Novel redox composited polymer electrodes for potential supercapacitors.

Submitted by

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Declaration.

The work described in this thesis is an account of the author’s research carried out at the University of Surrey from October 1998 to October 2001 and has not previously been submitted for a degree at any institution.

A. M. White
February 2002
"From the moment I picked your book up until I laid it down I was convulsed with laughter. Some day I intend reading it."

Groucho Marx (1895-1977)
Acknowledgements.

My thanks go to my parents, family and friends for their support and patience during the development of this work. To the IMSR group and other colleagues at the University of Surrey who have kept me sane and filled with beer. Special thanks go to J. R. Varcoe who helped in the development and correcting of this thesis and to B. Hook for engineering work. I would like to thank my supervisor Professor R. C. T. Slade for his guidance, thoughtful comments and ideas. I would like to thank Hannah, my partner, who has listened and supported me through the entire project and for the help given in correcting this thesis.

I would like to thank Innogy Technology Ventures Ltd for providing funding and materials in the final year of my PhD and for their interest in my work.

This thesis and all the work within it is dedicated to the memory of Millie and Michael White my grandparents.
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Abstract

Redox centred polymers have been chemically fabricated and evaluated for potential use as electrodes within a solid-state supercapacitor. A hydrated perfluorosulfonic acid Nafion® membrane acts as a solid electrolyte giving an environmentally ‘green’ system.

Thin-films were grown via vapour transport onto an aqueous oxidant solution and direct addition experiments were also performed. Successful combinations with polypyrrole and poly(N-methylpyrrole) gave black, conductive direct addition and thin-film products; oxidation involved either 12-molybdophosphoric acid, 12-molybdosilicic acid, 10-molybdo-2-vanadophosphoric acid, 14-vandophosphate, iron(III) chloride or potassium ferricyanide. Unsuccessful combinations used the monomers aniline, thiophene and 2-methylthiophene and / or the aqueous oxidants, 12-tungstophosphoric acid and 12-tungstosilicic acid.

Single electrodes were fabricated by vapour growth, onto a carbon paper support, with a polymer coating chosen from the successful candidates above. When multiple coats were applied to carbon paper, polymers doped with heteropolyacids and smooth surfaces were obtained which is essential for good contact with the Nafion® 115 membrane. On electrochemical analysis the heteropolyacids remain encapsulated within the polymer matrix due to their high charge and size. Cyclic voltammetry carried out in aqueous acid gave three dominant redox events associated with the heteropolyacids: 12-molybdophosphoric acid, 12-molybdosilicic acid and 10-molybdo-2-vanadophosphoric acid. The polypyrrole and 10-molybdo-2-vanadophosphoric acid based electrodes gave a high capacitance of 776 F g⁻¹ (with respect to active polymer material) and 0.79 F cm⁻² (geometric area of the electrode).
An evaluation of membrane electrode assemblies (MEAs, which are essentially capacitor devices without a casing) was carried out. MEAs were made by hot pressing of the electrodes onto the solid electrolyte membrane in a ‘sandwich’ configuration. The requirement for a supercapacitor is high specific capacitance accompanied by high energy density and by good power handling. The highest values per mass of MEA obtained were with electrodes incorporating polypyrrole doped with 10-molybdo-2-vanadophosphoric acid stored under damp conditions. For specific capacitance, energy density and specific power values obtained were 7 F g⁻¹, 0.5 W h kg⁻¹ and 3.3 W kg⁻¹. For the highest values per unit mass of active polymer, the combination of polypyrrole doped with 12-molybdosilicic acid gave 33.4 F g⁻¹, 2.12 W h g⁻¹ and 35.7 W kg⁻¹.
1 Introduction to novel redox composited polymer electrodes for potential supercapacitors

The aim of this project is to develop supercapacitor devices from polymer based electrodes, incorporating a Nafion® membrane as an electrolyte, forming an aqueous based solid-state system. The materials in the electrodes will be selected through a series of elimination reactions.

The field of supercapacitance, although developed, is small and fairly new compared to that of batteries and other similar devices. This section introduces the underlying phenomenon in a supercapacitor, which is capacitance. This forms a basis where supercapacitors can be introduced and their historical background and uses discussed. The introduction ends with a discussion on the types of supercapacitor that are mentioned, with some selected examples.

1.1 The historical background of capacitance and capacitors.

Humans have known since ancient times that when a piece of amber is rubbed with a soft cloth it will attract small fibres to its surface. This attraction is due to the creation of stored electrical charge on the amber’s surface. The basics of the phenomenon were not understood until the creation of apparatus that could harness the static electricity. The Leyden jar was developed by Dutch physicist Pieter van Musschenbroek (1692-1761) in 1745 at the university of Leyde and simultaneously, but independently, by Ewald Georg von Klaist (1700-1748) from Prussia in 1746 and was effectively the first capacitor. The Leyden jar came in various constructions; the one that most relates to a capacitor consisted of a glass bottle containing water in which a metal electrode was placed. The second electrode was a
tin coating around the glass container. Within the Leyden jar it was known that if a potential \( V \) was held between the charged plates, as charges \(+q\) and \(-q\), the Gibbs free energy is \( \frac{1}{2}qV \) and the capacitance \( C \) (in farads) is \( \frac{2G}{V^2} \), where \( q \) is the charge on the Leyden jar, \( V \) is the potential difference between the electrodes in volts and \( G \) is the Gibbs free energy in joules (J). It was not until one hundred and forty years later that work from J. J. Thompson, \(^2\) Millikan\(^3\) and Townsend led to electricity being understood in terms of the growth or decrease of charges. In 1881 von Helmholz concluded that Faraday’s laws referred to a fundamental unit of charge, which was normally involved in charge storage phenomena; this was something Faraday himself had failed to deduce.\(^4\) In the same year, Johnstone Stoney named this unit of electrical charge ‘electron’, which was derived from the Greek for amber (\( \epsilon\lambda\epsilon\kappa\tau\omicron\nu \)).\(^5\) After these deductions had led to the physical understanding of the electron, the research fields of electrochemistry and the electrical nature of matter developed.

At the start of World War Two, both the allies and Germany began the development of high quality capacitors. These capacitors incorporated such materials as paper with foil combinations, mica, glass and deposited zinc on dielectric paper. These designs were followed after the end of the war by the development in the United States of capacitors containing ceramics, tantalum, polyester and polystyrene. One of the first cases where electrical energy was stored in an electrochemical environment for practical purposes in a capacitor came from a patent filed by Becker in 1957.\(^6\) The electrochemical capacitor incorporated an acidic aqueous electrolyte, which penetrated a porous carbon electrode. This capacitor showed double-layer charge storage at the interfacial layer between the dielectric and electrode.

Between 1975 and 1981 work was carried out by B. E. Conway in which the use of base metals and solid oxides (such as RuO\(_2\)) formed the basis of a new type of electrochemical
capacitor.\textsuperscript{7,8} The base metal systems worked by the electrochemical adsorption of hydrogen at mono-layer levels.\textsuperscript{9} This movement of faradaic charge was not considered to be pure capacitance as it involved penetration of charge into the electrode and not just storage of energy on the surface. The term ‘pseudo-capacitance’ was therefore given to the ‘false capacitance’ shown with these electrode materials. Pseudo-capacitance and pseudo-capacitors will be described in more depth later on in this chapter. The term ‘supercapacitor’ was phrased by D. Craig who referred to the power and high energy storage capabilities of the electrochemical double-layer capacitor and pseudo-capacitor.\textsuperscript{10} These exhibit similar reversibility to electrostatic capacitors through static storage of energy.

1.2 The origin of capacitance and capacitors.

Capacitance is quite simply “the property of a system that comprises of conductors and insulators which allows them to store electrical static charge when a potential difference exists between the conductors.”\textsuperscript{11}

The capacitance of a body is defined as (Eqn. 1.1)

\begin{equation}
C = \frac{q}{V}
\end{equation}

where \( C \) is the capacitance on the surface and has the unit farad (F), \( q \) is the charge in coulombs (C) on the conductor and \( V \) is the potential difference in volts. A charged body is never fully isolated from other objects and can be influenced in some way. If, say, only one other conductor \( Y \) influences a conductor \( X \) with a magnitude of charge, all lines of force and electric fields from \( X \) will terminate at \( Y \). When defined using Gauss’s law, conductor \( Y \) must
therefore have a charge \( q \) which is of opposite sign but equal in magnitude to that of \( X \).\(^\text{12}\)

This arrangement of two conductors influencing only each other is known as a capacitor. This capacitance is defined as (Eqn. 1.2)

\[
C = \frac{q}{(V_x - V_y)}
\]

(Eqn. 1.2)

where \((V_x - V_y)\) represent the difference in potential between the conductors \( X \) and \( Y \). It can be seen that to achieve a perfect capacitor there must be as little influence from other conductors as possible. The ideal situation would be to have the body \( X \) completely surrounded by a shell of the conductor \( Y \); this would, however, prevent contact with the inner electrode (Fig. 1.1a). Examples of more practical constructions includes a concentric cylinder (Fig. 1.1b) (the type of arrangement in a coaxial cable) and a parallel plate device (Fig 1.1c), which is the type that will be considered within this project. To create as close to an ideal capacitor as possible using a parallel plate device, it is important that there is as little electrical field leakage as possible between the conductors. This requires:

- The conductors to run parallel to one another with little or no variation in the separation distance. This would prevent point charge build up and spread the charge on the whole area.
- The conducting plates must be of equal area and the diameter must be many times larger than the separation between the plates.
- The separation between the plates must be as small as possible so the electric field is concentrated between the plates, reducing leakage around the sides of the device.
Fig 1.1a - c. Schematic pictures of (a) ideal capacitor arrangement, (b) coaxial capacitor, (c) parallel plate capacitor.

Capacitance of a static capacitor can be defined in terms of the geometry and permittivity of the dielectric (Eqn. 1.3); \( S \) is the electrode surface area, \( D \) is the relative permittivity of the dielectric \((D = 1\) for vacuum or 78 for liquid \(H_2O)\), \( d \) is the electrode separation and \( \varepsilon_0 \) is the vacuum permittivity \((8.8 \times 10^{-12} \text{ F m}^{-1})\).

\[
C = S \varepsilon_0 \left( \frac{D}{d} \right)
\]

Equation 1.3

The potential voltage difference between the electrodes in an electrostatic capacitor can be quite high (sometimes up to the magnitude of kV). The stored energy density is, however, very low \((1 \text{ mW h kg}^{-1} \text{ to } 0.5 \text{ W h kg}^{-1})\), as the capacitance is quite low \((\text{in the range of pF to } \mu\text{F})\). The stability of a static capacitor during lifetime cycling is good, as the polarization of the electrode occurs with no change to the electrode surface. The energy storage and power handing of a static capacitor is defined by (Eqn. 1.4 to 1.6)

\[
E = \left( \frac{q^2}{C} \right) \quad \text{or} \quad E = \frac{1}{2} CV^2
\]

Equations 1.4 and 1.5

\[
P = VI
\]

Equation 1.6
where $E$ is energy in joules (J), $P$ is power in watts (W) and $I$ is current in amperes (A).

Electrode materials in an electrostatic capacitor are generally metals, such as aluminium or nickel, with a separator known as the dielectric, which can be mica, paper or ceramics. When designing a capacitor for a required application it is important to achieve the required capacitance, energy storage and power. Individual capacitor cells are inadequate, as they do not possess the capacitance, energy and power for practical applications. There are two main configurations that overcome this problem:

1. Roll capacitors maximise the surface area in a small space and therefore the capacitance of the capacitor. The voltage remains the same, being limited only by the dielectric.

2. A series stack of cells increases the energy storage in an additive manner (Eqn. 1.7); this has the effect of reducing the overall capacitance dramatically (Eqn. 1.8). Stack cells are generally combined in parallel to restore the capacitance of the original cell (Eqn. 1.9).

$$V_{\text{stack}} = V_n + V_{n+1} + \ldots + V_{n+\infty} \quad \text{Equation 1.7}$$

$$C_{\text{stack}} = \frac{1}{1/C_n + 1/C_{n+1} + \ldots + 1/C_{n+\infty}} \quad \text{Equation 1.8}$$

$$C_{\text{parallel}} = C_n + C_{n+1} + \ldots + C_{n+\infty} \quad \text{Equation 1.9}$$

1.3 **Supercapacitors and comparison to batteries.**

As already mentioned supercapacitors, which are also known as ultracapacitors and electrochemical capacitors, get their name from the high energy density they can retain and power output they can deliver, which are much higher than with conventional capacitors. Supercapacitors work in a similar way to normal capacitors, storing energy non-chemically
Chapter 1. Introduction to novel redox composited polymer electrodes for potential supercapacitors

in the form of static charge separation. This allows quick charge / discharge and long-term cycling stability characteristics. This is a useful property when compared to a battery construction, which has slow charge / discharge arising from the irreversibility in the materials microstructure and chemical irreversibility. Additional problems arise when the charging and recharging process of the battery causes polarisation of the materials. This leads to the lowering of the maximum voltage with increasing charge and discharge rates. The shelf life of a battery is another problem, as several months without use can result in the degradation from self-discharge and corrosion effects caused by electrolyte materials. Supercapacitors do self-discharge to very low levels of energy, but can be recharged quickly to their original levels of energy storage and power levels without degradation.

Batteries store energy in chemically active electrode materials according to the equation \( \Delta G = -Q \cdot \Delta V \), where \( Q \) is the total charge of the discharge of a battery and \( \Delta V \) is the potential difference between the anode and cathode. Batteries can therefore store a large amount of energy but, because of the problems highlighted, are incapable of releasing the power required by pulse applications. Pulse batteries have been developed, but these show poor cycling life times and much lower energy density compared to conventional batteries. Within a supercapacitor the electrode potentials are a continuous function of charge, limited only by the breakdown in the electrolyte. In a battery a thermodynamic response is observed, limiting the extent of the potential window. Aqueous electrolyte systems are limited theoretically to 1.23 V at 298 K, whereas organic systems using toxic solvents such as acetonitrile give up to 3 V.

Supercapacitors can solve these disadvantages by completely replacing the battery but are, however, not suitable for high energy applications, as supercapacitors can theoretically hold
only 20% of the energy of a battery. A more realistic method of using a supercapacitor is to combine it in parallel with a battery (section 1.4). This groups the advantages of the battery’s high energy storage and the high power output of the supercapacitor.

**1.4 Uses of supercapacitors and present technology.**

The capabilities of a supercapacitor can be applied to a large range of technologies, from power creation to mobile phones. This section gives a brief overview of the current status in research and industrial applications. The main areas of interest are as follows:

**i. Load levelling in power creation and protection devices on sensitive equipment.**

Supercapacitors have been considered for use in controlling power generation during daytime peak use by reducing the pressure caused by demand. This would save on investment and enhance the reliability of the power supply, which would lead to stable service and maintenance charges. The basis of the system is to store the energy during the night, when little power is used and then to release the power during the daytime, when it is most needed. The utilisation of a supercapacitor was predicted to be cheaper and more reliable when compared to a heat-regenerated heat pump system, superconducting magnetic energy storage, flywheel energy storage and secondary battery systems. The utilisation of supercapacitors in the power sector has been considered, taking into account spinning reserve, area and frequency control, transmission line stability, voltage regulation and power quality. Properties that must be considered include size, availability, cost, design, efficiency, cycle life, self-discharge rate, equalisation and excess discharge to 0 V.
ii. **Power boosting in electrically driven cars.**

At present there is growing concern at the use of the conventional internal combustion engine and diesel units, both from an ecological view and from fluctuating crude oil costs. Governments and car companies have invested a great deal of money into the development of new devices that will one-day replace existing technologies; these devices include fuel cells, batteries and ‘ultracapacitors’ (the term most often given to supercapacitor devices in industry). Many combinations coupling supercapacitors with other energy sources in vehicles have been considered, including those with fuel cells, batteries and conventional diesel engines. Supercapacitors coupled in parallel with batteries provide increased life span and a reduction in the overall cost of the system. This is achieved by transferring high power requirements to the supercapacitor. In situations such as hill climbing and overtaking manoeuvres in a vehicle, the fast discharge of the battery may damage the chemical balance, leading to shorter life and poor performance. The pairing of a diesel engine and supercapacitors has been successfully demonstrated by EPCOS Components on a bus in Nürnberg, Germany. The 56 V stack / parallel supercapacitor, developed by EPCOS Components, gave a 25% decrease in fuel consumption.

iii. **Supercapacitor / Fuel Cell hybrid systems.**

Due to the capability of producing a high energy density, Fuel Cells (FC) have been seen as a viable way of producing portable power that is both cheap and environmentally friendly. During continuous operation the power performance of a fuel cell is good, but during pulse applications problems begin to arise. It takes approximately five minutes to reach an optimal steady state for Polymer Electrode Membrane Fuel Cell (PEMFC) and Direct Methanol Fuel Cells (DMFC); in that time individual cells become polarised, which means that if there is a
sudden power increase the operating potential of the PEMFC will not recover. By placing a supercapacitor in parallel with the Fuel Cell, pulsed loads may be managed by combining the energy density benefits of a FC and the power handling of a supercapacitor.

iv. Electrical cranking devices.

Tantalum oxide hybrid capacitors have been developed by the Evans Capacitor Company (USA) for incorporation into tactical combat vehicles. These are relatively expensive devices compared to polymer and carbon based systems, but have gained customers in the military sector where their small weight and size is important.

v. Portable computer and mobile phone applications.

As both portable computers and mobile phones get smaller with increasing complexity, the requirement is for a lighter more efficient battery. A simple way of improving a battery, as stated earlier, is to group it in parallel with a supercapacitor.

vi. Space applications.

There has been recent interest in the development of supercapacitors for use within satellites. This has been shown to be one of the most challenging areas, as the requirements for design include resilience against extreme cold and total reliability. The supercapacitor would be coupled with a solar array (the most common form of power generation on space probes), where it would provide more efficient power transport. Main tasks that have been considered include short-term supply of high power pulses, fast recharging during pulse operation and the stabilisation of the power supply during possible operational failures.
These properties will deal with power supplies of pulse-power lasers, satellite antennae, communication systems, servo components, computer memory backup, safety and reliability of components during failure.

