENTIAL DEPOSITION OF Pb ONTO Au; (B) REDOX PSEUDOCAPACITANCE OF HYDROGEN IONS INSERTING INTO RuO2; (C) INTERCALATION PSEUDOCAPACITANCE OF Li INTO Nb2O5. ADAPTED FROM [79] .................................................................................................................... 26

FIGURE 2.9 SCHEMATIC DRAWING OF (A) GRAPHITIC LAYERS AND (B) LITHIUM INTERCALATION BETWEEN GRAPHITIC LAYERS [84].......................................................................................................... 28

FIGURE 2.10 COMMON EC CONFIGURATIONS. (A) EDLC, (B) PSEUDOCAPACITOR, (C) HYBRID EDLC – PSEUDOCAPACITOR (D) HYBRID EDLC – INTERCALATION (E) HYBRID PSEUDOCAPACITOR – INTERCALATION. ADAPTED FROM [85], REPRODUCED WITH PERMISSION ............................................................................. 30

FIGURE 2.11 SCHEMATIC OF CHARGE-DISCHARGE PROCESSES IN AN EDLC BASED ON ACTIVATED CARBON. DURING CHARGE AND DISCHARGE, IONS ARE ELECTROSTATICALLY ADSORBED AND RELEASED, RESPECTIVELY. .......................................................... 31
Chapter 0: List of Figures

Figure 2.12 Schematic of charge-discharge processes in an extrinsic redox pseudocapacitor based on transition metal oxides. During charge and discharge, ions are electrochemically absorbed and released, respectively. ................................................................. 32

Figure 2.13 Schematic of charge-discharge processes in an carbon-carbon LIC hybrid device. During charge and discharge, negative ions are electrostatically adsorbed and released, respectively, while positive lithium ions are intercalated (absorbed) and released, respectively. ................................................................. 32

Figure 2.14 Gravimetric energy and power capabilities of commercially available electrochemical and capacitor devices including specific EC configurations. Dashed lines indicate RC time constant; red and green areas indicate batteries. Adapted from Ref [6]. ........................................................................................................... 35

Figure 2.15 (A) Schematic of microporous graphitic planes, present as a substantial component in AC, representing relative pore size and ion size. (B) Schematic of AC with a hierarchical pore structure. ........................................................................................................ 40

Figure 2.16 SEM images of (A) powdered activated carbon [114] reproduced under CC BY-NC 3.0 licence; (B) activated carbon monolith [115]; and (C) activated carbon fibres [116] reproduced under CC BY 3.0 licence. ........................................................................................................ 41

Figure 2.17 Example of SWCNT with an open-tip structure. By Begemotv2718, reproduced under CC BY 3.0 licence. ........................................................................................................ 43

Figure 2.18 (A) Experimental data of CDCs and template carbons in ACN electrolyte versus specific capacitance normalised by BET SSA. ●TEA-BF₄ 1.5 M [64], ■:TEA-BF₄ 1 M and 1.4 M [157] and ▲: TEAMS 1.7 M [163]. (B to D) Schematics of solvated ions residing in pores with distance d between adjacent pore walls (B) greater than 2 nm, (C) between 1 and 2 nm, and (D) less than 1 nm. Adapted from [64]. ........................................................................................................ ERROR! BOOKMARK NOT DEFINED.

Figure 2.19 Schematic of CCCD charge-discharge processes for one EDLC device with symmetric cell capacitance and one with asymmetric cell capacitance, up to a peak voltage of 2.7 V. Oxidative and reductive boundaries represent ESPW for TEA-BF₄ solvated in ACN [164]. ........................................................................................................ 48

Figure 2.20 Schematic of charge-discharge processes in an LIC from an initiation voltage (i.e. nonzero base voltage) of ~2.95 V up to a peak voltage of 4.3 V, as derived from [86]. Oxidative and reductive boundaries represent ESPWs found in common used organic electrolytes [34]. ........................................................................................................ 51

Figure 2.21 Theoretical gravimetric energy density (per total electrode mass) of LICs, based on both GC and Si, utilising different percentages of their negative electrodes theoretical maximum charge capacity. ........................................................................................................ 54

Figure 2.22 Schematic of spin-coating process. Taken from Ref [198] under CC-BY 3.0 licence. .......... 59

Figure 2.23 Schematic of dip-coating process. ........................................................................................................ 60