1.5 Types of capacitor.

The diversity of capacitors is large, spanning normal electrostatic capacitors, supercapacitors based on double layer charge separation and those showing pseudocapacity (faradaic charge processes). A selection of capacitor types and examples of fabrication materials are shown below (Table 1.1). The bottom three, double-layer capacitors and two types of pseudocapacitor, are discussed in the following section.

<table>
<thead>
<tr>
<th>Type of capacitor</th>
<th>Type of charge storage</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>Electrostatic</td>
<td>Electrode: metal foil of plates</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dielectric: vacuum.</td>
</tr>
<tr>
<td>Dielectric</td>
<td>Electrostatic</td>
<td>Electrode: metal foil or plates</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dielectric: mica, paper, ceramics.</td>
</tr>
<tr>
<td>Electrolytic oxide</td>
<td>Electrostatic</td>
<td>Electrode: aluminium oxide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electrolyte: aqueous acid or organic.</td>
</tr>
<tr>
<td>Electrostatic double-layer</td>
<td>Electrostatic</td>
<td>Electrode: carbon, metal foams.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electrolyte: aqueous acid or organic.</td>
</tr>
<tr>
<td>Redox oxide or nitride films</td>
<td>Faradaic charge transfer</td>
<td>Electrode: RuO₂, Mo₂N.</td>
</tr>
<tr>
<td></td>
<td>process</td>
<td>Electrolyte: aqueous acid or organic.</td>
</tr>
<tr>
<td>Conducting polymer film</td>
<td>Faradaic charge transfer</td>
<td>Electrode: polyaniline, polypyrrole</td>
</tr>
<tr>
<td></td>
<td>process</td>
<td>Electrolyte: aqueous acid or organic.</td>
</tr>
</tbody>
</table>

Table 1.1. Summary of capacitor types with example materials.
1.5.1 **Double-layer capacitors.**

In a double-layer supercapacitor the electrodes are considered to be chemically and electrochemically inert. In the discharged capacitor the potential energy is stored in the electrolyte (Fig 1.2). When the capacitor is charged the ions migrate *via* diffusion through the electrolyte onto the electrode surface. This forms a double-layer between the electrolyte and available surface area.

![Schematic of a charged double-layer capacitor with ions penetrating highly porous carbon.](image)

*Fig 1.2. Schematic of a charged double-layer capacitor with ions penetrating highly porous carbon.*

Two models are used to describe this interaction of charge at the surface of the electrode. The Helmholtz layer is where the charges are accumulated parallel to the interface. This accumulation is often known as the Helmholtz plane (HPE).\(^{22}\) The Gouy-Chapman model extends the HPE into the dielectric taking into account the diffuse layer.\(^{23,24,25}\) Only a small portion of the electrode’s surface is generally accessible, this being due to ions in the electrolyte solution being unable to access the micropores, which can represent 80% of the
total surface area. Porosity is further reduced when binders are used to form the electrodes. The effective surface area is therefore (Eqn. 1.10):

$$S_{\text{effective}} = S_{\text{total}} - S_{\text{occupied}} - S_{\text{micropores}}$$

Equation 1.10

where $S_{\text{effective}}$ is the actual available surface area, $S_{\text{total}}$ is the theoretical maximum, $S_{\text{occupied}}$ is the surface area which filled with binder or other materials and $S_{\text{micropores}}$ represents the surface area where the pores are too small to be penetrated by the electrolyte. To obtain a large specific capacitance an electrode possessing a high effective surface area and high conductivity is required. Electrode materials that have these properties include carbon aerogels, catalytically grown nanotubes\textsuperscript{26, 27}, activated glassy carbon electrodes, carbon felts and the most commonly used activated carbon\textsuperscript{28}.

In double layer capacitors as much as 10% of the overall capacitance is due to pseudo-capacitance, which arises from active sites on the electrodes surface. The energy (Eqn. 1.11) and power (Eqn. 1.12) within a double layer device are defined by the following equations:

$$E = \frac{1}{2} C(V_i^2 - V_f^2)$$

Equation 1.11

$$P = \frac{1}{2} I(V_i + V_f)$$

Equation 1.12

where $C$ is the capacitance (F), $V_i$ is the initial voltage (V), $V_f$ is the final voltage, $E$ is the energy in joules (J), $P$ is the power in watts (W) and $I$ is the current in amperes (A).

Advantages of double layer capacitors include high voltage operation with organic electrolytes, high power operation, infinite reversibility with no chemical reactions and, a capacitance which is constant with varying voltage.
1.5.2 Redox pseudocapacitors.

Redox pseudo-capacitance works by the dispersion through faradaic charge-transfer of electro-active species into the crystalline or amorphous electrode structure after being deposited from the electrolyte (Fig. 1.3). On discharge the reverse of the above applies.

![Diagram showing charge/discharge process in faradically driven electrodes in a pseudo-capacitor.](image)

In this three-dimensional mechanism the energy stored is proportional to the amount of electroactive species that can be absorbed by the electrode. This leads to much larger values of energy storage (W h kg\(^{-1}\)) and specific capacitance (F g\(^{-1}\) or F cm\(^{-3}\)). This capacitance can range from 10 to 100 times larger per square centimetre than could be achieved from any double-layer process reliant solely on accessible surface area.

To maximise power the electrostatic resistance (e.s.r.) must be kept to a minimum. This can be achieved by having porous systems with high electronic conductivity and good contact with the electrolyte, allowing the fast transfer of charge. Using an electrode with a fine
microstructure (giving a high electrode / electrolyte area) can increase the rate of charge transfer.

Among the disadvantages of pseudo-capacitors are low voltage, capacitance not being constant with voltage and power being limited by kinetic factors:

Example pseudo-redox capacitor systems include;

1. Systems based on RuO$_2$, where the insertion and expulsion of electrons and protons into the oxide matrix takes place via faradaic pathways.
2. Conductive polymer electrodes that work on the transfer of charge, via redox-couples, along a conjugated chains in a doping and un-doping process.

Metal oxide, RuO$_2$.

Ruthenium oxide has been widely studied for use as a working electrode in supercapacitors.$^{30, 31}$ The main problem with RuO$_2$ incorporation in capacitors is the cost and much research has been aimed at alternative systems such as molybdenum nitrides$^{32}$ and porous nickel oxide films.$^{33, 34}$ Strontium ruthenate pervoskite materials have been developed to reduce the overall amount of ruthenium$^{35}$; in the same work it was found that the introduction of strontium, iron or cobalt will increase the stabilisation of the system with the alkaline aqueous electrolyte potassium hydroxide (3 mol dm$^{-3}$). The doping of lanthanum into the strontium site increases the capacitance of a standard SrRuO$_2$ electrode from 10 F g$^{-1}$ to 30 F g$^{-1}$. A 20% doping of lanthanum on the strontium site will give a 0.1 V increase in the stability window. Higher capacitance can be obtained by doping with manganese.$^{36}$ Another example is ruthenium / carbon aero-gels used for electrode materials which gave,
depending on Ru the content, 85 - 206 F g⁻¹ per electrode. Due to the high cost of ruthenium oxide, molybdenum nitrides have been studied and have been shown to possess similar properties.

**Conducting polymers.**

Conducting polymers have been studied for many years, with the first being polyacetylene and showing metallic type conductivity of $1 \times 10^6$ S cm⁻¹. This discovery was followed by the electrical characterisation of polymers such as polypyrrole, polythiophene and polyaniline, giving rise to the study of the preparation and analysis in electroactive polymer electrochemistry. These polymers utilise their π-conjugated backbones to transfer electrical charge from the current collector to the electrolyte. Conductive polymers are referred to as either n-doped (reduced state) or p-doped (oxidised state) relative to their neutral state. Electro-active polymer supercapacitors can be compared with solid oxide systems in that electrical charge transfer is faradaic and electrical storage properties are those of a capacitor.

There are advantages over other redox active electrode materials (e.g. RuO₂):

1) They are cost effective compared with expensive transition metal based electrodes.

2) They can be prepared readily onto supports *via* chemical or electrochemical methods (discussed in Chapter 2).

3) As with RuO₂, polymer electrolytes offer good capacitance, power output and energy storage.

4) Reversibility on cycling is adequate for most systems, although not as good as RuO₂.
5) Charge disperses well through the polymer and so the current collector need not be fully dispersed on the surface of the electrode.

6) Activated carbon electrodes have a slower charge / discharge rate compared to polymers such as polypyrrole.\textsuperscript{40} This phenomenon is caused by the inability of the ions to reach internal surfaces within the carbon matrix. Polypyrrole was found to give good rate of charge and discharge, making these materials more suitable for high power applications.

Polymers, which have been considered for study within a supercapacitor, include polypyrrole, polyaniline and polythiophene. These polymers are often modified either through structural derivatives or doping during growth, which can result in enhanced conductivity or $n$-type stabilisation. An example includes the doping of polypyrrole with the surfactant sodium dodecylbenzene sulfonate, which results in a micellar influence leading to a polymer with enhanced diffusion properties.

Most of the conductive polymers generated are in oxidised form, or lacking electrons, known as $p$-doped (for example polypyrrole and polyaniline, which can be reduced to a non-conductive state but not reduced to a conducting state). Polythiophene can be reduced to an $n$-doped state, which contains an excess of electrons, but is not stable in this form over a long cycling period. In recent work by Lafargue et al, the conducting polymer poly-$3$(4-fluorophenyl)thiophene was prepared and tested.\textsuperscript{41} By acting as an electron acceptor the fluorophenyl group was found to give good stabilisation to the $n$-doped state of the polymer when compared with simple polythiophene.
There are three types of supercapacitor based on the polymer redox configuration:\(^42,43\)

- **Type I:** A *p*-doped electronically conducting polymer in a symmetric form (e.g. polypyrrole / polypyrrole). When a type I supercapacitor is fully charged, one electrode will be completely *p*-doped and the other will be uncharged.

- **Type II:** Two *p*-doped electronically conducting polymers based in an un-symmetric form. This configuration is capable of doping over a range of potentials (e.g. polypyrrole / polythiophene).

- **Type III:** Two electronically conducting polymers, one *n*-doped and the other *p*-doped, in a symmetric configuration (e.g. polythiophene / poly-3(4-fluorophenyl) thiophene).\(^44\)

**Existing ‘state of the art’ systems:** As the area of supercapacitors progresses rapidly the following examples are taken from manufactures brochures at the time of writing.

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Power / W kg(^{-1})</th>
<th>Energy / Wh kg(^{-1})</th>
<th>Capacitance / F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ness 2.5 V</td>
<td>100 to 600</td>
<td>2.4 to 4</td>
<td>2600 to 4600</td>
</tr>
<tr>
<td>Panasonic 2.5 to 4 V</td>
<td>100</td>
<td>2.5 to 4</td>
<td>1200 to 2500</td>
</tr>
<tr>
<td>Skeltech 2.3 V</td>
<td>3500 to 5722</td>
<td>3.9 to 5.2</td>
<td>47 to 615</td>
</tr>
<tr>
<td>ESMA 1.3 V</td>
<td>156</td>
<td>1.1</td>
<td>10000</td>
</tr>
<tr>
<td>Montena 2.5 V</td>
<td>870</td>
<td>2.5 to 3.3</td>
<td>1800 to 2800</td>
</tr>
</tbody>
</table>

The development of a polymer based electrode system in this work will provide a cheaper system of power, energy and capacitance per unit mass compared with existing capacitor systems.
1.6 Conclusions.

This chapter has given a brief outline to the background of this project, with historical and technical information. The types of capacitors have been discussed with special emphasis on redox pseudocapacitance, an area of research still much less intense than that on carbon based double-layer technology. Although high surface area carbon based systems are cheap and show stable capacitive behaviour, pseudocapacitance can lead to higher energy storage. The area of pseudocapacitance is currently dominated by work involving oxides such as RuO₂, which tend to be very expensive and therefore may never reach a state of commercial viability. Work is being done in this field of supercapacitors to minimise the amount of oxide used, but this is still a relatively new area. Another alternative that was mentioned was the redox-conducting polymers such as polyaniline, polythiophene and polypyrrole. These can be both electrochemically and chemically grown (the nature and formation of these polymers will be explained in greater depth in chapter 2), the latter being a major emphasis in this study. These polymers are much cheaper relative to the cost of solid oxides and can lead to much higher capacitance, depending on the tailoring of the electrode and on cell design.

In the following pages the volatile monomers pyrrole, N-methylpyrrole, aniline, N-methylaniline, thiophene and 2-methylthiophene have been taken through an elimination process. Their suitability has been assessed for use as precursors to polymer electrodes in a new formulation for supercapacitors.
1.7 References.


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Chapter 2. The materials used for electrode fabrication, their selection and method of fabrication.

2 The materials used for electrode fabrication, their selection and method of fabrication.

2.1 Introduction.

The choice of the monomers and oxidants / dopants was made after an elimination process. These elimination steps are explained, with results, later on in this chapter. The first class of materials to consider are the oxidants / dopants, which react with the monomers to form the required polymers and which in some cases become trapped in the polymer matrix. Selected heteropolymetallates were used in this project to both oxidise the selected monomer to the corresponding polymer and to provide a fast proton conducting redox-centre, bound as a dopant, within the polymer matrix. The second part gives an overview of the redox-composited polymers involved; these include polypyrrole and poly(N-methylpyrrole) (and their related monomers). Structure, mechanism of formation and conduction process are considered. The way in which the polymer binds to the heteropolymetallate is mentioned and the properties that these composites possess have been characterised.
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2.2 The fabrication of conductive polymers.

Polypyrrole is grown chemically or electrochemically, with the first report of the anodic formation of polypyrrole in aqueous sulfuric acid having been in 1968.\(^1\) This was followed eleven years later by the electrooxidation of pyrrole in a 99% acetonitrile / 1% H\(_2\)O solution, leading to a free-standing film on the surface of the anode.\(^2\) In the electrochemical process, the pyrrole is oxidised to polypyrrole at the anode, giving high purity (Fig 2.1).\(^3\)

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{N} & \quad \text{N} \\
\text{H} & \quad \text{H}
\end{align*}
\]

\[
\text{H} - 2e^- \rightarrow \text{H} \quad \text{N} \quad \text{N} \quad \text{H} - 2H^+ \\
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{N} & \quad \text{N} \\
\text{H} & \quad \text{H}
\end{align*}
\]

\[
\text{H} - e^- \rightarrow \text{H} \quad \text{N} \quad \text{N} \quad \text{H} + 2nH^+ - yne^- \\
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{N} & \quad \text{N} \\
\text{H} & \quad \text{H}
\end{align*}
\]

Fig. 2.1. Mechanism of the electropolymerisation of pyrrole to polypyrrole. \(y\) is the degree of \(p\)-doping during the electropolymerisation.

The most accepted mechanism for the electrochemical growth of polypyrrole was proposed by Diaz and co-workers,\(^4,5\) with further evidence from theoretical work;\(^6,7\) a shortened form is shown above (Fig. 2.1). The electropolymerisation is generally carried out in an aqueous solution of neutral pH or weak acidity, or in a non-aqueous solution. A potential of between 0.65 V - 0.80 V is applied;\(^8\) if higher potentials or a higher pH is used the over-oxidation of the polymer may occur and this will result in the introduction of carbonyl, hydroxyl groups or unconjugated trimers into the polymer-backbone\(^9,10\). A golden coloured insulating polymer occurs if the polypyrrole is in a reduced form where there is no charge on the polymer chain; this is termed a reduced benzenoid or neutral form.
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If the pH is too low, a rough (almost powdery) film is made and so during an electrochemical reaction the pH must be carefully controlled.\textsuperscript{11} The final structure of the oxidised form of the polypyrrole is a close-packed backbone of organised linear chains for which, on average, every fourth pyrrole ring carries a positive charge.\textsuperscript{12} This $p$-doped state can be a radical cation (polaron state) or bipolaron state; these are black polymers with varying conduction properties (\textit{Fig. 2.2}).\textsuperscript{13}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{The neutral and conductive states of polypyrrole. Neutral (a.), polaron (b.), bipolaron (c.)}
\end{figure}

The first chemically produced polypyrroles were low molecular weight oligomers, generally trimers made using aqueous HCl.\textsuperscript{14} The formation of solid, chemically prepared polypyrrole was achieved in 1916 using acidified H$_2$O$_2$.\textsuperscript{15} The chemical oxidation of pyrrole has been the subject of research for several decades.\textsuperscript{16} The chemically prepared polymer has a lower conductivity, but is cheaper and easier to produce by large-scale fabrication, compared to its electrochemical counterpart.

An example of the above mechanism is the use of oxidant potassium ferricyanide (K$_3$Fe(CN)$_6$) reported by Torres-Gómez et al (\textit{Fig. 2.3}).\textsuperscript{17}
Chapter 2. The materials used for electrode fabrication, their selection and method of fabrication.

\[
\begin{align*}
\text{nPy} + n(2 + y)\text{K}_2\text{Fe(CN)}_6 & \rightarrow \{-\text{Py}^{y^+} \left[\text{Fe(CN)}_6^{\text{y}^+}\right]_{y/3}\} + 2n\text{H}^+ \\
& + 2n(1 + y/3)\text{Fe(CN)}_6^{4-} + 3n(2 + y)\text{K}^+
\end{align*}
\]

*Fig 2.3. Chemical oxidation of pyrrole by the oxidant hexacyanoferrate (III).*

2.3 Pathways for electronic conduction in polymers.

As has already been mentioned there are various forms of polypyrrole that can be fabricated. The insulating polymers are golden in colour, with no charge separation and can be described as defect free. The conducting polymers are black with a polaron or bipolaron state for every four pyrroles within the \(\pi\)-system. As polypyrrole is made up of long conjugated chains, the polaron is able to hop along the backbone causing a transfer of charge *via* the redox-couples, leading to electronic conduction (*Fig 2.5*). The process is complex but can be explained by a transport mechanism termed *variable range hopping* (VRH). This results from the electron hopping between neighbouring monomers through high and low energy level units along the polymer chain.\(^{18}\) Deoxyribonucleic acid (DNA) also exhibits VRH in which the electrons are transported between localised sites in the double helix.\(^{19}\)

Other pyrroles that have been N-substituted have been synthesised\(^{20,21}\) and then polymerised, allowing the study of their conductivity.\(^{22,23}\) Most electrochemically polymerised N-substituted polypyrroles possess low conductivity and are generally brown to golden in appearance. The formation of poly(N-methylpyrrole) gives a black polymer of slightly lower conductivity than the polypyrrole material.\(^{24}\)
Fig. 2.4. Schematic of the transport of an electron through redox couples in an electro-active polymer film. Current collector (grey), electro-active polymer (yellow), electrolyte (blue). The black dots represent repeated redox couple reactions.