Figure 2.24 Schematic of tape casting process using a doctor blade. ........................................................................................................ 61

Figure 2.25 Schematic of (A) traditional coin cell structure (B) a coin cell structure which incorporates a reference electrode. ........................................................................................................ 64

Figure 2.26 (A) Schematic of internal structure for a pouch cell [218]; (B) image of external structure for a pouch cell [219] reproduced with permission from Cadex Electronics Inc. ........................................................................................................ 65

Figure 3.1 Image of coin cell components with labels above. ........................................................................................................ 78
Capacitive Energy Storage:
Filling the gap

Figure 3.2 IUPAC classifications of physisorption isotherms, arrows indicating increasing relative pressure indicate adsorption while arrows indicating decreasing relative pressure indicate desorption. Each is labelled above with commonly associated pore structures [236].

Figure 3.3 Nitrogen adsorption isotherms, with a logarithmic P/P₀ scale, comparing BELSORP Max and Mini instruments. Inset: full isotherm profiles with linear scale.

Figure 3.4 CCCD response of an EDLC showing voltage variation versus time. The key to variables is given in the text.

Figure 3.5 Schematic of resistance analysis method based upon multiple CCCD test currents, identified as points [249].

Figure 3.6 Example cyclic voltammetry plot for a two electrode EDLC device at a scan rate of 10 mV s⁻¹ between 0 and 2.5 V. Note that both current density and capacitance may also be represented specifically.

Figure 3.7 Example Nyquist plot for EDLC based EC. Each marker represents a unique frequency, decreasing left to right; and R_{esr} determination methods are marked in red. Adapted from [93].

Figure 3.8 Calculated impedance for various shapes of a single pore assuming a capacitive interface. From ref [260].

Figure 3.9 Cyclic voltammogram exemplifying current response issues. Note that the top and bottom current plateaus are not smooth.

Figure 4.1 SEM image of Kynol ACC at (a) x100 and (b) x20,000 magnification.

Figure 4.2 SEM image of Sigma PAC at (a) x200 and (b) x16,000 magnifications.

Figure 4.3 SEM image of TS Elgab MWCNT at nanometric scales.

Figure 4.4 SEM image of Silicon Electrode NXA-513 at (a) x500 magnification and (b) x20,000 magnification.

Figure 4.5 SEM image of Silicon Electrode NXA-513 under EDX examination; POIs are elementally quantified in Table 4.1.

Figure 4.6 SEM image of Alfa Aesar Graphite 325 Mesh at (a) x500 magnification and (b) x950 magnification.

Figure 4.7 Nitrogen adsorption (Ads) and desorption (Des) isotherms with a logarithmic P/P₀ scale. Inset: full isotherm profiles with linear scale. Isotherms were produced by a BELSORP Max.

Figure 4.8 Nitrogen adsorption (Ads) and desorption (Des) isotherms with linear scale. Isotherms were produced by a BELSORP Mini.

Figure 4.9 Microporous PSD of Kynol ACC 507-15 and Sigma PAC C9157 from nitrogen adsorption isotherm on a BELSORP Max with GCMC analysis and slit assumptions. (a) Bare BF⁺ ion diameter, (b) bare TEA⁺ ion diameter, (c) ACN solvated BF⁺ ion diameter, (d) ACN solvated TEA⁺ ion diameter. (Left) Differential pore volume, (right) Incremental pore volume.

Figure 4.10 Mesoporous PSD of Kynol ACC 507-15 and Sigma PAC C9157 from nitrogen adsorption isotherm on a BELSORP Max with GCMC analysis.
Chapter 0: List of Figures

**Figure 4.11** Mesoporous PSD of TS Elicarb MWCNT, NXA 513 and AA Graphite from nitrogen adsorption isotherm on a BELSORP Mini with GCMC analysis; the assumed porous structure is stated in the legend. .........................................................................................................................111

**Figure 4.12** Toyal Carbo® (A) cross-sectional SEM image at x1,500 magnification and (B) planar SEM image at x10,000 magnification. .................................................................................................................................112

**Figure 4.13** (A) Planar SEM image of Toyal Carbo® under EDX examination; POIs are elementally quantified in Table 4.4. (B) SEM image of possible Toyal Carbo® whisker tip at x80,000 magnification. .................................................................................................................................113

**Figure 4.14** Scatter plot comparing the doctor blade gap thickness and average coating thickness of electrodes fabricated by tape casting and dried at 80 °C. The active material consists of Sigma PAC (95 m%) and SBR/CMC binder (5 m%) while the current collector is Toyal Carbo®. .........................................................................................................................118

**Figure 4.15** Scatter plot (including linear fit) comparing the areal density and average coating thickness of electrodes fabricated by tape casting and dried at 80 °C. The active material consists of Sigma PAC (95 m%) and SBR/CMC binder (5 m%) while the current collector is Toyal Carbo®. .........................................................................................................................119

**Figure 4.16** SEM images of electrodes fabricated by tape casting and dried at 80 °C with thicknesses of (A) 150 mm, (B) 250 mm and (C) 310 mm. Image (D) is a close up of the area identified in (C), it is a composite image produced by overlaying two separate SEM images captured with differing brightness and contrast settings. The active material consists of Sigma PAC (95 m%) and SBR/CMC binder (5 m%) while the current collector is Toyal Carbo®. .........................................................................................................................120

**Figure 4.17** Coin cell layup schematics showing (A) a coin cell layup using a single spacer and (B) a coin cell layup using two spacers. ...........................................................................................................................................123

**Figure 4.18** Cyclic voltammograms of 5 mm with 0.1 M TEABF4 in ACN against an Ag QRE at a scan rate of 50 mV/s for five cycles. Arrows indicate oxidation potential. .........................................................................................................................125

**Figure 4.19** Image (A) shows a coin cell layup schematic showing a coin cell with an incorporated QRE. Image (B) shows a silver QRE device with Kapton® shielding, it has been bent to fit onto the lip of a partially complete coin cell. Image (C) shows the same device in-situ; note that the device rests upon the lip of a negative (-) cap containing a cone spring and spacer. .........................................................................................................................126

**Figure 5.1** The potentiostatic cell ageing process. Initial cell properties are deduced close to 0 hrs using 3 CCCC cycles and 3 CV cycles. The impacts of ageing are deduced by CCCD and CV after each 10 hour ageing period. .........................................................................................................................137

**Figure 5.2** Results of CCCD testing at 0.28 A g⁻¹ (3⁰ run) for material and mass symmetric cells containing (A) Sigma PAC and (B) Kynol ACC. ...........................................................................................................................................139

**Figure 5.3** Mass specific cell capacitance-voltage plots derived from CV testing at 5 mV s⁻¹ (3⁰ cycle) for material and mass symmetric cells containing (A) Sigma PAC and (B) Kynol ACC. .........................................................................................................................140

**Figure 5.4** Nyquist plot from EIS testing at 0 V for material and mass symmetric cells containing (A) Sigma PAC and (B) Kynol ACC. ...........................................................................................................................................142

**Figure 5.5** Bode mass specific cell capacitance (BMSC) plot from EIS testing at 0 V for material and mass symmetric cells containing (A) Sigma PAC and (B) Kynol ACC. .........................................................................................................................142

**Figure 5.6** Bode phase angle (BPA) plot from EIS testing at 0 V for material and mass symmetric cells containing (A) Sigma PAC and (B) Kynol ACC. ...........................................................................................................................................143
Capacitive Energy Storage:
Filling the gap

Figure 5.7 Material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54). Results of (A) CCCD testing at 0.28 A g⁻¹ (3rd cycle) and (B) mass specific capacitance-voltage plots derived from CV testing at 5 mV s⁻¹ (3rd cycle).

Figure 5.8 Material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54). Results of EIS analysis at 0 V presented as (A) a Nyquist plot and (B) a Bode mass specific capacitance (BMSC) plot. In (A) samples of m(1:0.54) are specifically identified.

Figure 5.9 Material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54). Results of EIS analysis at 0V presented as a Bode phase angle (BPA) plot.

Figure 5.10 CCCD performance at 0.28 A g⁻¹ (3rd run) relative to potentiostatic ageing at 2.7 V of material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54).

Figure 5.11 CV performance at 5 mV s⁻¹ (3rd cycle) after potentiostatic ageing at 2.7 V of material symmetric cells (Sigma PAC). Sample B represents m(1:1), sample C represents m(1:2) and sample E represents m(1:0.54).

Figure 5.12 Mass specific capacitance and areal resistance as a function of potentiostatic ageing at 2.7 V for material symmetric (Sigma PAC) cells with mass ratios of m(1:1), m(1:2) and m(1:0.54).