2.4 Uses of conducting redox polymers within supercapacitors

Conducting polymers are of great interest in the design of electrodes for supercapacitors. As introduced in Chapter 1, they are relatively inexpensive to produce compared with existing technologies such as the well studied RuO₂ electrode.²⁵, ²⁶ Use of a polymer leads to a pseudocapacitance enabling a much higher empirical capacitance and greater power output compared with standard carbon based double-layer devices.²⁷
2.5 Heteropolyacids.  

In 1826 the formation of a new inorganic material was reported when a mixture of molybdates and phosphates was acidified. The inorganic species was 12-molybdophosphoric acid; this was the first recorded heteropolyacid and is the most widely studied to date (Fig. 2.5).

\[
\begin{align*}
\text{nH}_2\text{O} + \text{PO}_4^{3-} + 12\text{MoO}_4^{2-} + 27\text{H}^+ & \rightleftharpoons \text{H}_3[\text{PMo}_{12}\text{O}_{40}].n\text{H}_2\text{O} + 12\text{H}_2\text{O} \\
\end{align*}
\]

Fig. 2.5. Formation of 12-molybdophosphoric acid.

Other heteropolyacids soon followed, such as 12-molybdosilicic acid and the tungsten analogues 12-tungstophosphoric acid and 12-tungstosilicic acid. The 12-molybdophosphoric acid and the 12-tungstophosphoric acid are often commercially available as "phosphomolybdic acid" and "phosphotungstic acid" respectively. Heteropolymetallates have become the most studied of the polyoxometallates and are a popular starting point for various applications. Their frequent use is due to the vast amount of detailed literature available, which studies both reactivity and the electrical properties. Commercial availability of these substances is plentiful at a low cost.

The structure of the 12-heteropolymetallates is based on the Keggin ion, which can be described as a cluster of oxides that forms a complex local framework (Fig 2.6). The anion of 12-tungstophosphoric acid was the first to be characterised using X-ray diffraction and the resultant structure was named after its discoverer (hence the name Keggin ion). At the base of the structure are metal ions that are co-ordinated to metal oxide clusters, forming a close
packed arrangement locally similar to a solid oxide. There are generally just a few metal ions that are studied; these are usually based on molybdenum, tungsten, vanadium or uranium.34 There is a large range of mixed molybdovanadophosphoric acids that have been made and many studies of their various properties have been carried out (many are catalytically active).35,36.

![Diagram of a 12-heteropolyacid](image)

**Fig 2.6. Structure of a 12-heteropolyacid:** The twelve octahedra (in red) represent the metal oxide clusters that form edge-sharing triads. These are bridged together via corner sharing. The metal atoms in this case are usually tungsten or molybdenum; alternatives that are studied can incorporate uranium or vanadium. The inner structure (in blue) is generally a hetero atom, such as silicon or phosphorus, surrounded by four oxygen atoms.

The heteroatom can be tailored to provide various properties; the most common heteroatoms are silicon or phosphorus at the centre of the heteroanion, surrounded by four oxygen atoms. Alternatives include arsenic, iodine, chromium, boron and tellurium.37 Stability varies with pH, with tungsten-containing systems being more stable in acidic environments (in contrast molybdenum based species decompose in one molar aqueous acid).38 The vanadium-
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containing polyanions are even less stable, forming heteropoly anions (such as in Na$_7$[PV$_{12}$O$_{36}$].38H$_2$O) that decompose above 60°C and are only stable at pH 1.5 - 6.0.$^{39}$ More stable heteropolyacids of tungsten and molybdenum have been obtained by replacing some of the respective metal ions with vanadium

2.6 Conduction properties of the heteropolymetallates.

The proton conduction in a heteropolyacid is due to its bulk structure and the high acidity. Each of the heteropoly anions is set in an aqueous medium, with the presence of water in the matrix holding individual heteropoly anions together.$^{41}$ Within this 'pseudo-liquid', an equilibrium is present in which the oxide, co-ordinated to the metal atom $X$, 'shares' a proton with a water molecule (Fig 2.7).

\[
\text{X}^n \text{O}^2- \text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{X}^2\text{O}^5^- + \text{H}_3\text{O}^+\]

Fig 2.7. Equilibrium within the heteropolyacid matrix. The $X$ is a metal atom such as molybdenum or tungsten. Water is found between the acid molecules / anions.

This equilibrium of the proton transfer reaction is shifted to the right due to high Brönsted acidity resulting from the bonding of polarised outer electrons from the oxygen to the Mo$^{VI}$ ion. This causes all oxygen atoms on the surface of the molecule to become strongly acidic. The heteropoly acid is therefore considered as three-dimensional acid with the acidic groups covering the complete, almost spherical surface. The water channels between the anions
form the second component of the conduction step; at room temperature the $\text{H}_2\text{O}$ and $\text{H}_3\text{O}^+$ may rotate and exchange protons freely in a Grotthus mechanism.\textsuperscript{42} The proton conductivity of these materials has been extensively studied elsewhere using techniques such as a.c. conductivity, pulsed field gradient NMR\textsuperscript{43,44} and quasielastic neutron scattering.\textsuperscript{45,46,47}

Within the supercapacitor the proton conduction properties of the heteropoly acid will interact with the protons from the electrolyte. This will cause the reduction or oxidation of the electrodes and therefore the charge and discharge.

### 2.7 Uses of heteropolymetallates within supercapacitors and other applications.

Katsoulis has reviewed the considerable literature on polyoxometallate chemistry, with much of this area dedicated to heteropolyacids.\textsuperscript{30} The uses of these acids are extensive and some of the main areas are as follows:

- Carbon electrode modification for capacitors, electrolytic capacitors.\textsuperscript{48,49}
- Coatings and primers that are resistant to corrosion.\textsuperscript{50}
- Pigments for metal-coating paints.\textsuperscript{51}
- Hardeners in epoxy resin.\textsuperscript{52}
- Electrochromism.\textsuperscript{53}
- Photochromism.\textsuperscript{54}
- Sensors.\textsuperscript{55}
- Fuel cells.\textsuperscript{56}

The list is long and this is due to the broad chemical and structural capabilities of the heteropoly anion. The major part of the research in this area is dedicated to catalysis.\textsuperscript{57,58}
with the supercapacitors taking only a small part. Yamada et al describe a study performed on 12-molybdophosphoric acid in which the heteropolyacid was an electrode, with a Nafion\textsuperscript{®} membrane as a separating electrolyte.\textsuperscript{59} It was found that the 12-molybdophosphoric acid supercapacitor gave a lower energy density compared to ruthenium oxide supercapacitors. Although the energy density was lower, the materials used in the fabrication of the 12-molybdophosphoric system were far cheaper per unit of energy, making the ruthenium oxide supercapacitor less economical. Patent literature contains a number of entries; one example uses the heteropolyacid salts of \([\text{H}_4\text{SiW}_{12}\text{O}_{40}]\) or \([\text{H}_4\text{SiMo}_{12}\text{O}_{40}]\) as the electrolyte material within a supercapacitor, as above.\textsuperscript{60}

### 2.8 Polymers and heteropolyacid combined.

The polymers that are mainly studied in this work are polypyrrole and poly(N-methylpyrrole) doped with various heteropolyacids. The most common ways for combining a polymer with a heteropolyacid are as follows:

- One-step reactions where the polymer is combined directly in a solution or on to the solid oxidant.
- Electrochemical growth onto the surface of a support.
- Through vapour transport onto the surface of an oxidant on a support.
- Impregnation of a support material with either the monomer or heteropolyacid, followed by a dipping step.

The combination of a conjugated polymer and heteropolyacid was first reported by Bidan et. al.\textsuperscript{61} This publication considered the combination of pyrrole or N-methylpyrrole with
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Tungstophosphoric acid, forming the respective polymers via electrochemical growth at an anode. The resultant polymer formed around the anion, giving a more regular structure compared to the undoped polymer system. On doping, the heteropolyacid increases the homogeneous separation of charges on the polymer by the delocalisation of its own negative charge. This leads to an increase of the electronic conductivity, which is further increased as the heteropolyacid aids the transfer of charge between the polymer chains.

Most interest in polyaniline or polypyrrole doped with various heteropolyacids is in the field of catalysis. Examples include the decomposition of isopropanol, the electrocatalytic reduction of oxygen and protons, ethanol conversion and many other applications. Lira-Cantú and co-workers combined polypyrrole and polyaniline with 12-molybdophosphoric acid to produce powders chemically and thin-films electrochemically. The polypyrrole was found to share nine pyrrole units with one heteropolyanion, implying that the polypyrrole studied was fully oxidised (Fig 2.8).

![Fig 2.8. The electrochemical synthesis of polypyrrole doped with 12-molybdophosphoric acid (after Lira-Cantú).](image)

Various properties of these quantitatively made polymers were explored using electrochemical and spectroscopic techniques and analysis showed that these materials were suitable as electrodes. Cyclic voltammetry (CV) of the polypyrrole and 12-molybdophosphoric acid polypyrrole composite showed similar responses for the electrochemically grown thin-films and chemically produced bulk polymer. The CV clearly
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showed three redox processes associated with the 12-molybdophosphate anion (0.324 V, 0.190 V, and -0.042 V on reduction and 0.404 V, 0.260 V and 0.042 V on oxidation relative to Ag/AgCl). These peaks almost hid the polypyrrole peaks, which appeared as shoulders at 0.460 V and 0.510 V on the reduction and oxidation scans respectively. The results from cyclic voltammetry showed that the heteropolyanion maintained the good conductivity of the host polymer matrix. Cycling tests on the retention of the heteropolyacids showed that, on reduction, 12-molybdophosphate anions remain within the polymer. The only degradation products found were believed to be partially oxidised monomers or oligomers originating from corrosion of polypyrrole. Infrared analysis provided further proof that 12-molybdophosphate is retained within the polypyrrole matrix. Heteropolytungstate is another example of this class that has been combined with polypyrrole via electrochemical growth. The dispersion of the heteropolyacid throughout a polymer matrix has been shown to enhance the catalytic activity relative to that of a heteropolyacid in its pure crystalline state.

2.9 The selection process to find a suitable electrode material.

This section will explain how, through a series of eliminations using direct addition and vapour transport reactions, the combinations of polymers, supports, heteropolyacids and other oxidants were chosen to complete the study.

2.9.1 Candidate polymers and heteropolyacids.

Monomers were selected from commercially available heterocycles that have in the past given conductive polymers through either electrochemical or oxidative chemical synthesis. The criteria by which they were chosen were that they possessed a low melting point and
high volatility, which led to thiophene, 2-methylthiophene, aniline, N-methylaniline, pyrrole and N-methylpyrrole. The oxidants that were chosen, for reasons that have been explained earlier, included the commercially available 12-molybdophosphoric acid, 12-molybdosilicic acid, 12-tungstophosphoric acid and 12-tungstosilicic acid. Two heteropolyacids were synthesised to provide comparison tests; these were 12-vanadophosphoric acid and 10-molybdo-2-vanadophosphoric acid. Anhydrous iron(III) chloride (FeCl₃) was included in the study, as it has been used as an oxidant to grow polypyrrole via chemical polymerisation. Materials that have been fabricated with FeCl₃ include thin-films of pure polypyrrole, doped polypyrrole composites or powders, from the chemical reaction by direct addition of FeCl₃ to monomer solutions. Potassium hexacyanoferrate(III) (K₃Fe(CN)₆) was included in this study as it, in common with FeCl₃, formed polypyrrole during both electrochemical synthesis and chemical direct-addition reactions.

2.9.2 Preparation of the monomers, heteropolyacids and other oxidants.

Each of the heterocyclic monomers (Aldrich) was distilled under nitrogen prior to use and stored in the dark at 4°C to 6°C. The oxidants (Aldrich, except for 10-molybdo-2-vanadophosphoric acid and 14-vanadophosphate synthesised as below) were kept in the dark at 4°C to 6°C and were used as received. Iron(III) chloride and potassium ferricyanide (K₃Fe(CN)₆).6H₂O (Aldrich) were used as received.

Due to the hygroscopic nature of heteropolyacid materials, thermogravimetry (TG) was performed on the samples to determine the amount of water present. This value was then used to calculate the amount of oxidant required to produce accurate concentration solutions and to identify the proportion of bound oxygen in the heteropolyacid. The full TG traces are
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TG was carried out using a Stanton Redcroft STA-781, coupled with differential temperature analysis (DTA). Heating rate was 10°C min⁻¹ in static air. Infrared (IR) analysis was carried out on samples prepared as KBr disks on a Nicolet 512 PS spectrometer.

TG for the 12-molybdophosphoric acid found the formula H₃PMo₁₂O₄₀·XH₂O, where X is ≈ 29.1, giving an overall RMM = 2349. IR analysis gave the peaks P-O 1065 cm⁻¹, Mo=O 963 cm⁻¹, Mo-O-Mo corner sharing 867 cm⁻¹ and Mo-O-Mo edge sharing 784 cm⁻¹. TG for the 12-molybdosilicic acid gave the formula H₃SiMo₁₂O₄₀·XH₂O, where X ≈ 19.1, giving an overall RMM = 2164. IR analysis gave the peaks Mo=O 955 cm⁻¹, Si-O 905 cm⁻¹, Mo-O-Mo corner sharing 865 cm⁻¹ and Mo-O-Mo edge sharing 766 cm⁻¹.

The mixed heteropolyacid 10-molybdoo-2-vanadophosphoric acid was chosen as a further comparison and as a possibility for a more stable heteropolyacid. The compound was made as follows using a previously reported method that used a simple extraction step: Sodium metavanadate (24.4 g, 0.2 mol) was dissolved in deionised water (100 cm³) at 80°C and mixed with a solution of dibasic sodium phosphate (7.15 g, 0.05 mol) in deionised water (100 cm³). When the mixture had cooled, concentrated sulfuric acid (5 cm³) was added, acidifying the solution and yielding a deep red colour. Sodium molybdate dihydrate (121.1 g, 0.5 mol) dissolved in deionised water (200 cm³) was added to the red solution. To the vigorously stirring solution concentrated sulfuric acid (85 cm³) was added with care and then the complete reaction mixture was allowed to cool to room temperature. The desired heteropolyacid was then extracted from the acidic aqueous mixture into diethyl ether (500 cm³). The diethyl ether was removed from the product in vacuo and the afforded solid
was recrystallised from water. The final filtered product was deep orange in colour. Yields of pure material for repeated reactions varied between 25 g (23%) and 35 g (32%). The recrystallisation and extraction steps caused the variation in yield.

The TG of the 10-molybdo-2-vanadophosphoric acid gave \( \text{H}_5\text{V}_2\text{Mo}_{10}\text{PO}_{40}.x\text{H}_2\text{O} \), where \( x \approx 24.9 \), giving an overall RMM = 2185. Elemental analysis: Mo 51.82; V 5.65; P 1.78 gives the ratio Mo : V : P as 10 : 2 : 1 as predicted. IR analysis gave the peaks P-O 1048 cm\(^{-1}\), Mo=O 957 cm\(^{-1}\), Mo-O-Mo corner sharing 878 cm\(^{-1}\), Mo-O-Mo edge sharing 788 cm\(^{-1}\) (Fig 2.9). The V-O-V peaks cannot be seen as the Mo-O-Mo peaks overlap.

The attempt at the fabrication of the sodium salt of 12-vanadophosphate \( 10\text{Na}_2\text{O}.\text{P}_2\text{O}_5.24\text{V}_2\text{O}_5.x\text{H}_2\text{O} \) was carried out using a method previously reported.\(^{37}\) Sodium vanadate (18.39 g, 0.18 mol) was dissolved in deionised water (100 cm\(^3\)) at 70°C and allowed to cool to room temperature. Any residual solid was removed by filtration. The NaVO\(_3\) solution was combined with a solution of dibasic sodium hydrogen phosphate (9.16 g, 0.315 mol) in deionised water (50 cm\(^3\)). To the stirring mixture cooled in an ice bath, aqueous nitric acid (73 cm\(^3\) ≈ 1.13 mol) was added slowly to prevent over heating and the release of noxious gas. The resulting deep red solution was allowed to cool to room temperature and then acetone (20% of the volume of the reaction mixture) was added and the solution was cooled further to 5°C. After 24 h a red crystalline product was obtained in yields of 5.3 (21%) to 7.5 g (29%).
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Fig 2.9. Infrared spectra of the four heteropolymetallates under study. Absorbance / % is shown on an arbitrary scale. 14-vanadophosphate –, 12-molybdosilicic acid –, 12-molybdophosphoric acid –, 10-molybdo-2-vanadophosphoric acid –.

Elemental analysis for the vanadium heteropoly salt is Na 5.94; V 41.90; P 1.79. When errors associated with elemental analysis are taken into account this composition is consistent with the formula PV$_{14}$O$_{42}$$^{9-}$, known in the literature; Kato et. al isolated the guanidinium salt and identified this 14-vanadium based heteropolyacid.$^{78}$ The 14-vanadophosphate is a bicapped, 5-coordiante Keggin ion. This is not observed when molybdenum or tungsten heteropolyacids form. The formation of PV$_{12}$O$_{40}$$^{15-}$ was not successful as the high negative charge prevents this; the bicapped PV$_{14}$O$_{42}$$^{9-}$ is favoured as it is stabilised by the capping of two VO$_{3}^{+}$ units. The bicapped system is allowed, as the vanadium is capable of 5-coordination. Others confirmed this system in preference to the PV$_{12}$O$_{40}$$^{15-}$. Further solution NMR analysis by Kato confirmed the results. The TG of this product gave number of water molecules $\approx$ 29.6 leading to an overall RMM 2050.44. IR analysis gave the peaks P-O 1066 cm$^{-1}$, V=O 965 cm$^{-1}$, V-O-V corner sharing 875 cm$^{-1}$, V-O-V edge sharing 827 cm$^{-1}$ and P-O wagg. 592 cm$^{-1}$ (Fig 2.9).
2.9.3 Preparation of doped polymers via direct addition.