Figure 5.13 Charge storage efficiency and energy storage efficiency as a function of potentiostatic ageing at 2.7 V for material symmetric cells (Sigma PAC) with mass ratios of m(1:1), m(1:2) and m(1:0.54).

Figure 5.15 Material asymmetric (*ACC:PAC*) cells with mass ratios of m(1:0.93) and m(0.51). Results of (A) CCCD testing at 0.28 A g⁻¹ (3rd cycle) and (B) mass specific capacitance-voltage plots derived from CV testing at 5 mV s⁻¹ (3rd cycle).

Figure 5.16 Material asymmetric (*ACC:PAC*) cells with mass ratios of m(1:0.93) and m(0.51). Results of EIS analysis at 0V presented as (A) a Nyquist plot and (B) a Bode mass specific capacitance (BMSC) plot. In (A) samples specifically identified.

Figure 5.17 Material asymmetric (*ACC:PAC*) cells with mass ratios of m(1:0.93) and m(0.51). Results of EIS analysis at 0V presented as a Bode phase angle (BPA) plot.

Figure 5.18 CCCD performance at 0.28 A g⁻¹ (3rd run) relative to potentiostatic ageing at 2.7 V of material asymmetric (*ACC:PAC*) cells with mass ratios of m(1:0.93) and m(0.51).

Figure 5.19 CV performance at 5 mV s⁻¹ (3rd cycle) after potentiostatic ageing at 2.7 V of material asymmetric (*ACC:PAC*) cells. Sample A represents m(1:0.93) and sample C represents m(1:0.51)...170

Figure 5.20 Mass specific capacitance and areal resistance as a function of potentiostatic ageing at 2.7 V for material asymmetric (*ACC:PAC*) cells with mass ratios of m(1:0.93) and m(0.51)...170

Figure 5.21 Charge storage efficiency and energy storage efficiency as a function of potentiostatic ageing at 2.7 V for material asymmetric (*ACC:PAC*) cells with mass ratios of m(1:0.93) and m(0.51). ...171

Figure 5.22 Thermogravimetric analysis (TGA) of Kynol ACC and Sigma PAC samples between room temperatures of 0 and 600 °C under a flow of nitrogen at a rate of 10 °C per minute.

Figure 5.25 Results of CCCD analysis for material and mass asymmetric (*ACC:PAC*) cells with a range of mass ratios at 0.28 A g⁻¹ (3rd cycle), this includes the electrode specific voltage as determined by the incorporated silver QRE.
Chapter 0: List of Figures

Figure 5.26 Temporal stepwise mass specific capacitance for each electrode versus electrode voltage for material and mass asymmetric (*ACC:PAC) cells with a range of mass ratios. Derived from CCCD charge analysis of a cell incorporating a quasi-reference electrode (QRE) such as the relative voltage of each electrode could be determined. ......................................................... 181

Figure 5.27 Electrode voltage versus to cell mass ratio for material and mass asymmetric (*ACC:PAC) cells. X is mass of the negative electrode relative to the mass of the positive electrode. ......................... 182

Figure 5.28 Mass specific capacitance-voltage plots derived from CV testing at 5 mV s⁻¹ (3rd cycle) for material and mass asymmetric (*ACC:PAC) cells with a range of mass ratios. ........................... 183

Figure 5.29 Nyquist plot from EIS testing at 0 V for material and mass asymmetric (*ACC:PAC) cells with a range of mass ratios. ......................................................................................... 184

Figure 5.30 Bode mass specific capacitance (BMSC) plot from EIS testing at 0 V for material and mass asymmetric (*ACC:PAC) cells with a range of mass ratios. ........................................ 185

Figure 5.31 Bode phase angle (BPA) plot from EIS testing at 0 V for material and mass asymmetric (*ACC:PAC) cells with a range of mass ratios. ................................................................. 186

Figure 5.32 Mass specific capacitance relative to mass ratios for material and mass asymmetric (*ACC:PAC) cells. Theoretical values are presented in Table 5.12 and actual values are presented in Table 5.13. ................................................................................................................................. 187

Figure 5.33 CCCD performance at 0.28 A g⁻¹ (3rd run) relative to potentiostatic ageing at 2.7 V of material asymmetric (*ACC:PAC) cells with mass ratios of m(1:1), m(0.53) and m(0.48) ....................... 188

Figure 5.34 CV performance at 5 mV s⁻¹ (3rd cycle) after potentiostatic ageing at 2.7 V for material asymmetric (*ACC:PAC) cells with mass ratios of m(1:1), m(0.53) and m(0.48) ....................... 189

Figure 5.35 CV performance at 5 mV s⁻¹ (3rd cycle) after potentiostatic ageing at 2.7 V for material asymmetric (*ACC:PAC) cells with mass ratios of m(1:1), m(0.53) and m(0.48) ....................... 190

Figure 5.36 Part A (left) Mass specific capacitance and areal resistance as a function of potentiostatic ageing at 2.7 V and (right) charge storage efficiency and energy storage efficiency as a function of potentiostatic ageing at 2.7 V for material asymmetric (*ACC:PAC) cells with a range of mass ratios. .................................................................................................................. 191

Figure 5.40 Schematic representations of carbon/electrolyte interfaces (A) a protruding tip which is ideally one atomic layer thick (i.e. graphene), (B) a planar surface with extensive depth, (C) a pore extensively surrounded by carbon and wide enough for ions to enter .................................................. 197

Figure 6.1 Example of the formation cycling technique implemented for LIC research. In essence, the cell is repeatedly driven to high voltage followed by long periods of self-discharge. ................. 208

Figure 6.2 Relative power and energy density as a function of the mass ratio of the electrodes for LICs utilizing AC as positive electrode and graphite as negative electrode. Note, this graph associates only with the materials used in [91]. ........................................................................................................... 209

Figure 6.3 Analysis of formation cycling by CV testing at 5 mV s⁻¹ (3rd cycle) of samples GC LIC A-1 and GC LIC A-2. The 1st, 2nd and 3rd CV plots associate with those presented previously in Figure 6.1. .... 215

Figure 6.4 Results of CV testing at 5 mV s⁻¹ (3rd cycle) of a single LIC type EC device using Sigma PAC as the positive electrode and graphitic carbon as the negative electrode combined with a LiPF₆ EC/DEC
Capacitive Energy Storage:
Filling the gap

50/50 (v/v). The negative electrode charge capacity utilization has been previously calculated as 50%.

**Figure 6.5** Results of CV testing at 5 mV s⁻¹ (3rd cycle) and 100 mV s⁻¹ of a single LIC type EC device using Sigma PAC as the positive electrode and graphitic carbon as the negative electrode combined with a LiPF₆ EC/DEC 50/50 (v/v).

**Figure 6.6** CCCD testing at 0.1 A g⁻¹ (3rd cycle) of a single LIC type EC device using Sigma PAC as the positive electrode and graphitic carbon as the negative electrode combined with a LiPF₆ EC/DEC 50/50 (v/v). The negative electrode charge capacity utilization has been previously calculated as 50%.

**Figure 6.7** Ragone plot for a graphite based LIC with a mass ratio of m(7:44:1) where the positive electrode is Sigma PAC with a mass specific capacitance estimated to be 50 F g⁻¹ and the negative electrode is graphite carbon with a specific capacity of 380 Ah g⁻¹. Test current densities were 100 (right), 250, 500, 1000 and 2500 (left) mA g⁻¹ of graphite material.

**Figure 6.8** CCCD testing at 2 C-rate theoretical charge capacity (5th cycle) from 0 to 4.6 V of differing LIC type EC devices using either Sigma PAC or Kynol ACC as the positive electrode and silicon based NXA-513 as the negative electrode combined with a LiPF₆ EC/DEC 50/50 (v/v). The time taken for samples to complete a full cycle in minutes was (A) 157, (B) 65, (C) 46, (D) 69 and (E) 60.

**Figure 6.9** Three formation cycles performed on differing LIC type EC devices (Table 6.8) using the preliminary technique of charging at C/20 followed by three hours open circuit self-discharge.

**Figure 6.10** CCCD testing at 0.5 C-rate theoretical charge capacity (5th cycle) from 0 to 4.3 V of silicon based LIC type EC devices with varying silicon utilization, post formation cycling. This is compared against the preliminary 'fresh' results taken from sample 1 devices.

**Figure 6.11** CV analysis at 5 mV s⁻¹ (5th cycle) of type E LIC devices using Kynol ACC as the positive electrode and silicon based NXA-513 as the negative electrode combined with a LiPF₆ EC/DEC 50/50 (v/v). Individual samples have experienced differing degrees of electrochemical testing as stated in the legend.