The monomer (0.05 mol) was poured into deionised water (50 cm$^3$) and stirred vigorously to form an emulsion. To this stirring mixture the oxidant (0.1 mol dm$^{-3}$) in deionised water was added rapidly. The reaction mixture was allowed to stir for 12 h. Any precipitates obtained were washed repeatedly with deionised water and then ethanol, until the washings became clear and colourless. The resultant polymer was dried overnight in vacuo.

To determine the conductivity of the direct addition product an appropriate amount of each polymer powder was ground into a homogeneous mixture and then pressed into a pellet (diameter, 1.3 cm). The pellets were made by pressing the powder under 15 tonnes cm$^{-2}$ for 10 min using a Specac KBr press. Pellets were between 1 and 2 mm in thickness. The pressed polymers were then brought to equilibrium water content over 24 h in a desiccator within an atmosphere of 51% relative humidity at 20°C (above a saturated aqueous solution of Ca(NO$_3$)$_2$.4H$_2$O). The pellets were placed into a two-electrode cell and impedance spectroscopy was used to determine the total resistance, these values were used to calculate the conductivity. Conductivity measurements were carried out using a Solartron SI 1260 impedance analyser coupled with a SI 1287 electrochemical interface. Infrared analysis was carried out as KBr disks on a Nicolet 512 PS. Conductivity is calculated using the following formula (Eqn 1),

$$K = \frac{1}{R \times 1/A}$$

Eqn 1.

Where $K$ is the conductivity in S cm$^{-1}$, $R$ is the total resistance in Ohms (determined from the total conductivity found by the impedance analysis), $l$ is the thickness of the sample pellet in cm and $A$ is the area in cm$^2$. Measurement were carried out at 20°C.
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Results of direct addition reactions involving aniline and N-methylaniline.

The reaction of aniline or N-methylaniline with $\text{K}_3\text{Fe(CN)}_6$, $\text{FeCl}_3$, 12-tungstophosphoric acid and 12-tungstosilicic acid generally resulted in waxy golden brown polymers which were insulating. All other oxidants gave no reaction or intense blue solutions with no precipitate resulting from the mixture. This was due to the formation of aniline oligomers (with no polymer formation), although it is known to be possible to form the polymer through further oxidation of this solution. The result of this reaction indicates that these candidates are not suitable for the formation of thin-films using the method proposed.

Results of direct addition reactions involving thiophene and N-methylthiophene.

The reaction with both thiophene and N-methylthiophene with all the oxidants gave no reaction. Only after several days did the thiophene and 12-molybdophosphoric acid selection give any colouration to the solution. This was indicative of short chain oligomer formation. Strong acids such as a heteropolyacid do not completely oxidise thiophene via direct chemical reaction and so do not form the polymer. The results from this reaction set indicate that they are unlikely to give thin-films and therefore were not further studied.

Results of direct addition reactions involving pyrrole and N-methylpyrrole.

The reaction of pyrrole and N-methylpyrrole gave a precipitate with all oxidants. The polymers varied depending on the aqueous oxidant properties being summarised in Table 2.1 and Table 2.2.

The ratios of polymer unit to heteropoly anion (found in Chapter 2 and Chapter 3) were calculated by,
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1) Dividing the percentages of the elements present by their corresponding molecular mass.

2) Dividing the resultant values by the lowest value (in this work, normally phosphorous or silicon as only one in general).

3) Dividing the value for the molybdenum content by number of molybdenum atoms found in the heteropolyacid dopant (determined by elemental analysis).

4) The value for the nitrogen content is then divided by the value for the molybdenum content, obtained in 3. This gives the number of monomer units per heteropolyacid.

The direct addition products made with 12-tungstophosphoric acid and 12-tungstosilicic acid were insulating waxy golden products. A similar outcome is seen from other very strong oxidants, which tend to over-oxidise the polymers to less conductive states.\textsuperscript{75} This is also the outcome from an electrochemical reaction, which is too anodic.\textsuperscript{12} The infrared data for 12-tungstophosphoric within polypyrrole gave peaks at 792, 874, 972 and 1098 cm\textsuperscript{-1} and in poly(N-methylpyrrole) at 803, 893, 986 and 1079 cm\textsuperscript{-1}. These were assigned to the W-O-W edge sharing, W-O-W corner sharing, terminal W=O and P-O band respectively. Similar stretching bands were seen in the 12-tungstosilicic acid doped polymers; as expected the P-O band was absent with an Si-O peak appearing at 920 cm\textsuperscript{-1}. The 12-tungstosilicic acid doped polypyrrole gave peaks at 794, 883, 920 and 972 cm\textsuperscript{-1} and with poly(N-methylpyrrole) 796, 873, 924 and 970 cm\textsuperscript{-1}. From the elemental analyses the ratios of monomer units to heteropolyacids are calculated. For the polypyrrole doped samples 12-tungstophosphoric acid resulted in a doping of 11.4 : 1 and 12-tungstosilicic acid gave a similar ratio of 12.8 : 1. The poly(N-methylpyrrole) samples gave the indication that more of the heteropolyacid was trapped during the direct addition reaction. 12-Tungstophosphoric acid with poly(N-methylpyrrole) gave an average ratio of polymer units to anions of 3.7 : 1 and the
12-tungstosilicic acid gave a ratio of 9.2 : 1. Due to the insulating nature of the tungsten-based products, these materials were not studied further. Conductivity measurements carried out at 20°C. ‘Insulating’ in this case means the material under consideration failed to conduct.

The direct addition products of polypyrrole and poly(N-methylpyrrole) grown with iron(III) chloride or potassium ferricyanide were all black and conductive. These products were found to absorb large amounts of water when exposed to the air and this caused problems when pressing pellets for conductivity tests (cracks tended to appear in the samples). Results shown in Table 2 and Table 3 are from successful pressing.

The direct addition products of polypyrrole and poly(N-methylpyrrole) prepared with 12-molybdophosphoric acid, 12-molybdosilicic acid, 10-molybdo-2-vanadophosphoric acid and 14-vanadophosphate gave black fine powdered polymers that varied in conductivity (Table 2 to 3). 12-molybdophosphoric acid with polypyrrole gave a ratio of 10.5 : 1; in the poly(N-methylpyrrole) case the ratio is slightly higher at 11.3 : 1. Polypyrrole prepared with 12-molybdosilicic acid gave a ratio of 13.4 : 1 and the N-methyl derivative a higher 15.4 : 1. The 10-molybdo-2-vanadophosphoric acid gave similar ratios to the other heteropolyacids, with polypyrrole 11.4 : 1 and poly(N-methylpyrrole) 13.3 : 1. The sodium salt of the 14-vanadophosphate gives ratios of 20.1 : 1 for polypyrrole and 25.6 : 1 poly(N-methylpyrrole). Taking into account that the ratios are an average of the doping and therefore approximate for the whole polymer the charge is shared between three or four repeat units on average.

Infrared analysis gave distinctive peaks for the encapsulated heteropolyacids in polypyrrole materials: these were (M = Mo or V), M-O-M edge sharing, M-O-M corner sharing, M=O
terminal, Si-O or P-O stretching (Table 2.3). In the spectra of the polymers doped with the 10-molybdo-2-vanadophosphoric acid, V-O vibrations were hidden by the Mo-O stretches. The P-O band in the doped polypyrrole is overlapped by a strong C-H band which is absent from the poly(N-methylpyrrole) spectra. The V-O-V edge sharing and corner sharing vibrations are either absent or unresolved in the spectra.

<table>
<thead>
<tr>
<th>Oxidant in aqueous solution</th>
<th>Conductivity / S cm⁻¹</th>
<th>Appearance</th>
<th>Elemental analysis %</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>1.83 x 10⁻⁴</td>
<td>Fine black powder</td>
<td>C: 20.79; H: 1.60; N: 5.79</td>
</tr>
<tr>
<td>12-Molybdosilic acid</td>
<td>1.07 x 10⁻⁶</td>
<td>Fine black powder</td>
<td>C: 24.34; H: 2.40; N: 6.84</td>
</tr>
<tr>
<td>12-Tungstophosphoric acid</td>
<td></td>
<td>Waxy golden brown lumps</td>
<td>C: 15.74; H: 1.82; N: 4.34</td>
</tr>
<tr>
<td>12-Tungstosilic acid</td>
<td></td>
<td>Waxy golden brown lumps</td>
<td>C: 17.26; H: 1.92; N: 4.74</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>9.12 x 10⁻⁷</td>
<td>Fine black powder</td>
<td>C: 31.13; H: 2.34; N: 7.17</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>5.24 x 10⁻⁸</td>
<td>Fine black powder</td>
<td>C: 33.74; H: 2.29; N: 9.94</td>
</tr>
<tr>
<td>Potassium ferricyanide</td>
<td>9.47 x 10⁻⁷</td>
<td>Soft, slightly rubbery texture black powder</td>
<td>C: 45.73; H: 3.10; N: 17.69</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>3.04 x 10⁻⁵</td>
<td>Soft, slightly rubbery texture black powder</td>
<td>C: 57.27; H: 3.53; N: 16.26</td>
</tr>
</tbody>
</table>

Table 2.1. Properties of polymer materials made via direct chemical reaction between pyrrole and a specified aqueous oxidant. Measurements taken at RH = 52%.
<table>
<thead>
<tr>
<th>Oxidant in aqueous solution</th>
<th>Conductivity / S cm(^{-1})</th>
<th>Appearance</th>
<th>Elemental analysis %</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>(3.01 \times 10^{-7})</td>
<td>Fine black powder</td>
<td>C: 25.15; H: 2.48; N: 5.70</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>(3.56 \times 10^{-9})</td>
<td>Fine black powder</td>
<td>C: 30.60; H: 2.54; N: 6.96</td>
</tr>
<tr>
<td>12-Tungstophosphoric acid</td>
<td></td>
<td>Waxy golden brown lumps</td>
<td>C: 7.56; H: 0.98; N: 1.55</td>
</tr>
<tr>
<td>12-Tungstosilicic acid</td>
<td></td>
<td>Waxy golden brown lumps</td>
<td>C: 17.41; H: 2.17; N: 3.86</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>(5.33 \times 10^{-8})</td>
<td>Fine black powder</td>
<td>C: 25.17; H: 1.70; N: 7.06</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>(6.44 \times 10^{-9})</td>
<td>Fine black powder</td>
<td>C: 43.84; H: 3.65; N: 9.93</td>
</tr>
<tr>
<td>Potassium ferricyanide</td>
<td>(1.75 \times 10^{-7})</td>
<td>Soft, slightly rubbery texture black powder</td>
<td>C: 58.83; H: 4.19; N: 15.85</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>(2.45 \times 10^{-8})</td>
<td>Soft, slightly rubbery texture black powder</td>
<td>C: 58.18; H: 4.67; N: 13.41</td>
</tr>
</tbody>
</table>

Table 2.2. Properties of polymer materials made via direct chemical reaction between N-methylpyrrole and a specified aqueous oxidant. Measurements taken at \(RH = 52\%\).
### Table 2.3. Infrared peak positions of heteropoly anions doped in polypyrrole and poly(N-methylpyrrole). Infrared peak positions are given as wavenumber (cm⁻¹), M is Mo or V, full assignments can be found in appendix 1.
2.9.4 Thin-film fabrication

Tests were carried out to examine monomer / oxidant combinations for forming suitable thin films which could then be grown onto a support giving potential electrodes. The monomers pyrrole and N-methylpyrrole were used as they gave black conductive polymers as a result of the direct addition reactions. The monomers where required to be volatile at room temperature, a feature exhibited by pyrrole and N-methyl pyrrole. All the previously used oxidants were studied as all had produced powders. The method of thin film fabrication was as follows,

![Schematic picture of the reaction vessel used for the growth of the redox-centred polymer films. An aqueous solution of oxidant (in red) and liquid monomer (in green) are shown.](image)

A solution of the oxidant ($20 \text{ cm}^3, 0.100 \text{ mol dm}^{-3}$) prepared with deionised water was poured into a glass petri dish (5 cm diameter). The selected monomer (1 g) was placed into another glass petri dish. The dish containing the oxidant and the dish containing the heterocyclic monomer were placed into a clean sealed desiccator (Fig 2.10). The reaction was allowed to proceed for 24 h at approximately $20^\circ\text{C}$. The resultant product (generally a
thin film) was carefully washed repeatedly with separate deionised water and ethanol until the washings became colourless.

The resultant films, which formed at the vapour / liquid boundary, were very mixed in integrity and appearance. Methods to study selected thin films included scanning electron microscopy (SEM), elemental analysis and infrared spectroscopy; these techniques are described in varying detail later on in this work.

Films made with polypyrrole doped with potassium hexacyanoferrate (Plate 2.1a) were very thin, very fragile and difficult to handle. This was the case with of poly(N-methylpyrrole) doped with 12-molybdophosphoric acid, 12-molybdosilicic acid, 10-molybdo-2-vanadophosphoric acid, potassium ferricyanide, 14-vanadophosphate and grown with iron(III) chloride. These thin-films were further studied grown on various support materials, as discussed later in this work.

Plate 2.1a to c. Thin-films of polypyrrole doped with metal containing compounds. Doped with (a) potassium ferricyanide, (b) 12-tungstophosphoric acid and (c) 12-molybdophosphoric acid.
Polypyrrole or poly(N-methylpyrrole) doped with 12-tungstophosphoric acid or 12-tungstosilicic acid gave brittle golden brown polymers that were difficult to handle (Plate 2.1b). These fragmented films were insulating (as found earlier with direct addition reactions) and were therefore not suitable as electrode materials. The polymers containing the heteropolytungstic acids were therefore studied no further.

Polypyrrole doped with 10-molybdo-2-vanadophosphoric acid, 12-molybdosilicic acid, 14-vanadophosphate or formed with iron(III) chloride gave black thin films that showed good strength and thickness [similar in appearance to the film made with the 12-molybdophosphoric acid and pyrrole (Plate 2.1c)]. The films could be removed from the surface of the water, but required support because they became inflexible, brittle and curled when dried. All the thin-films of this type grew quickly and were visible on the surface of the oxidant solution after about one hour.

Secondary-electron and some backscattered electron, scanning electron microscopy (SEM) images are shown in the following pages. Images with plates numbers that include the letter ‘S’ are secondary electron images and those that are signified by ‘B’ are backscatter electron images. The infrared bands relating to the heteropolyacid component of the material are also presented; more detailed data for the thin films is in appendix 1. Elemental analysis of selected polypyrrole thin-films grown on aqueous oxidant surfaces is also given.

**Thin-film of polypyrrole doped with 12-molybdophosphoric acid.**

The results of elemental analysis gave C: 24.59%, H: 1.67%, N: 6.69%, Mo: 38.64% and P: 0.72%. Ratio of pyrrole units to heteroanions ≈ 14 : 1. Infrared data: Mo-O-Mo edge
sharing at 795 cm\(^{-1}\), Mo-O-Mo corner sharing 880 cm\(^{-1}\), Mo=O terminal 973 cm\(^{-1}\), P-O stretch 1062 cm\(^{-1}\).

The side of the thin-film in contact with the pyrrole vapour (Plate 2.2S) shows a crinkled morphology with features approximately 40 µm in length and 7 - 10 µm in width. The backscattered image (Plate 2.4B) shows amorphous areas of high heteropoly acid content (light colour) with a pores of 40 - 50 µm in length and up to 5 µm in width. The appearance of the aqueous oxidant side reflects that seen from the vapour side. The pores are again seen in the secondary and backscattered image (Plate 2.3S and Plate 2.5B), in between the nodular structures that have formed.

Plate 2.2S. Thin-film side in contact with the pyrrole vapour, grown on aqueous oxidant 12-molybdophosphoric acid.

Plate 2.3S. Thin-film side in contact with aqueous oxidant 12-molybdophosphoric acid.
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Plate 2.4B. Thin-film side in contact with the pyrrole vapour, grown on aqueous oxidant 12-molybdophosphoric acid.

Plate 2.5B. Thin-film side in contact with aqueous oxidant 12-molybdophosphoric acid.

The nodules, which are between 2 - 5 µm in diameter, appear to have formed on top of each other. From the secondary image, the film appears to have formed from individual platelets that have become interwoven. When viewed with the naked eye, the side that has been in contact with vapour appeared to be grey in colour, implying that more light was reflecting from the black surface. The aqueous oxidant side was matt black with little light reflection. This is explained by the smooth morphology of the vapour side surface and the nodular surface of the liquid-formed side.
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**Thin-film of polypyrrole doped with 12-molybdosilicic acid.**

The results of elemental analysis gave C 24.81%, H 2.33%, N 6.52% and Mo 37.41%, ratio of pyrrole units to heteroanions 14.3 : 1. Infrared data shows the encapsulated heteropolyanion peaks with Mo-O-Mo edge share 800 cm⁻¹, Mo-O-Mo corner share 876 cm⁻¹, Si-O 913 cm⁻¹, M=O 957 cm⁻¹.

![Plate 2.6S. Thin-film side in contact with pyrrole vapour grown on aqueous oxidant 12-molybdosilicic acid.](image1)

![Plate 2.7S. Thin-film side in contact with aqueous oxidant 12-molybdosilicic acid.](image2)

The morphology of the thin film is very different to that of the 12-molybdophosphoric acid / polypyrrole combination. Both the backscatter and secondary images (Plate 2.6S and Plate 2.8B) of the thin film show that the surface in contact with the vapour is smoother and is pock marked with nodules of 6 to 10 µm in diameter. The side in contact with the aqueous liquid is very rough with nodules of 10 - 20 µm; this side appears matt black to the naked eye (Plate 2.7S and Plate 2.9B). The surface in contact with the vapour was very smooth, more so that any of the other thin films. With the naked eye this appeared jet black and shiny.
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Thick-film of polypyrrole doped with 10-molybdo-2-vanadophosphoric acid.

The results of elemental analysis gave: C, 26.52%; H, 2.41%; N, 7.35%; Mo, 35.20% and V, 1.27%, ratio of pyrrole units to heteroanions of 14.3 : 1. Infrared data: Mo-O-Mo 807 cm⁻¹, Mo-O-Mo 884 cm⁻¹, M=O terminal 950 cm⁻¹, P-O stretch 1065 cm⁻¹.