**Figure 6.12** Formation cycling of differing Si based LIC type EC devices (Table 6.8) using an advanced method; the initial charge phase was conducted with a current density of 125 mA g⁻¹ (relative to total Si content). Only the last two cycles, those which operate up to 4 V, of this pre-lithiation process are displayed. These devices incorporated silver (Ag) QREs; the voltage of the positive and negative electrodes have been evaluated relative to this QRE. The concluding voltage at the end of formation cycling is displayed to the right of each plot.

**Figure 6.13** Analysis of formation cycling by CV testing at 5 mV s⁻¹ (5th cycle) of differing Si based LIC type EC devices (Table 6.8). The 1st, 2nd and 3rd CV plots associate with pre-, mid- and post- formation.

**Figure 6.14** Formation cycling of differing Si based LIC type EC devices (Table 6.8) using an advanced method. Only the last cycle of this pre-lithiation process, which operates up to 4 V, are displayed.

**Figure 6.15** CCCD testing at 200 mA g⁻¹ (relative to total Si content) (3rd cycle) from 1.5 to 4 V of differing LIC type EC devices with varying silicon utilization combined with a LiPF₆ EC/DEC 50/50 (v/v) electrolyte.
Chapter 0: List of Figures

Figure 6.16 CCCD testing at 200 mA g⁻¹ (relative to total Si content) (3rd cycle) from 1.5 to 4 V of the sample type E-3 which contains a Kynol ACC based positive electrode and an NXA-513 based negative electrode. This plot includes data captured through the use of a silver QRE device, as defined by the legend. This marker indicates the transition point between differing electrochemical discharge processes. .............................................................................................................. 246

Figure 6.17 Ragone plot for a silicon based LIC with a mass ratio of m(5:1) where the positive electrode is Kynol ACC with a mass specific capacitance estimated to be 97 F g⁻¹ and the negative electrode is NXA-513 with an estimated specific capacity of 4200 Ah g⁻¹. Test current densities were 200 (right), 500, 1000, 2000 and 5000 (left) mA g⁻¹ of silicon material. .................................................................................................................. 250

Figure 6.18 Comparison of CCCD testing at 4 mA (3rd cycle) of GC and Si based LIC devices. Note that GC based LIC devices contained a Sigma PAC negative electrode while the Si LIC device contained a Kynol ACC negative electrode. .................................................................................................................. 253

Figure 6.19 Comparative Ragone plot between the GC and Si based LIC devices fabricated in this study. Test current densities were 100 (right), 250, 500, 1000 and 2500 (left) mA g⁻¹ of graphite material and 200 (right), 500, 1000, 2000 and 5000 (left) mA g⁻¹ of silicon material. .................................................................................................................. 254

Figure 7.1 Scatter plot (including linear fit) relating the areal density to the average coating thickness of electrodes fabricated by spray deposition (three coating layers) and dried at 80 °C. The active material consists of Sigma PAC (95 m%) and SBR/CMC binder (5 m%) while the current collector is Toyal Carbo®. .................................................................................................................. 265

Figure 7.2 Cross-sectional SEM image showing an electrode fabricated by spray deposition (three coating layers) and dried at 80 °C. The active material consists of 95 m% Sigma PAC and 5 m% SBR/CMC binder while the current collector is Toyal Carbo®. (A) cavernous internal void and (B) tall non-planar structure. .................................................................................................................. 266

Figure 7.3 Planar SEM image showing an electrode fabricated by spray deposition (three coating layers) and dried at 80 °C. The active material consists of 95 m% Sigma PAC and 5 m% SBR/CMC binder while the current collector is Toyal Carbo®. .................................................................................................................. 267

Figure 7.4 SEM image of spray deposited electrode containing 95% Sigma PAC under EDX examination; POIs are elementally quantified in Table 7.3. The active material consists of 95 m% Sigma PAC and 5 m% SBR/CMC binder while the current collector is Toyal Carbo®. .................................................................................................................. 268

Figure 7.5 Results of CCCD testing at (A) 100 mA g⁻¹ (3rd run) and (B) 2,500 mA g⁻¹ (3rd run) for EDLC cells containing electrodes fabricated by spray deposition. .................................................................................................................. 272

Figure 7.6 Mass specific capacitance-voltage plots derived from CV testing at (A) 10 mV s⁻¹ (3rd cycle) and (B) 1,000 mV s⁻¹ (3rd cycle) for EDLC cells containing electrodes fabricated by spray deposition. .................................................................................................................. 272

Figure 7.7 Cells containing spray deposited electrodes based upon 95% Sigma AC and 5% SBR/CMC binder. (A) Mass specific capacitance with respect to current density during CCCD analysis. (B) Charge and energy efficiency with respect to current density during CCCD analysis. Indicated current densities are 0.1, 0.25, 0.5, 1, 2.5 and 5 A g⁻¹. .................................................................................................................. 276

Figure 7.8 Cells containing spray deposited electrodes based upon 95% Sigma AC and 5% SBR/CMC binder. (A) Mass specific energy density with respect to current density during CCCD analysis. (B)
Areal resistance and mass specific power with respect to current density during CCCD analysis.

Indicated current densities are 0.1, 0.25, 0.5, 1, 2.5 and 5 A g⁻¹.

**Figure 7.9** SEM images of an electrode fabricated by spray deposition containing 2% MWCNT, 93% Sigma PAC, and 5% SBR/CMC binder; (A) shows an area sparsely covered and (B) shows an area of agglomeration.

**Figure 7.10** SEM images of an electrode fabricated by spray deposition containing 5% MWCNT, 90% Sigma PAC, and 5% SBR/CMC binder; (A) shows MWCNTs bridging between particles and (B) shows particle covering by MWCNTs.

**Figure 7.11** SEM images of an electrode fabricated by spray deposition containing 10% MWCNT, 85% Sigma PAC, and 5% SBR/CMC binder; (A) shows multiple MWCNT interparticle bridges and (B) shows an extremely long bridge.

**Figure 7.12** SEM images of an electrode fabricated by spray deposition containing 20% MWCNT, 75% Sigma PAC, and 5% SBR/CMC binder. (A) shows MWCNTs bridging between particles and (B) shows particle smothering by MWCNTs.

**Figure 7.13** Results of CCCD testing at (left plots) 100 mA g⁻¹ (3rd run), (right plots) 2,500 mA g⁻¹ (5th run) for EDLC cells containing electrodes fabricated by spray deposition. All electrodes contain 5% SBR/CMC alongside (A) and (B) 2% MWCNT, (C) and (D) 5% MWCNT, (E) and (F) 10% MWCNT, (G) and (H) 20% MWCNT with the remaining electrode material content being Sigma PAC.

**Figure 7.14** Mass specific capacitance-voltage plots derived from CV testing at (left plots) 10 mV s⁻¹ (3rd run) and (right plots) 1,000 mV s⁻¹ (5th run) for EDLC cells containing electrodes fabricated by spray deposition. All electrodes contain 5% SBR/CMC alongside (A) and (B) 2% MWCNT, (C) and (D) 5% MWCNT, (E) and (F) 10% MWCNT, (G) and (H) 20% MWCNT with the remaining electrode material content being Sigma PAC.

**Figure 7.15** Mass specific capacitance of cells containing spray deposited electrodes with varying degrees of MWCNT content. (Left) 100 mA g⁻¹ (3rd run), (right) 2,500 mA g⁻¹ (5th run).

**Figure 7.16** Charge and energy storage efficiency of cells containing spray deposited electrodes with varying degrees of MWCNT content. (Left) 100 mA g⁻¹ (3rd run), (right) 2,500 mA g⁻¹ (5th run).

**Figure 7.17** Areal resistance and mass specific power of cells containing spray deposited electrodes with varying degrees of MWCNT content. (Left) 100 mA g⁻¹ (3rd run), (right) 2,500 mA g⁻¹ (5th run).

**Figure 7.18** Mass specific energy density of cells containing spray deposited electrodes with varying degrees of MWCNT content. (Left) 100 mA g⁻¹ (3rd run), (right) 2,500 mA g⁻¹ (5th run).

**Figure 7.19** Comparative Ragone plot of cells containing spray deposited electrodes with varying degrees of MWCNT content. Test current densities were (right to left) 0.1, 0.25, 0.5, 1, 2.5 and 5 A g⁻¹.

**Figure 7.20** Relationship between change in discharge current and resulting drop in voltage during CCCD analysis as per IEC 62576. Both plots relate to cells containing electrodes with 20% MWCNT content (by mass). (A) is sample A and (B) is sample D.