The surface that was in contact with the vapour has a swirled appearance from creases (Plate 2.10S and Plate 2.12B), which are ≈ 10 µm in length. The side in contact with the aqueous oxidant has the nodular appearance that is common to these thin-film samples, each nodule being 2 – 4 µm in diameter (Plate 2.11S). From the backscattered image at magnification (500 x), large almost crystalline formations of polymer can be seen (Plate 2.13B). The large nodules are 10 – 35 µm in diameter and could result from small amounts of the 10-molybdo-2-vanadophosphoric acid crystallising on the bottom of the thin-film during growth. The crystals might then have promoted the growth of the polymer forming these granular structures.
Plate 2.10S. Thin-film side in contact with pyrrole vapour, on aqueous oxidant 10-molybdo-2-vanadophosphoric acid.

Plate 2.11S. Side in contact with aqueous oxidant 10-molybdo-2-vanadophosphoric acid.

Plate 2.12B. Thin-film side in contact with pyrrole vapour, on aqueous oxidant 10-molybdo-2-vanadophosphoric acid.

Plate 2.13B. Side in contact with aqueous oxidant 10-molybdo-2 vanadophosphoric acid.
Thin-film of polypyrrole doped with 14-vanadophosphate:

The elemental analysis gave: C, 34.28%; H, 1.88%; N, 10.35%; P, 0.93%; V, 23.35%. Ratio of pyrrole units to heteroanions is 22.6 : 1, which was similar to that of the direct addition products. Infrared data: V-O-V edge share 807 cm⁻¹, V-O-V corner share 877 cm⁻¹, P-O stretch 1057 cm⁻¹; the M=O is overlapped with a strong band attributed to the polypyrrole.

The thin-film has a similar morphology to that seen with the 10-molybdo-2-vanadophosphoric acid and polypyrrole combination. The surface exposed to the pyrrole vapour shows an amorphous arrangement of interlocking swirls made up of Y and X shape creases (Plate 2.14S). The growth of this morphology in an electrochemical manner onto the surface of an electrode has been studied previously. Small grains of polymer form on the surface of the electrode and the growth of polymer spreads outwards across the surface of the electrode. When the expanding grains meet the ridges begin to form Y and X patterns. The same process may give the similar result seen here with the growth of the grains on the surface of the aqueous oxidant (Plate 2.15S). These structures are better seen in the backscattered image (Plate 2.16B). The side in contact with the aqueous solution (Plate 2.17B) gave a nodular surface with formations measuring 2 - 5 μm in diameter.
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The pyrrole vapour, grown on aqueous oxidant 14-vanadophosphate.

Thin-film of polypyrrole grown with iron(III) chloride:

The SEM images show a very rough surface on the side in contact with the vapour, with large pores 100 µm in length and up to 30 µm in width (Plate 2.18S). The “liquid side” shows amorphous nodular formations of 2 - 5 µm in diameter (Plate 2.19S). To the naked
eye both sides appear matt black, with the side in contact with the aqueous oxidant a little
darker than the vapour side, a result of the highly nodular surface.

Plate 2.18S. Thin-film side in contact with pyrrole vapour grown on aqueous oxidant
FeCl₃.

Plate 2.19S. Side in contact with aqueous oxidant FeCl₃.

The elemental analysis gives: C, 58.26%; H, 2.48%; N, 16.18% and Fe, 0.45% indicating
only a small amount of iron(III) chloride present.

2.9.5 Support materials.

The results from the thin-film experiments indicated that the materials were too fragile to be
used as free-standing electrodes. This led to the testing of a range of supports, including
insulating and conductive materials to gain information on the enhancement of strength and
flexibility. Polymer growth was carried out via vapour transport onto the surface of the
support using a method similar to that of the stand-alone thin-film process and is explained in
more detail within Chapter 3. Toray carbon paper (E-tek Inc.), cellulose membranes
(Millipore), and glass filters (Whatman, GF/C) were tested.
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Plate 2.20. The three supports tested using pyrrole monomer vapour and 12-molybdophosphoric acid aqueous oxidant solution. (a) Paper membrane, (b) glass fibre and (c) carbon paper.

Paper membrane coated well with the black conductive polymers but became very brittle and curled when dried (Plate 20a). The polymer did not penetrate the glass filter membranes and gave a poor coating only on the surface (Plate 20b); after drying they generally peeled, yielding polymer pieces. The paper membrane and glass membrane supports are therefore unsuitable for supercapacitor electrodes. Polymers coated onto the surface of the carbon paper gave good coverage and adhesion, with no curling or peeling (Plate 20c). The carbon paper became more flexible when coated, which was a useful property when pressing the electrodes to form the supercapacitor cell. It is interesting to note that polypyrrole adheres well to other materials such as iron or steel and has been considered for use as an adhesive and as a corrosion protector.
2.10 Conclusions.

This chapter has provided an insight into the various reactions that take place between selected monomers and dopants. From the direct addition tests and thin-film tests it was possible to select a range of materials that might give doped conductive polymers, which could be used as electrode materials in supercapacitors.

The powders obtained from direct addition reactions were either golden brown and insulating or black polymers that had poor conductivity.

The information gained from the scanning electron microscope (SEM) gave useful information on the type of thin-film formed with the vapour deposition method. SEM images of the thin-films formed from the heteropolyacids, in secondary and backscatter modes showed a similar morphology for the side grown in contact with the liquid oxidant. Surfaces in general appeared rough with nodules of 2 - 20 µm; this gave a matt black appearance to this side of the film. Surfaces in contact with the vapour were smoother and either grey or shiny black in appearance. The materials chosen were as follows:

**The support material:** Toray carbon paper was chosen as it did not curl or peel during the coating processes. The result was a successful coating of polymer that increased the flexibility of the carbon paper. Carbon paper is conductive and will act as a current collector, reducing the electronic resistance of the electrode.
The heterocyclic monomer: From the tests, pyrrole and N-methylpyrrole were the only monomers that produced conductive black polymers with oxidants in both the direct addition and thin-film tests. Films could be removed from the surface and could be handled for SEM analysis. The films were still prone to easy tearing and curling, making it difficult to make conductivity measurements. The poly(N-methylpyrrole) gave very thin-films that could not easily be handled and will be further studied only on the chosen support. The monomers aniline, N-methylaniline, thiophene and 2-methylthiophene at this point were no longer considered, as there were no reactions judged to have a positive outcome.

The oxidant / dopant: The 12-tungstophosphoric and 12-tungstosilicic acids were found to yield golden brown, insulating, direct addition and thin-film products. All other oxidants were taken forward as they produced black conductive polymers of varying qualities, which would be interesting to compare in electrode studies.

To summarise the conclusions, the following materials were selected for further study:

- Pyrrole and N-methylpyrrole as the heterocyclic monomers.

- 12-Molybdophosphoric acid, 12-molybdosilicic acid, 10-molybdo-2-vanadophosphoric acid, 14-vanadophosphate, iron(III) chloride and potassium ferricyanide as oxidants.

- Toray carbon paper as support.
2.11 References.


32 12-Molybdophosphoric acid at costs £19.80 per 100g at the time of writing (Sigma-Aldrich catalogue 2002).


Chapter 2. The materials used for electrode fabrication, their selection and method of fabrication.


Chapter 2. The materials used for electrode fabrication, their selection and method of fabrication.


Chapter 2. The materials used for electrode fabrication, their selection and method of fabrication.


3 The fabrication and testing of polymer coated carbon electrodes.

3.1 Fabrication of electrodes and materials used.

The following types of electrode were fabricated during the course of this work:

1. Lone electrodes for study within a three-electrode cell. Measurements were taken using cyclic voltammetry to study the various electron transfers and stability of the heteropolymetallate centre in the polymer matrix.

2. Electrodes grown in a ‘hung’ manner, where both sides of the oxidant-coated electrode were exposed to monomer vapour. This is suitable for supercapacitor use.

3. Electrodes grown in a ‘flat coat’ manner, with one side of the oxidant coated electrode exposed to monomer vapour. This will also be suitable for supercapacitor use.

4. Electrochemically grown films were included for comparison. Such films were grown for both lone electrode and supercapacitor use.

The study of the interaction between the monomer and oxidant, as discussed within the conclusions of Chapter 2, allowed the selection of appropriate materials for further study. Most reactants are available from commercial sources; some heteropolyacids studied required synthesis as has been outlined in the previous chapter.
The 12-molybdophosphoric acid and the 12-molybdosilicic acid (Aldrich) were stored in a fridge and used as received. Iron(III) chloride, potassium ferricyanide hexahydrate and sodium dodecylbenzene sulfonate (Aldrich) were used as received. The monomers pyrrole and N-methylpyrrole (Acros Organics) were distilled prior to use and stored under nitrogen in the dark at 0 - 5°C.

Toray carbon paper (E-Tek Inc.) was shown to be the best support tested, as discussed in the conclusions of Chapter 2. The papers were prepared by cutting them in such a way as to suit either lone electrode analysis or supercapacitor construction (see later). To remove grease and other surface impurities the uncoated carbon paper electrodes were washed with acetone (Merck) and then 30% hydrogen peroxide (Acros Organics). After soaking in deionised water for 1 h, the supports were dried in air and coated as described below.

3.1.1 Lone electrode growth.

Multiple exposures onto the carbon paper of monomer and oxidant were carried out in an attempt to increase the amount of polymer coating, leading to more suitable electrodes.

![Diagram of coating process](image)

**Fig 3.1. Schematic picture of the coating process of carbon paper lone electrodes.**

*The electrode 'square' is 0.5 x 0.5 cm.*
Electrodes were cut into a flag shapes (Fig. 3.1a.) and treated with acetone and hydrogen peroxide as detailed above. The flag tail was then painted with silver conductive paint (Fig. 3.1b) (RS Components) and cured at 80°C for 10 min. Solutions (usually 0.1 mol dm\(^{-3}\)) of the required oxidants were made up in deionised water: 12-molybdophosphoric acid, 12-molybdosilicic acid, 10-molybdo-2-vanadophosphoric acid, 14-vanadophosphate and FeCl\(_3\) (exceptionally 1.0 mol dm\(^{-3}\)). The flag part of the electrode was then coated with the selected oxidant solution using a glass rod to spread the liquid and then hung from a cotton thread in an open plastic pot (Fig. 3.1c). The coated electrode was exposed to monomer vapour for up to 24 h at autogenous pressure and 20°C. The electrode was washed using deionised water in an ultrasonic bath for 30 min, removing any loose oligomers and unabsorbed oxidant. The coating process was carried out a total of three times on each electrode; the washing process was used between each coat and the final coat was followed by refluxing treatment in ethanol for 30 min. The fully treated flag electrode was dried and attached to a tin-coated copper wire using silver epoxy resin (RS Components) (Fig. 3.1d) and cured overnight at room temperature and pressure.

3.1.2 Supercapacitor electrode fabrication.

The ‘flat coat’ method (Fig. 3.2a).

The Toray carbon paper rectangles (60 x 35 mm) were cut out and washed as previously explained, using acetone and hydrogen peroxide and were then treated with an aqueous solution of oxidant (as used in the fabrication of the lone electrodes). The carbon papers were then laid flat in a glass petri dish and put into a sealed container in the presence of
monomer vapour at room temperature and pressure. The source of the vapour was a small dish filled with the monomer liquid below the petri dish. After 24 h the carbon papers were removed and washed with deionised water in an ultrasonic bath for 30 min until the washings remained clear and colourless. Wet carbon papers were then blotted with filter paper, removing any residual surface water, and allowed to dry in air for 2 h. The papers were then re-coated as before, this treatment process being repeated four or five times. The final coated paper was cleaned in an ultrasonic bath with deionised water for 30 min to remove any loose solids and was then washed in refluxing ethanol. After the washing process the electrodes were allowed to dry in air.

*Fig 3.2. Schematic picture of oxidant coated Toray carbon paper (red) exposed to pyrrole vapour (yellow): a) ‘Flat coating’ in a glass petri dish, b) ‘Hung’ on a cotton thread in an open plastic pot.*

The ‘hung coat’ method (Fig. 3.2b).

This method is similar to the ‘lone electrode’ method. The Toray carbon paper electrodes (60 mm x 35 mm) were hung on cotton thread while exposed to pyrrole vapour. This results in the even coating of both sides.
3.1.3 Electrochemically grown electrodes.

To compare results with the vapour-grown redox-centred polymers; lone electrodes and supercapacitor electrodes were fabricated with electrochemically deposited polypyrrole doped with sodium dodecylbenzene sulfonate. The chosen method is similar to the one mentioned previously by Naoi. The surfactant sodium dodecylbenzenesulfonate (6.967 g, 0.020 mol) was dissolved into deoxygenated, deionised, water (200 cm$^3$) to give a clear colourless solution. To this rapidly stirring solution, freshly distilled pyrrole (1.340 g, 0.020 mol) was added. The well-mixed solution was then poured into an electrochemical cell and covered with a blanket of flowing nitrogen. A carbon paper electrode was introduced into the solution as the working electrode, with a platinum wire as the auxiliary electrode. The polymer films were grown onto the carbon paper electrode under galvanostatic conditions at $\approx 2.93$ mA cm$^{-2}$. The above experiment was repeated for freshly distilled N-methylpyrrole (1.62 g, 0.020 mol). To form black conducting films with reasonable coverage, polypyrrole took approximately 1 h reaction time and poly(N-methylpyrrole) 2 h. The electrodes were washed by soaking in deionised water with slight agitation for several hours and then dried in air.
Chapter 3. The fabrication and testing of polymer coated carbon electrodes.

3.2 **Electron microscopy of the carbon paper electrodes with doped polymer coatings.**

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) of the electrodes are discussed below.

3.2.1 **Scanning electron microscopy (SEM) analysis of single electrodes.**

By considering the coverage and morphology determined using SEM, important decisions and conclusions can be drawn concerning the integrity of the fabricated electrode. The clarity of SEM is better than that of a conventional optical microscope, as electrons give a greater depth of field, thereby creating the impression of a three dimensional image. SEM is similar, in principle, to an optical microscope in that it has a lens, but instead of light waves being manipulated by glass optics, SEM has an electron beam that is bent by an electromagnetic field.

The sample to be analysed is mounted and then sputter coated, under argon, with carbon (or gold) and then placed in the sample stage at a pressure of \( \approx 1 \times 10^{-6} \) mmHg. The samples in this work were not sputter coated, as they were already conductive. The vacuum prevents the tungsten filament from burning out and prevents any degradation of the image that could arise from reactions between gas molecules and the sample.\(^4\) When the incident electrons hit the sample many photon and electron signals are discharged. These include cathodoluminescence, Auger electrons\(^5\), X-rays, primary backscattered electrons and secondary electrons. The latter two are the most often used in morphology studies.
Backscattered electrons are an example of elastic scattering (where no energy is lost when an electron enters the sample), the only change is in the momentum vector. Electrons in the beam are attracted to the atoms’ positively charged nucleus causing the ejection in a curved trajectory of that same electron at an unchanged velocity (Fig 3.3). The amount of backscattering is dependent on atomic number, with a larger atom having a higher chance of giving backscattering; this technique can therefore be used to gain an image of the elemental distribution in a sample. The backscatter electron detector is a disk placed over the sample in front of the objective lens, incident electrons pass though a hole in the centre onto the sample.

![Backscatter detector diagram](image)

*Fig 3.3. A schematic representation of a backscattered electron passing onto a detector.*

Weakly bound electrons in the conduction or valence bands of an atom may be expelled from the sample if beam electrons cause a powerful repulsion whilst passing through. The resulting emission is a secondary electron, which has less kinetic energy than the incident electron. Due to the relatively low speed of a secondary electron the positively charged secondary electron detector (SED) can easily capture them. The electrons extracted from cracks and corners are detected by the SED, giving a three-dimensional image and this technique is therefore useful for topographical studies. The intensity and formation of the final image is dependent on the number of secondary electrons that come from the surface of the sample. A secondary electron is one example of an inelastic interaction, others include
ionisation of inner shells, plasmon excitation (oscillations in the free electron gas of a metal), phonon excitation and X-ray generation.

3.2.2 X-ray microanalysis in electron microscopes.

Fig 3.4. Schematic representation of X-ray creation. An incoming high-energy electron (A) displaces an inner shell photoelectron (B) leading to an electron (C) inside the atom replacing the lost electron and creating an X-ray via fluorescence.

X-rays are a result of the inelastic collisions of electrons with the target atom in the sample (Fig 3.4) and can be collected by an energy dispersive X-ray detector (EDX). The X-rays pass through a window, which must be strong enough to support a vacuum. In this project a Pentafet Plus Si(Li) SuperATW window detector was used, although a beryllium window can be used. After the X-ray has passed through the window, it is converted into a pulse of electricity and this charge is converted to a voltage which is then amplified by a pre-amplifier. The stronger signal is then sent to a pulse processor where it is measured digitally and a spectrum is obtained using a Multi-Channel Analyser (MCA).

The X-rays are a combination of background radiation and characteristic radiation; these vary in energy between zero and that of the incoming electron. When the number of counts is plotted against energy, along with data obtained from the characteristic radiation, information
on the elemental composition is gained (Fig 3.5). The magnitude of the ‘Counts’ is related to
the concentration of the elements in the sample and the positions of the energy peaks identify
individual elements.

The values that are obtained can give information of the following type:-

1) Qualitative analysis, which determines the elements present. This is the principal use in
this project.

2) Quantitative analysis, which is achieved through the ZAF correction. To achieve a
quantitative analysis a large amount of data must be known about the sample. Geometry
of the bulk specimen must be known and the count rate depends on other elements in the
sample. A material must have a flat polished surface so that various penetration affects
can be measured. As the samples in this project show surface roughness this technique is
not strictly applicable.

Fig 3.5. Examples of EDX microanalysis spectra. (a) Plain Toray carbon paper and (b)
coated with poly pyrrole doped with 10-molybdo-2-vanadophosphoric acid.
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3.2.3 Results of scanning electron microscopy (SEM) on polymer electrodes.

The following are examples of the typical results obtained from analysis of the surface of the polymer coated Toray carbon papers. The images shown are only a small number taken from many scanned samples, results of EDX analysis are also presented. SEM experiments were carried out on a LEO 4401 with an Oxford Instruments Link ISIS X-ray microanalysis system (EDX).

Plain washed Toray carbon paper.

Plate 3.1. SEM images of the cross-section and surface of untreated Toray carbon paper.

SEM images of washed Toray carbon paper show a mesh (≈ 90 μm thick) of carbon fibrils (≈ 8 μm in diameter) giving the paper its strength (Plate 3.1). This tight network of carbon fibres allowed the polymer to form a complete coverage on the surface, making it suitable for use as an electrode support. X-ray microanalysis showed only one peak at 0.3 keV (for carbon Fig. 3.5a).
‘Hung’ coat samples.

Plate 3.2. SEM (secondary electron) images showing the successive coatings of Toray carbon paper with polypyrrole doped with 12-molybdophosphoric acid. Moving clockwise from top left, coatings 1 to 4 respectively.

Electrodes such as carbon paper coated with polypyrrole doped with 12-molybdophosphoric acid all gave very similar morphology results when grown using the ‘hung’ coating method (Plate 3.2). The first coating of the carbon paper showed the first signs of growth between the carbon fibrils. The second coat built on the first coat with a reduction in the carbon paper pores. The third coat showed a further closure of the pores, with plate-like coverage. The
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forth and final coat resulted in total coverage of a smooth ‘skin-like’ morphology. There
were small cracks and wrinkles of $\approx 2 \mu m$ and $\approx 4 \mu m$ in width, respectively. Further coats
were avoided, as this generally resulted in unpredictable rough powdery surfaces. A
wrinkled surface has also been observed in a detailed study into the electrochemical growth
of polypyrrole onto the surface of poly(methyl methacrylate) (PMMA).\textsuperscript{9} In the case of
polypyrrole electrochemically grown onto the surface of indium-tin oxide (ITO) anodes, the
wrinkles were attributed to the vertical growth of the polymer from the surface of anode.\textsuperscript{10}
This irregular three-directional growth was caused by small point areas on the anode, which
had higher conductivity than the rest of the electrode. This growth finally resulted in a
collection of Y- or T- shaped structures. The wrinkles in the chemically grown polymers
may originate from the multiple coating processes, which puts down layer after layer
building up various areas on the polymer surface. The chemically formed wrinkles and small
cracks may alternatively be attributed to the shrinkage caused by the drying of the electrode.
The backscattered image clearly shows the carbon paper fibrils where the polymer has not
fully coated, and the same wrinkled surface effects seen from the secondary image (Plate 3.3
left). The light shade of the polymer is due to the heavy molybdenum atoms in the included
heteropolyanions, which give strong backscattering intensities. The cross-sectional image
collected in backscatter mode highlights the polymer coating on the surface of the fibrils,
which is $\approx 2 \mu m$ in thickness (Plate 3.3 right). Other hung coat electrodes had polymer
thickness that varied in the range 1.5 - 5.0 $\mu m$.

The resultant coating of carbon paper by the poly(N-methylpyrrole) materials is again
smooth in all cases using the ‘hung’ coat method (Plate 3.4 left). In this instance the surface
is not as wrinkled as the polypyrrole coat, but there is still slight creasing forming out from
the carbon fibrils. A cross-sectional analysis shows the even formation of the polymer on
both sides of the carbon paper (Plate 3.4 right). In the growth of the polypyrrole and poly(N-methylpyrrole) coatings there is a lack of growth within the actual carbon paper with most of the polymer on the outer parts of the carbon paper. These voids arise from the pyrrole or N-methylpyrrole vapour having restricted access to the central portion of the carbon paper during polymer growth. One possibility is as follows; vapour coming into contact with the oxidant solution forms a thin film, which restricts the vapour penetration into the rest of the solution. The little vapour that did penetrate through the thin-film coating reduced the remaining oxidant, forming only short chain oligomers that were eventually removed in the washing stage. A similar observation had been made with the growth of the thin-films where the thin-film formed and the oxidant solution continued to react forming a strong blue solution of oligomers (see Chapter 2).

Plate 3.3. Toray carbon paper backscatter of hung samples 12-molybdophosphoric acid and polypyrrole; surface (left) and cross-section (right).

The carbon papers coated with either polypyrrole or poly(N-methylpyrrole) doped with any of the heteropolyacids gave light grey to shiny black coatings. This is also seen from the analysis of the thin-films (Chapter 2).
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Plate 3.4. SEM of carbon Toray carbon paper coated with poly(N-methyl pyrrole) doped with 12-molybdophosphoric acid.

During the initial coating potassium ferricyanide oxidant solution is repelled by the carbon paper. The opposite is true for the heteropolyacid-based oxidant solutions, which coat easily. This repulsion may explain why the multiple coating of the carbon papers with K$_3$Fe(CN)$_6$ was unsuccessful resulting in poor coverage and a slight nodular growth (Plate 3.5). It cannot be the growth process itself that gives this result as products of thin-film and direct addition K$_3$Fe(CN)$_6$ with pyrrole form just as readily as those using N-methylpyrrole with a selected heteropolyacid.

Plate 3.5. SEM images of Toray carbon paper coated with polypyrrole formed with K$_3$Fe(CN)$_6$ after first coat (left) and after fourth coat (right).
The polymer coatings made using iron(III) chloride gave very rough surfaces and appeared matt black when viewed with the naked eye (Plate 3.6). A similar observation had been made with the thin-film SEM analysis, which had shown a rough surface. This may cause problems during supercapacitor fabrication, as contact with the electrolyte will be poor.

Plate 3.6. SEM images of Toray carbon paper coated with polypyrrole doped with FeCl₃ after four coats.

‘Flat’ coated samples:

Unlike the ‘hung’ coated carbon papers, the ‘flat’ coating method resulted in unpredictable results. Although smooth surfaces formed occasionally, the general outcome was a rough pockmarked face on the side in contact with the vapour and a thick rough coating on the side which has contact with the glass (Plate 3.7). A nodular appearance is seen for coating of poly(N-methylpyrrole) doped with 12-molybdophosphoric acid on the side in contact with the glass, and each nodule as seen from the cross-sectional analysis is \( \approx 60 \, \mu\text{m} \) in diameter (Plate 3.8).
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Plate 3.7. SEM images of Toray carbon paper “flat” coated with polypyrrole doped with 12-molybdosilicic acid. Side exposed to vapour (left) and side in contact with the dish (right).

Plate 3.8. SEM images of Toray carbon paper “flat” coated with poly(N-methylpyrrole) doped with 12-molybdophosphoric acid: Cross-section SEM (left), surface in contact with the glass dish (right).
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Electrochemically grown polymer electrodes:

Plate 3.9. SEM backscatter analysis of polypyrrole doped with sodium dodecylbenzene sulfonate electrochemically grown onto Toray carbon paper, surface (left) and cross-sectional (right) images.

The electrochemical growth of polypyrrole and poly(N-methylpyrrole) doped with the surfactant sodium dodecylbenzene sulfonate (SDBS) resulted in a nodular growth outward from the carbon fibrils (Plate 3.9 left). The cross-section shows the extent of the growth is ≈70 µm thick (Plate 3.9 right). The nodules appear to have grown outward from the carbon fibrils with each nodule to be between 2 - 5 µm in diameter. The formation of these nodular growths, through micellar influence, has previously been studied by Noai, who grew the polymer and SDBS onto a indium tin oxide plate. The columnar structures of the doped polymer were thought to form independently of each other and grow directly upward. If the micellar concentration was large compared with the number of monomers, as was the case in experiments in this work, this would result in the stabilisation of the micelles on the surface of the electrode. An increase in the concentration of the pyrrole was observed at the electrode surface, as the monomers, which are hydrophobic in nature, are considered to be more soluble in the micellar assembly. Defects which arose in the aggregated micellar /
pyrrole layer during the passing of the current caused the pyrroles to aggregate into columnar structures. The columnar structures did not join together as there is electrostatic repulsion of the bi-layer on the surface of the column structures. These observations relate to the results seen in this work where, instead of a flat surface, columnar structures will have grown outward from the conductive carbon fibres.

**Energy dispersive X-ray analysis (EDX).**

EDX microanalysis of the polymer electrodes gave prominent peaks at 0.3 keV (carbon), 0.5 keV (oxygen), 2 keV (phosphorus) and 2.2 keV (molybdenum) for the polymer doped with 12-molybdophosphoric acid. Additionally, peaks attributed to other heteropolyacids are found at 0.85 keV (silicon) and 4.47 keV (vanadium). Qualitative analysis showed that all the required elements were present in the spectra; these are presented in appendix 4.

### 3.3 Infrared and elemental analysis of the polymer coated electrodes.

Infrared analysis was used for structural analysis of the polymer and to assess the environment of the heteropolyacid. Samples of the electrode were ground to a fine powder and then pressed with KBr to produce disks suitable for analysis. Reflectance infrared analysis was attempted, but the black nature of the electrodes resulted in low intensities. Experiments were carried out as before on a Nicolet 512P over 128 scans at a resolution of 2 cm⁻¹. Studies by Singh *et. al*¹³ and Kang *et. al*¹⁴ were used to assign the bands present in the spectra. Infrared bands found with the polymers doped with heteropolyacids are summarised in *Table 3.1*. The observations were as follows:
Chapter 3. The fabrication and testing of polymer coated carbon electrodes.

1) Polymers encapsulated with 12-molybdophosphoric, 10-molybdo-2-vanadophosphoric and 12-molybdosilicic acids, all gave peaks relating to the heteropoly anion centres.

2) Polymers with encapsulated 14-vanadophosphoric acid did not give the expected peaks, which indicates a breakdown in the heteropolyacid structure.

3) The polypyrroles doped with heteropolyacids containing phosphorus centres gave P-O stretching bands, which overlapped with the C-H band of the pyrrole ring. The overlap did not occur in the poly(N-methylpyrrole).

4) Peaks relating to polymer backbones were present in all of the electrodes (summarised in appendix 1, table A1.4 and A1.5).

<table>
<thead>
<tr>
<th>Heteropolyacid</th>
<th>M-O-M Edge share</th>
<th>M-O-M Corner share</th>
<th>M=O Terminal</th>
<th>Si-O</th>
<th>P-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-Molybdophosphoric</td>
<td>782</td>
<td>870</td>
<td>942</td>
<td></td>
<td>1062</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric</td>
<td>798</td>
<td>865</td>
<td>965</td>
<td></td>
<td>1062</td>
</tr>
<tr>
<td>12-Molybdosilicic</td>
<td>799</td>
<td>863</td>
<td>962</td>
<td>913</td>
<td></td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>Absent</td>
<td>Absent</td>
<td>964</td>
<td></td>
<td>1065</td>
</tr>
<tr>
<td>12-Molybdophosphoric</td>
<td>813</td>
<td>894</td>
<td>969</td>
<td></td>
<td>1074</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric</td>
<td>799</td>
<td>883</td>
<td>969</td>
<td></td>
<td>1071</td>
</tr>
<tr>
<td>12-Molybdosilicic</td>
<td>799</td>
<td>883</td>
<td>968</td>
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</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>Absent</td>
<td>Absent</td>
<td>Abrent</td>
<td></td>
<td>Absent</td>
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</table>

*Table 3.1. Main infrared bands (cm\(^{-1}\)) identified as belonging to the heteropolyacids encapsulated in the polymer matrix coating. Polymer on carbon paper support.*
Elemental analysis was carried out as before on each of the electrodes. This gave an indication as to the loading of the heteropolyacid in the polymer matrix; the result is quoted as a ratio between heteropolyacid and monomer unit in the following text. Details on the calculation of the ratio can be found in Chapter 2. The amount of polymer on the carbon paper is calculated from the nitrogen content figure. Elemental analysis of the electrodes lead to the following observations (Table 3.2):

1) Electrodes chemically grown with the iron(III) chloride were shown to have only small amounts of iron, which was effectively an impurity. This is because the iron(III) chloride does not become encapsulated within the polymer.

2) All polypyrroles doped with the heteropolyacids gave lower doping levels compared with the literature values\textsuperscript{15} (e.g. the ratio of 12-molybdophosphoric acid to pyrrole units is 1 : 12.8, whereas Gomez et. al, calculated a ratio of 1 : 9, with a single charge on every third pyrrole ring). The result indicates the charge on every fourth pyrrole ring, which has been indicated by others.\textsuperscript{16} The highest doping level obtained for doped polypyrrole was with 10-molybdoo-2-vanadophosphoric acid.

3) The level of encapsulation of heteropolyacids in poly(N-methylpyrrole) was higher than the polypyrrole derivatives. The better retention in the poly(N-methylpyrrole) has been seen previously for electrochemically grown electrodes containing iron and molybdenum based heteropoly acids.\textsuperscript{17}
<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Elemental analysis / %</th>
<th>Ratio*</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>C: 10.90; H: 0.96; N: 3.17; Mo: 20.31;</td>
<td>12.83 : 1</td>
</tr>
<tr>
<td></td>
<td>P: 0.49. Carbon paper ≈ 48.21.</td>
<td></td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>C:14.06 ; H: 1.27; N: 4.10; Mo: 24.24;</td>
<td>13.90 : 1</td>
</tr>
<tr>
<td></td>
<td>Si: 0.65. Carbon paper ≈ 39.12.</td>
<td></td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>C: 8.49; H: 0.92; N: 2.52; Mo: 16.98;</td>
<td>10.17 : 1</td>
</tr>
<tr>
<td></td>
<td>V: 1.20; P: 0.39. Carbon paper ≈ 53.1</td>
<td></td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>C: 10.08; H: 0.60; N: 2.94; V: 6.45; P: 0.31. Carbon paper ≈ 67.59.</td>
<td>23.22 : 1</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>C: 8.09; H: 0.55; N: 2.36; Fe: 0.11.</td>
<td>1027 : 1</td>
</tr>
<tr>
<td></td>
<td>Carbon paper ≈ 81.56.</td>
<td></td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td>C: 48.90; H: 5.40; N: 5.71; S: 4.36.</td>
<td>3.00 : 1</td>
</tr>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>C: 7.50; H: 0.83; N: 1.75; Mo: 21.19;</td>
<td>6.79 : 1</td>
</tr>
<tr>
<td></td>
<td>P: 0.49. Carbon paper ≈ 53.09.</td>
<td></td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>C: 6.47; H: 1.09; N: 1.51; Mo: 33.48;</td>
<td>3.71 : 1</td>
</tr>
<tr>
<td></td>
<td>Si: 0.91. Carbon paper 38.03.</td>
<td></td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>C: 8.49; H: 1.09; N: 1.98; Mo: 14.72;</td>
<td>9.21 : 1</td>
</tr>
<tr>
<td></td>
<td>V: 0.45, P: 0.42. Carbon paper ≈ 58.1</td>
<td></td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>C: 6.30; H: 0.54; N: 1.47; V: 2.68; P: 0.18 Carbon paper ≈ 83.30.</td>
<td>27.94 : 1</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>C: 17.66; H: 1.49; N: 4.12; Fe: 1.86.</td>
<td>106.1 : 1</td>
</tr>
<tr>
<td></td>
<td>Carbon paper ≈ 55.16.</td>
<td></td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td>C: 52.12; H: 5.32; N: 7.07; S: 3.19.</td>
<td>5.10 : 1</td>
</tr>
<tr>
<td></td>
<td>Carbon paper ≈ 13.17.</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2. Elemental analysis of the carbon paper electrodes coated with either polypyrrole or poly(N-methylpyrrole), each doped with a different oxidant. *Ratios are monomer units per counter anion.
3.4 Cyclic voltammetry and analysis of the lone electrodes\textsuperscript{18,19}

The single most important technique now used to study electrochemical redox processes is cyclic voltammetry (CV), which has in most cases replaced polography and was first used by the Czech chemist Jazroslav Heyrovsky in the early 1920's. The electrochemical phenomena that can be studied, range from simple electron transfers in inorganic chemistry to complex many electron mechanisms in biological processes. The popularity of CV is mainly due to the knowledge that has built up over years of study on voltammetric responses of redox processes. The information gained from CV provides an accurate method of determining the electrochemical processes present within a system.

A standard cyclic voltammetry experiment involves a cell made up three electrodes, a working electrode (WE), a reference electrode (RE) and an auxiliary electrode (AE), also known as a counter electrode. These electrodes are connected via a potentiostat, which gives an output to a XY recorder or computer. A voltage scan generator or ramp generator is joined internally or externally to the potentiostat; this allows a range of potentials to be scanned linearly at a given sweep rate. This is an important aspect of the method because the sweep rate controls the time scale of the experiment. The three electrode configuration is used as it overcomes a number of problems seen when the cell is under a large current. Only small currents are allowed to pass through the reference electrode, as any reaction at the reference will cause the reference potential to shift. Typically only nano amperes pass through a reference electrode, this is achieved by using an electrometer of high impedance. The third electrode is the AE, which receives current flowing from the WE such that negligible current flows through the RE. This action is achieved by using a potentiostat with a high impedance on the RE, forcing the current between the AE and WE. Secondly, it deals
with the increasingly high current, which causes a drop in the potential at the WE as a result of internal resistance in the electrolyte. That is, the applied cell voltage will be higher than that at the WE by an ohmic potential drop; the RE is placed as close to this WE as possible, to reduce the potential drop as to a minimum.

Starting at an initial potential of $E_i$, a linear potential ramp is applied to the WE causing capacitive charging of the electrochemical double layer. When the ramp reaches a switching potential $E_s$, the direction is reversed and potential is returned to its original value. The RE is used to give a value of the potential $E$ between the WE and AE, which would be impossible to measure if only the WE was used on its own. The potentiostat sets the potential difference $E$ to a required voltage $E_d$. The current, known as the excitation signal, is converted by the potentiostat using a current-follower into the voltage $E_i$. The measurement of the voltage sweep $E_d$ (x-axis) and the current as a voltage $E_i$ (y-axis) relative to the potential gives a plot in the form of a cyclic voltammogram. The appearance of this can vary a great deal, as there can be reversible, quasi-reversible and non-reversible (Fig 3.6a to c) processes.