**Figure 7.21** Comparative Ragone plot of cells containing spray deposited electrodes with varying degrees of MWCNT content, samples with erratic voltage/current relationships have been removed (see text). Test current densities were (right to left) 0.1, 0.25, 0.5, 1, 2.5 and 5 A g⁻¹.
**Chapter 0: List of Figures**

**Figure 7.22** Schematic of the electrode structures fabricated by targeted spray deposition. The SBR/CMC binder was held constant at 5% in all samples with the remaining electrode material content being Sigma PAC. 

**Figure 7.23** SEM images of a base-coated electrode fabricated by spray deposition containing (A) a single top layer coating of 20% MWCNT, 75% Sigma PAC, and 5% SBR/CMC binder, (B) a single middle layer coating of 5% MWCNT, 90% Sigma PAC, and 5% SBR/CMC binder and (C) a triple base layer coating of 0% MWCNT, 95% Sigma PAC, and 5% SBR/CMC binder.

**Figure 7.24** SEM images of a top-coated electrode fabricated by spray deposition containing (A) a triple base layer coating of 0% MWCNT, 95% Sigma PAC, and 5% SBR/CMC binder, (B) a single middle layer coating of 5% MWCNT, 90% Sigma PAC, and 5% SBR/CMC binder and (C) a single top layer coating of 20% MWCNT, 75% Sigma PAC, and 5% SBR/CMC binder.

**Figure 7.25** Results of CCCD testing at (left plots) 100 mA g⁻¹ (3rd run), (right plots) 2,500 mA g⁻¹ (5th run) for EDLC cells containing electrodes fabricated by targeted spray deposition. Plots (A) and (B) relate to cells with a top-coating of MWCNTs while plots (C) and (D) relate cells with a base-coating of MWCNTs.

**Figure 7.26** Results of CV testing at (left plots) 10 mV s⁻¹ (3rd run), (right plots) 1,000 mV s⁻¹ (5th run) for EDLC cells containing electrodes fabricated by targeted spray deposition. Plots (A) and (B) relate to cells with a top-coating of MWCNTs while plots (C) and (D) relate cells with a base-coating of MWCNTs.

**Figure 7.27** Mass specific capacitance as a function of current density for cells containing spray deposited electrodes with MWCNT deposition targeted at either the top layers (left) or base layers (right).

**Figure 7.28** Areal resistance as a function of current density for cells containing spray deposited electrodes with MWCNT deposition targeted at either the top layers (left) or base layers (right).

**Figure 7.29** Charge and energy storage efficiency as a function of current density for cells containing spray deposited electrodes with MWCNT deposition targeted at either the top layers (left) or base layers (right).

**Figure 7.30** Mass specific power density as a function of current density for cells containing spray deposited electrodes with MWCNT deposition targeted at either the top layers (left) or base layers (right).

**Figure 7.31** Mass specific energy density as a function of current density for cells containing spray deposited electrodes with MWCNT deposition targeted at either the top layers (left) or base layers (right).

**Figure 7.32** Comparative Ragone Plot of cells containing spray deposited electrodes with either no MWCNT content, an MWCNT top-coat or an MWCNT base-coat. Test current densities were (right to left) 0.1, 0.25, 0.5, 1, 2.5 and 5 A g⁻¹ and the average electrode thickness is stated in the legend.

**Figure 9.1** Gravimetric energy and power capabilities of electrochemical and capacitor devices. Dashed lines indicate RC time constant; red and green areas indicate batteries. From Ref [6].
## Abbreviations and Acronyms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AA</td>
<td>Alfa Aesar</td>
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<tr>
<td>AC</td>
<td>Activated Carbon</td>
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<td>a.c.</td>
<td>Alternating Current</td>
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<td>Activated Carbon Cloth</td>
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<td>Activated Carbon Fibre</td>
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<td>ACM</td>
<td>Activated Carbon Monolith</td>
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<td>ACN</td>
<td>Acetonitrile</td>
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<td>ASTM</td>
<td>American Society for Testing and Materials</td>
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<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
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<tr>
<td>BF₆⁻</td>
<td>Tetrafluoroborate</td>
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<td>BMSC</td>
<td>Bode Mass Specific Capacitance</td>
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<td>BPA</td>
<td>Bode Phase Angle</td>
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<td>CC</td>
<td>Current Collector</td>
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<td>CCCC</td>
<td>Constant Current Charge-Discharge</td>
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<td>CMC</td>
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<td>CV</td>
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<td>d.c.</td>
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<td>DEC</td>
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<td>DIW</td>
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Richard Fields - February 2018