![Cyclic voltammogram of a reversible reaction.](image)

**Fig 3.6a.** Cyclic voltammogram of a reversible reaction.
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Reversible reactions (Fig 3.6a).\textsuperscript{20}

For a reversible reaction the shape of the cyclic voltammogram is independent of the scan rate and will only vary in current density. If $i / \nu^{1/2}$ is plotted verses $E$ (where $i$ is the current, $\nu$ is the scan rate and $E$ is the potential) then the voltammograms should be identical. A typical cyclic voltammogram for a 1 e\textsuperscript{-} transfer is shown in Fig 3.6a. Reversible reactions carried out at 298 K can be identified using a set of diagnostic tests (symbols refer to those given for Fig 3.6a);
1) \[ \Delta E_p = E_{pA} - E_{pc} = 2.3RT / nF = 0.059 \, \text{V} / \, n \] (Where \( \Delta E_p \) is the potential separation, \( E_{pA} \) anodic potential, \( E_{pc} \) cathodic potential, \( R \) is the gas constant, \( n \) is the number of electron transferred and \( F \) is the Faraday constant).

2) \[ E_p - E_{p/2} = 0.059 \, \text{V} / \, n \] (where \( E_{p/2} \) is the half wave potential)

3) \[ -i_{pc} / i_{pa} = 1 \] (where \( i_{pc} \) is the cathodic current response and \( i_{pa} \) the anodic response both opposite signs)

4) \[ i \propto v^{1/2} \]

5) \( E_p \) is independent of \( v \).

6) \[ i^2 \propto t \] at potentials beyond \( E_p \).

The formal electrode potential may be calculated from a reversible cyclic voltammogramme (Eqn 3.1);

\[ E^\circ = (E_{pa} + E_{pc}) / 2 \]

*Eqn 3.1*

And the diffusion may be calculated using the Randles-Sevick equation for a mobile active component (Eqn 3.2);

\[ i_p = 0.446nF(nF/RT)^{1/2}AD^{1/2}v^{1/2} \]

*Eqn 3.2*

where \( A \) is the area of the electrode and \( D \) is the diffusion coefficient. The plot of \( i_{pa} \) vs \( v^{1/2} \) is linear for a diffusion limited / solution species. If the electroactive species is immobilised on an electrode the equation for the peak potential becomes,

\[ i_p = n^2F^2\alpha C_{surf}v / 4RT \]

*Eqn 3.3*
where $\alpha$ is the area under the peak and $C_{\text{surf}}$ is the concentration of immobilised species on the surface of the electrode. The current response, $i$ at any point on the curve is proportional to $v$, where as in the diffusing case (*Eqn 3.4*) $i$ is proportional to $v^{1/2}$. The plot of $i_{pa}$ verses $v$ is linear for a surface confined species.

**Quasi reversible (Fig 3.6b).**

For a quasi reversible reaction the electron transfer is appreciably slow compared with the reversible case. From the diagnostic tests used to identify a reversible systems for a $1e^-$ transfer at 298K would be $\Delta E_p > 0.059$ V; the peak current ratio $-i_{pc} / i_{pa} < 1$; and $E_p$ is dependent on $v$. For a reaction to happen which involves quasi reversibility, a small amount of potential in addition the thermodynamically required potential value. This value known as overpotential, results in the cathodic peak shifting to more negative values. (Reversible reactions do not require overpotential, driven only but thermodynamic potential).

**Irreversible reactions (Fig 3.6c).**

This arises when a reaction involves very slow kinetics or if the scan rate is increased to such a speed as to prevent equilibrium of electron transfer. In an irreversible reaction the overpotential is much greater than that required for a quasi reversible reaction. This results in a cyclic voltammogram, which is completely distorted, with the cathodic peak at a very negative potential to the anodic peak.
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The diagnostic steps for an irreversible reaction are:

1) \[ \Delta E_p = E_{pA} - E_{pc} \gg 0.059 \text{ V} / n \]
2) \[ E_p - E_{p/2} = 0.048 \text{ V} / \alpha n \]
3) \[ -i_{pc} / i_{pa} = 1 \]
4) \[ i_p \text{ increases with } v. \]
5) \[ E_p \text{ shifts with increasing } v. \]

The reproducibility of the voltammogram is dependent on the purity of the electrolyte, the identity of the electrode material, the scan rate and the switching potentials.

An electrode that is considered suitable for the construction of a supercapacitor must be electronically conducting and show an almost reversible image in its cyclic voltammogram over a reasonable potential range. Pseudocapacitance gives cyclic voltammograms which become less reversible as \( s >> s_0 \) (where \( s \) is the sweep rate and \( s_0 \) is the critical sweep rate at which the oxidation and reduction electron transfers become reversible).

When assembling the cell it is important to remove as many of the impurities as is possible, as even trace amounts will affect the appearance of the final cyclic voltammogram. On reduction in the range of -0.2 to -0.8 V oxygen gives water and \( \text{H}_2\text{O}_2 \).

This means oxygen is electrochemically active and therefore must be removed from aqueous solutions; water must similarly be removed from aprotic solvents. Prior to electrochemical analysis, lone electrodes were soaked overnight in aqueous sulfuric acid (1.2 mol dm\(^{-3}\)). The electrode was then placed in the glass cell containing aqueous sulfuric acid (1.2 mol dm\(^{-3}\)) electrolyte, which was purged of air using flowing nitrogen gas. During the experiment, nitrogen was slowly bubbled through the acid to prevent the adsorption of air. The auxiliary electrode was
a home-made coiled platinum electrode wire (0.4 mm diameter and 290 mm length) (Heraeus). Measurements were taken against a Ag / AgCl reference electrode (197 mV against SHE) (Bioanalytical Inc., with NaCl(aq), 3 mol dm$^{-3}$). The instrument used was an analogue Princeton EG&G 173 potentiostat / galvanostat coupled with a Sycope PC-100 which generated a digital signal suitable for full computer control. To study the reversibility and redox reactions of the electrodes the scan rates were; 1, 10 and 100 mV s$^{-1}$.

The CV taken at 1 mV s$^{-1}$ are shown (Fig 3.14 to 3.25). The cyclic voltammograms are given against two y-axes, firstly $A g^{-1}$ of electroactive material (unit mass of polymer coating) and secondly $A cm^{-2}$ of the geometrical area of the electrode. Where possible, capacitances are calculated from the mean of the magnitude of the oxidation peak and the corresponding reduction peak. Full peak positions (Table A3.1 to A3.3) and specific capacitances are tabulated in appendix 3 (Table A3.4 to A3.6) and are referred to in the text as necessary. The voltage peak separation between the oxidant peak and the corresponding reduction curve, which indicates reversibility, is given as the mean of the peak separations for each scan rate (if more than one present). The top, positive in current, sweep relates to the oxidation of the polymer and dopant (if active) and the bottom sweep is the reduction.

Electrode coatings are the polymers polypyrrole (Ppy) and poly(N-methylpyrrole) (Pmpy) grown with various oxidants. Capacitance of the lone electrode was calculated from the cyclic voltammogram using the equation (Eqn. 3.1):

$$C = \frac{i}{s}$$  \hspace{1cm} \text{Equation 3.4}

where $C$ is the capacitance in farads (F), $i$ is the mean peak current in amperes (A) of the maximum and minimum and $s$ is the scan rate in V s$^{-1}$. Results of capacitance are given per unit mass of the redox-active polymer and per unit area of the electrode [the area of the electrode is the geometrical area and does not take account porosity or surface roughness].
Chapter 3. The fabrication and testing of polymer coated carbon electrodes.

Results of the cyclic voltammetry are as follows:

1) The cyclic voltammograms for the Toray carbon paper, measured at 100 to 1 mV s⁻¹, show a reversible response typical of a carbon double layer response (Fig. 3.7). The shape and peaks, which are clearly seen in the oxidation scan at 500 mV, relate to the small amount of pseudocapacitive charge obtained from the carbon electrode which was previously observed with glassy carbon and activated carbon felt.²², ²³ The pores in the carbon paper, as seen from the scanning electron microscopy (Plate 3.1), are very large and therefore do not hinder the movement of the electrolyte. The capacitance arising from the double layer interaction is low 3.0 x 10⁻⁴ F cm⁻² for 10 mV s⁻¹.

![Fig 3.7. CV's of Toray carbon paper, showing results for various scan rates.](image)

2) The polypyrrole electrodes containing 12-molybdophosphoric (Fig. 3.11 to 3.13), 12-molybdsilicic (Fig. 3.20) and 10-molybdo-2-vanadophosphoric (Fig. 3.22) anions all gave three characteristic peaks in their cyclic voltammograms. These peaks associated with the heteropolymetallates reducing to more negative anions and the reverse on the oxidation cycle. Peaks associated with the polypyrrole were not visible, this being due to
dominant heteropolyacid peaks. The three peaks and their positions compare favourably with work done by Gómez-Romero et. al and Wang et. al, who studied both electrochemically and chemically grown polypyrrole doped with 12-molybdophosphoric acid. Their work also agrees with the observation that the 12-molybdophosphoric acid becomes entrapped within the polymer, as a result of its size and high charge. This prevents the complete exchange with HSO₄⁻ ions and results in stabilised CVs.

3) When a heteropolyacid in solution is reduced, it is changed to a more negatively charged species. When a heteropolyacid is encapsulated in polypyrrole (Ppy) and poly(N-methylpyrrole) (or aniline) the overall charge is maintained by the simultaneous stabilisation from protonation by the polymer backbone. For example, in the case of 12-molybdophosphoric acid the charge is kept at -3 as in the formula Ppy.[PMo₁₂O₄₀]⁻³ (Fig. 3.8). The 10-molybdo-2-vanadophosphoric acid has previously been encapsulated in polyaniline, another well studied conductive polymer. It was noted that the vanadium is reduced first (with more ease than the molybdenum) within any heteropolyacid which contains a phosphorus heteroatom (Fig. 3.10). The electron and protonation schemes for the polypyrroles doped with heteropolyacids are shown over (Fig 3.8 to 3.10).

The peak positions are in the same order for all the polypyrroles and poly(N-methylpyrrole)s doped with 12-molybdophosphoric acid, 10-molybdo-2-vanadophosphoric acid and 12-molybdosilicic acids. CVs of electrodes coated with polypyrrole doped with 12-molybdophosphoric acid (Fig. 3.11 to 3.13) are shown as examples and are compared with the corresponding charge transfer mechanism using A, B and C on the oxidation curve and A', B' and C' on the reduction curve (Fig 3.11 to 3.13).
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A. \[ \text{PPY.}[\text{PMo}_{12}\text{VI}O_4]^{3-} \xrightleftharpoons{+2e^- , +2H^+}{-2e^- , -2H^-} \text{PPY.H}_2[\text{PMo}_{10}\text{VI}Mo_2\text{V}O_4]^{3-} \]

B. \[ \text{PPY.H}_2[\text{PMo}_{10}\text{VI}Mo_2\text{V}O_4]^{3-} \xrightleftharpoons{+2e^- , +2H^+}{-2e^- , -2H^-} \text{PPY.H}_4[\text{PMo}_8\text{VI}Mo_4\text{V}O_4]^{3-} \]

C. \[ \text{PPY.H}_4[\text{PMo}_8\text{VI}Mo_4\text{V}O_4]^{3-} \xrightleftharpoons{+2e^- , +2H^+}{-2e^- , -2H^-} \text{PPY.H}_6[\text{PMo}_6\text{VI}Mo_6\text{V}O_4]^{3-} \]

Fig 3.8. Mechanism for the reduction and oxidation of electrodes coated with
12-molybdophosphoric acid doped polypyrrole.

A. \[ \text{PPY.}[\text{SiMo}_{12}\text{VI}O_4]^{4-} \xrightleftharpoons{+2e^- , +2H^+}{-2e^- , -2H^-} \text{PPY.H}_2[\text{SiMo}_{10}\text{VI}Mo_2\text{V}O_4]^{4-} \]

B. \[ \text{PPY.H}_2[\text{SiMo}_{10}\text{VI}Mo_2\text{V}O_4]^{4-} \xrightleftharpoons{+2e^- , +2H^+}{-2e^- , -2H^-} \text{PPY.H}_4[\text{SiMo}_8\text{VI}Mo_4\text{V}O_4]^{4-} \]

C. \[ \text{PPY.H}_4[\text{SiMo}_8\text{VI}Mo_4\text{V}O_4]^{4-} \xrightleftharpoons{+2e^- , +2H^+}{-2e^- , -2H^-} \text{PPY.H}_6[\text{SiMo}_6\text{VI}Mo_6\text{V}O_4]^{4-} \]

Fig 3.9. Mechanism for the reduction and oxidation of electrodes coated with
10-molybdo-2-vanadophosphoric acid doped polypyrrole.

A. \[ \text{PPY.}[\text{PMo}_{10}\text{VI}V_2\text{IV}O_4]^{5-} \xrightleftharpoons{+2e^- , +2H^+}{-2e^- , -2H^-} \text{PPY.H}_2[\text{PMo}_{10}\text{VI}V_2\text{IV}O_4]^{5-} \]

B. \[ \text{PPY.H}_2[\text{PMo}_{10}\text{VI}V_2\text{IV}O_4]^{5-} \xrightleftharpoons{+2e^- , +2H^+}{-2e^- , -2H^-} \text{PPY.H}_4[\text{PMo}_8\text{VI}Mo_2\text{V}_2\text{IV}O_4]^{5-} \]

C. \[ \text{PPY.H}_4[\text{PMo}_8\text{VI}Mo_2\text{V}_2\text{IV}O_4]^{5-} \xrightleftharpoons{+2e^- , +2H^+}{-2e^- , -2H^-} \text{PPY.H}_6[\text{PMo}_6\text{VI}Mo_6\text{V}_2\text{IV}O_4]^{5-} \]

Fig 3.10. Mechanism for the reduction and oxidation of electrodes coated with
12-molybdosilicic acid doped polypyrrole.
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Fig 3.11. CV of electrode run at 100 mV s\(^{-1}\). Electrode coating: polypyrrole doped with 12-molybdophosphoric acid.

Fig 3.12. CV of electrode run at 10 mV s\(^{-1}\). Electrode coating: polypyrrole doped with 12-molybdophosphoric acid.

Fig 3.13. CV of electrode run at 1 mV s\(^{-1}\). Electrode coating: polypyrrole doped with 12-molybdophosphoric acid.
4) A lowering of the scan rate from 100 to 1 mV s\(^{-1}\) results in an increased reversibility of the electrodes. For polypyrrole doped with 12-molybdophosphoric acid (Fig 3.11 to 3.13) \(\Delta E_p\) for 100 mV s\(^{-1}\) = 196 to 212 mV, \(\Delta E_p\) for 10 mV s\(^{-1}\) = 92 to 97 mV and \(\Delta E_p\) for 1 mV s\(^{-1}\) = 43 to 45 mV (the separation for a reversible 2e\(^{-}\) reaction is \(\Delta E_p\) = 30 mV). This was due to the diffusion caused by the slow electron transfer reactions seen with these thick film polymers. The chemically grown films in this work are considered thick and this results in the electron transfer reactions becoming dependent on the diffusion through the active material coating on the carbon paper electrode.\(^{28}\)

5) Polypyrrole based polymers in general gave the highest capacitances per unit area and mass. The exception was poly(N-methylpyrrole) doped with 12-molybdosilicic acid. For polypyrrole doped with 10-molybdo-2-vanadophosphoric acid the reduction in scan rate to 1 mV s\(^{-1}\) gave an increase in the individual specific capacitance of the electrode, with the peak specific capacitances (occurring at 409 mV on the oxidation curve, second redox peak) of 776 F g\(^{-1}\) and 0.79 F cm\(^{-2}\) (Fig. 3.22). This was the highest value for both the specific capacitance per unit mass and geometrical area of all the polymers (this heteropolyacid is considered to be the most stable in this work, and high doping levels may also be a contributory factor).

6) The poly(N-methylpyrrole) electrodes containing 12-molybdophosphoric (Fig. 3.19), 12-molybdosilicic (Fig. 3.16) and 10-molybdo-2-vanadophosphoric (Fig. 3.23) anions all gave three characteristic peaks in their cyclic voltammograms. The peaks were generally better defined than with the polypyrrole based coatings. The heteropolyacids, 12-tungstophosphoric acid and 12-tungstosilicic acid, have also been encapsulated within a poly(N-methylpyrrole) by Bidan et. al.\(^{29}\)
7) Electrochemically grown polypyrrole doped with SDBS (Fig. 3.14) and polypyrrole chemically grown with iron(III) chloride (Fig. 3.16) or 14-vanadophosphate (Fig. 3.24) gave only one visible peak, showing only one electron transfer reaction present. The electron transfer was attributed to the polypyrrole, which is similar to that found in the literature. 30

8) Electrochemically grown poly(N-methylpyrrole) (Fig. 3.15) and poly(N-methylpyrrole) chemically grown with iron(III) chloride (Fig. 3.17) or 14-vanadophosphate (Fig. 3.25) gave irreversible profiles. This indicates the likelihood of poor cycling in the capacitor devices.
Key to the CV figure numbers: carried out at 1 mV s$^{-1}$, of carbon paper electrodes with polymer coatings chemically and electrochemically grown:


3.15. Electrode coating: poly(N-methylpyrrole) with sodium dodecylbenzene sulfonate.

3.16. Electrode coating: polypyrrole with iron(III) chloride.

3.17. Electrode coating: poly(N-methylpyrrole) with iron(III) chloride.

3.18. Electrode coating: polypyrrole with 12-molybdophosphoric acid.


3.20. Electrode coating: polypyrrole with 12-molybdosilicic acid.


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3.14

3.15

3.16

3.17

3.18

3.19

potential / mV
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3.20

3.21

3.22

3.23

3.24

3.25
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3.5 Conclusions.

Chapter 3 has discussed the use of results from a series of investigations (carried out in Chapter 2) to achieve successful growth of the polymer coatings onto the surface of the carbon paper support. Using a variety of analytical techniques, information on the coatings has been obtained, especially from scanning electron microscopy (SEM), which allowed the study of the morphology of the supported polymers. Infrared spectroscopy, elemental analysis and X-ray microanalysis provided the compositional data of the electrode materials. The successful development of the lone electrodes allowed the electrochemical study of the supported polymers that had a variety of encapsulated dopants. The conclusions drawn from the results are as follows:

1) The successful transfer of the chemical growth of unsupported thin films (Chapter 2) onto growth on the surface of a support was observed for nearly all of the monomer / oxidant combinations. All polymers gave good adhesion to the surface of the carbon paper. The number of coatings varied depending on the monomer used; generally pyrrole required four coatings and poly(N-methylpyrrole) required five coatings.

2) Heteropolyacid dopants were permanently anchored within the polymers as a result of their size and charge. On reduction, the charge was stabilised by the simultaneous protonation from the polymer backbone.

3) Smooth and complete polymer coatings were formed via “hung coating” chemical methods with 12-molybdophosphoric, 12-molybdosilicic, 10-molybdo-2-
vanadophosphoric acids and 14-vanadophosphate (Plate 3.2 to 3.4). This should ensure good contact with the current collector and a solid electrolyte.

4) "Flat coat" systems were rough and irreproducible and would result in poor contact with the electrolyte. This method of fabrication was not used from this point onward.

5) Polymer coatings acquired through chemical growth of iron(III) chloride were very rough in appearance (Plate 3.6). This would inhibit their use as electrodes in the fabrication of capacitor devices, as a good contact with both the electrolyte and current collector is highly important.

6) The unsuccessful formations included polymers grown with potassium ferricyanide, which gave only poor coverage after four coats (Plate 3.5). This combination will not be studied further.

7) Polypyrrole and poly(N-methylpyrrole) were successfully electrochemically grown onto carbon paper using sodium dodecylbenzene sulfonate as a dopant. Surfaces were nodular and complete (Plate 3.7), as previously observed and discussed by Noai and co-workers. 

8) The development, fabrication and electrochemical testing of the lone electrodes was successful. The simple method of construction allowed easy coating and provided reproducibility when fabrication was performed with a constant atmosphere and temperature.
9) The cyclic voltammetry of the single electrodes gave information on the electron transfer reactions and specific capacitance. Polypyrrrole doped with 10-molybdo-2-vanadophosphoric acid gave the individual specific capacitance of the electrode of 776 F g\(^{-1}\) and 0.79 F cm\(^{-2}\). This was the highest value for both the specific capacitance by unit mass and by geometrical area of all the polymer coated electrodes.

All combinations of materials, except polymers incorporating potassium ferricyanide, were taken forward to study in potential capacitor devices. Although many of the chosen polymers give irreversible cyclic voltammograms, they may prove useful in comparison devices.
3.6 References.


4 Fabrication and investigation of single cell supercapacitors.

4.1 Existing cell designs that are relevant to the project.

There are few literature discussions of the construction of supercapacitor cells. This could be seen as a problem, as it is not just the chemical nature of the capacitor but also the geometrical construction of the cell that can determine the final performance. The chemical literature often fails to mention this important factor. There are, however, several patents that include a description of the cell design and various conference proceedings that have discussed the topic. Some examples of cell designs are discussed below.

The most convenient starting point for construction of the capacitors in this project was a simple single cell type in which the polymer coated carbon papers press onto a solid electrolyte. Although single cells provide no usable benefit for energy storage or useful capacitance levels, they do allow the careful study of electrode / electrolyte configurations, allowing the rational design of later devices. General one-cell designs use a sandwich configuration in which electrodes are separated by a solid polymer or a separator impregnated with either a liquid or gel electrolyte. Electrodes can be polymeric, metallic, metal oxide or carbon based. An example of a single coin cell supercapacitor was patented by Yen and co-workers, who developed a design made up of two metallic carbon electrodes separated by a polymer film which contained a non-aqueous solution of conducting salts. Other examples of coin cells include a polyacenic semiconductor on aluminium current collector foil (these have been compared with roll designs) and coin capacitors using polymer electrodes. The Evans Company often gives details of cell designs, such as carbon supercapacitors, and compares a standard packaging and a sealed design. The standard design, often used by manufacturers, comprises conductive rubber current collectors and
rubber gasket seals, which are placed inside a metal casing. Leakage was found to occur through the rubber seals at temperatures above 80°C, limiting the capacitors' use. Using a laser welded hermetic casing prevented leakage of the electrolyte. However, this was found to cause further problems with the associated pressure build up of carbon dioxide within the chamber; to overcome this problem the pressure was alleviated using a permselective valve, which allowed gases to escape but prevented leakage of electrolyte. Another Evans design is the tantalum hybrid design in which a folded tantalum foil (acting as the negative current collector) coated with ruthenium oxide is wrapped around a tantalum pellet (the positive electrode). The device was laser sealed with a positive feed wire from the positive electrode. The electrolyte was sulfuric acid gelled with fused silica, giving a device with a capacitance of 7.1 mF at 5.5 V. For further tests three electrode capacitors were used, an example using vanadium pentoxide as electrode material in two- and three-electrode devices. The two-electrode device was used in a.c. impedance and galvanic cycling tests. Cyclic voltammetry in the three-electrode design was taken using a lithium reference sandwiched in a glass fibre separator soaked in lithium perchlorate electrolyte solution.

Although only a single cell configuration is studied in this work, Chapter 1 has some detail of the use of bipolar and roll designs (in series and parallel) which give more practically useful supercapacitors. Bipolar stack and roll configurations utilising nickel oxide electrodes were used to assess a range of current collectors. The roll capacitor gave enhanced capacitance due to the increased geometrical area of the electrodes; this design was easily fabricated, as the chosen current collector was nickel foil. Similar comparisons have been made with carbon based designs. In bipolar stack designs using a rigid nickel mesh as the current collector and carbon based electrodes, the main problem arose from leakage of the electrolyte materials caused by over pressurisation. Other comparisons have been made with
ruthenium oxide from which supercapacitors were constructed using spiral wound and coin configurations.¹⁵

4.2 Nafion®-based polyelectrolytes for use within the membrane electrode assemblies.

The development of proton conductors has been motivated by the need to replace methods of energy production that can produce large volumes of noxious gases (e.g. CO₂ and NOₓ), such as the internal combustion engine and fossil fuel burning power generation. Devices utilising proton conductors work by converting chemical energy into electrical energy, overcoming the inefficient thermodynamic (constant limited) combustion processes. Proton conductors are being used in electrochromic devices¹⁶, fuel cells¹⁷, batteries, high temperature work¹⁸ and supercapacitors¹⁹. The most useful solid polyelectrolyte for this project is the commercially available polyelectrolyte Nafion® 115, (Fig 4.1). The number 115 represents an equivalent weight of 1100 and a thickness of 5 x 25 µm (≈ 125 µm when dry).²⁰

\[
\text{H}_2\text{O} \quad \text{H}_2\text{O} \\
\text{H}_2\text{O} \\
\text{H}_2\text{O}
\]

\[
\begin{array}{c}
\text{H}_2\text{O} \\
\text{H}_2\text{O} \\
\text{H}_2\text{O}
\end{array}
\]

(a) Structure of Nafion® and (b) schematic representation of the internal phase distribution of H₂O and polymer chains. Hydrophobic medium with hydrophobic channels formed by −SO₃H + H₂O.
Nafion®, a perfluorosulfonic acid membrane, is one of the most studied of the solid electrolytes which was developed as a solid proton conductor for 1972 Gemini earth-lunar fuel cell system. Du Pont manufacture the Nafion® membrane, which is available in several different forms (e.g. Nafion® 112, 115 and 117).

Nafion® is made through a series of complicated steps, which include the rearrangement of a cyclic sultone and copolymerisation; the resulting XR resin is hydrolysed to form the membrane. This process gives a long-chain thermoplastic with a fluorinated carbon backbone that has good chemical resistance and is thermally inert. The membrane’s backbone is branched, with fluorinated ether chains at various intervals terminated with sulfonic acid bunches that are distributed randomly leading to effective proton transport in moist films (Fig. 4.1a.). These ionisable acid groups are in contact with zones of counterions and water (enabling strong acid behaviour), which are linked by channels forming an inverted micellar structure; this is referred to as the three-phase model (Fig. 4.1b).

The conduction mechanism in Nafion® as an electrolyte has been extensively studied using conductivity and NMR methods. The ability of the protons to move within the Nafion® relies on the amount of water present; this does not need to be very high as the water, the second phase, has an effective phase separation. Mineral acids are often used in a pre-treatment of Nafion® as they heighten initial conductivity, which may then decrease on d.c. use. The effect of pre-treatment is most pronounced at T > 260 K as the amount of water that can be present in the pores increases and leads to lowered conductivity activation energy. This movement of protons is directly related to the number of sulfonic acid sites, controlling the equivalent weight for the Nafion®. As the equivalent weight decreases, the degree of crystallinity increases and conductivity rises due to the water in the membrane.
becoming more liquid-like. Conduction in Nafion® is related to the diffusion of the hydrated protons; these are present in many forms, including H$_3$O$^+$ and H$_5$O$_2^+$. There are two modes of proton transfer in the membrane; these are as follows:

1. Conduction involving counter ions, protons with other cations and lone protons. These included the jumping of protons from one nearby sulfonic group to another via H$_2$O.

2. Sorbed acids may be dissociated, forming anionic species that can add to the conduction process. In water-rich Nafion® various species, such as H$_3$O$^+$ and H$_5$O$_2^+$, transfer protons to and from the polymer chain by rotation and proton hopping. This transfer of species is known as the Grotthus mechanism and involves a proton jump at a critical distance of 2.8Å, which has been previously confirmed by infrared spectroscopy. The Grotthus mechanism has been observed for other electrolyte materials such as CsHSO$_4$, (BPEI)$_x$H$_2$SO$_4$ (BPEI is branched polyethyleneimine) and (PAAM)$_x$H$_2$SO$_4$. (PAAM is polyacrylamide)

The use of Nafion® is not restricted to electrolyte applications; the membrane can also be used as a permselective cation-exchange membrane. An example in the chlor-alkali industry is the membrane preventing the flow of hydroxyl and chloride ions (allowing only sodium cations to pass through). The main problem for large-scale applications utilising Nafion® is the cost of fabricating the membrane. Future development of cheaper membranes will require a better understanding of the conduction processes within the system. Future alternatives may come from grafted polystyrene sulfonic acids, which at the time of writing are still under development but may suffer from long term lack of durability in use.
this work Nafion® will be used as a standard electrolyte, allowing each of the different electrode systems to the studied on the same basis.

Prior to use within the supercapacitor cells, Nafion® 115 was pre-treated: Nafion® 115 (donated by Innogy Technology Ventures Limited) was cut into squares of 1.5 x 1.5 cm². Membranes were boiled in hydrogen peroxide (30% by volume) for 5 h and then washed three times in boiling deionised water. The Nafion® was then refluxed in aqueous nitric acid (4 mol dm⁻³) for 3 h to fully acidify the sulfonic acid groups. The washing process with water was repeated as above, and membranes were stored in deionised water until required.

![Graph showing conductivity and thickness of T Nafion and UT Nafion](image)

**Fig 4.2.** Conductivity tests carried out on Nafion® 115 at various humidity levels (@ 24 °C). Treated (T) and untreated (UT) Nafion® 115.

The conductivity and thickness of the treated Nafion® are compared to untreated membrane (Fig. 4.2). It was found that the treatment of the Nafion® increased the conductivity at high relative humidities, this being due to the removal of organic impurities and further
conversion to sulfonic acid groups. It was noted that the thickness of the untreated Nafion®, unlike the treated form, did not reach the optimum 150 µm. This difference in thickness was an indication that the pores within the Nafion® swell during treatment, allowing more water molecules to interact with the bound ion exchange groups, leading to a further increase in conductivity. Conductivity measurements were carried out in a two-electrode test cell as explained later.

4.3 Fabrication of the single cell using a hot-press method.

The cells were fabricated using a hot pressing method, a simple technique giving reproducibility of the final supercapacitor. The following procedure was developed and used as a protocol:

1) The electrodes were cut onto a plastic sheet from the rectangular coated carbon papers using a carefully machined cork borer. Electrode disks were 1.35 cm in diameter (area 1.42 cm²).

2) The electrodes were washed for 1 h in refluxing water and refluxing ethanol to remove any remaining heteropolyacid residue and loose polymer fragments.

3) The electrodes were dried in air and then matched by mass (to within +/- 0.5 mg) so that the electrodes would form a symmetrical construction on fabrication.
4) One side of each circular electrode was coated several times with perfluorinated Nafion® milk (5 % mass in mixed alcohols, Aldrich) and dried between each coat until 0.7 mg cm\(^{-2}\) of Nafion® was deposited.

5) A rectangle of Nafion 115® (2.25 cm\(^2\)) was sandwiched between two electrodes. This membrane-electrode assembly (MEA) was then placed between thin PFTE sheets and put into the pressing device, a KBr disk press with two aluminium heater plates and insulating mats that prevented heat transfer to the press (Fig 4.3).

6) The cell was pressed for 15 min under 1 T cm\(^{-2}\) at 70\(^{\circ}\)C (temperature control provided by a Eurotherm 1115 controller with heater elements and a thermocouple).

7) After pressing, the cell was cut from excess Nafion® 115 using a cork borer to give MEAs 1.51 cm in diameter (area 1.79 cm\(^2\)). The cell was then hydrated overnight in deionised water and placed into a two-electrode test cell for charge / discharge analysis (the in-house developed two-electrode test cell is discussed later in the chapter).

Fig 4.3. Schematic of hot pressing, with the supercapacitor membrane-electrode assembly (MEA) in the centre. (a) heat resistant mat, (b) PTFE sheet, (c) disk press, (d) thermocouple and (e) membrane electrode assembly.
4.4  Analysis and results for MEA test cells.

Many techniques can be used to study supercapacitors, and all have their individual advantages. Within this project four electrochemical methods were chosen to yield information concerning the charge transfer, capacitance, stability, resistance, reproducibility and effectiveness of the MEA configuration. The results that are given use the analytical techniques of scanning electron microscopy (SEM), cyclic voltammetry (CV) and a.c. impedance measurements. These are all discussed briefly. Charge / discharge and open circuit studies are presented in Chapter 5.

4.4.1  Scanning electron microscopy.

Scanning electron microscopy (SEM) has already been introduced (Chapter 3), highlighting its value in identifying a satisfactory electrode surface. The heavy elements that are present, in this case molybdenum (and sometimes vanadium), affect the appearance of the polymer, giving it a light hue. This phenomenon, which is caused by the backscattering of electrons, can be put to good use when viewing the cross section of a supercapacitor (Plate 4.1). To fabricate the sample for cross-sectional SEM, the supercapacitor MEA was moulded into epoxy resin and then sliced cleanly to form an acceptable surface for analysis.

The cross-section of the supercapacitor device showed good contact between the Nafion® and the polymer electrodes. The polymer coating in this case was ≈ 15 µm thick on the carbon paper. The thickness of the carbon weave decreased by over 30% from ≈ 90 to ≈ 60 µm due to the compression on hot pressing. The Nafion® was compressed to ≈ 115 µm thick, lower than any of the unpressed Nafion® membranes tested at various humidities (Fig. 4.2). Total MEA thickness is ≈ 0.3 mm.
Plate 4.1. Cross-sectional SEM images of a typical hot-pressed MEA in backscattered mode.

This example is of two ‘hung’ coated carbon paper electrodes impregnated with polypyrrole doped with 12-molybdophosphoric acid. Nafion® 115 is the sandwiched electrolyte.

4.4.2 Electrochemical methods discussed.

To characterise a supercapacitor cell a number of electrochemical procedures are used to give information on its stability, charging etc. These include:

- Cyclic voltammetry. This has already been introduced (Chapter 3) as a useful technique for defining the effect of heteropolyacid inclusion in the polymer. Here it provides an insight into the capacitor type and determination of the associated capacitance.
- AC impedance will give details on the MEA and associated resistances in the cell.
- Charge / discharge curves. These will give information on capacitance, internal resistance and power / energy storage and are discussed in Chapter 5.
- Open circuit (self-discharge). This indicates how potential varies as a function of time at zero current and is discussed in Chapter 5.
4.4.3 Cyclic voltammetry in the design of test cells.

A small modification of the cell assembly was made during the hot pressing procedure; a small piece of electrode was removed to form an area on which a reference electrode may contact the solid electrolyte (Fig 4.4). A small rectangular piece of PTFE sheet was used to ensure that the Nafion® membrane was pressed onto the lower electrode. The pressing then followed in the usual manner.

![Figure 4.4](image.png)

Fig 4.4. Schematic to show the removal of a small piece of electrode from the working electrode side. The brown rectangle represents a slice of PTFE, which helped to maintain the 1 T cm⁻² pressure across the Nafion® in the cell.

The MEAs constructed from the electrochemically grown or uncoated carbon paper electrodes were not hot-pressed, but were simply pressed at 5 N m under ambient conditions: hot pressing otherwise caused the polymer coating to deform on the surface of the carbon paper and the carbon paper electrodes then disintegrated.

The author developed a three-electrode cell in-house to study cyclic voltammetry of supercapacitor cells to gain a greater insight into the electrochemical processes involved (Fig. 4.5).
The PTFE coated silver wire (Advent Inc.) electrode acts as a Ag / Ag2O quasi-reference electrode (QRE), which is sometimes termed a pseudo-reference electrode (Fig. 4.5a). A QRE is normally used with non-aqueous solutions to help prevent contamination of dry electrolyte solvents. In this work a silver QRE has been chosen as it can easily access the cell and make effective contact with the electrolyte. Platinum and diamond have also been used as alternative probes to silver, but do not provide such a well defined couple.40,41 During a cycle the silver wire forms a layer of silver oxide at the tip that acts as a redox couple of type $\text{Ag} = \text{Ag}^1 + e^-$, which does not change potential during an experiment. The potential window of a QRE may vary by up to 30 mV, and so calibration is required before
results are shown. The calibration of the QRE can be carried out against a reversible redox-couple and compared to the response from a known reference electrode under the same conditions. Ferrocene has been used as the redox couple for calibration in organic systems, as it shows a Nernstian-type curve.\cite{42} In this work the QRE was calibrated in aqueous sodium hydroxide solution (1 mol dm$^{-3}$) against a Ag / AgCl reference (Bioanalytical Inc.) in a similar cell to those used in the electrode work in Chapter 3. PTFE O-rings are used to seal the top and bottom of the cell, preventing leaks of electrolyte material which would lead to drying of the Nafion$^\circledR$ (Fig. 4.5b). The auxiliary electrode has a groove cut in its circumference to prevent shorting (Fig. 4.5c). A PTFE washer is used to insulate further and to add support to any materials that may overhang. A small groove has been cut in the circumference of the working electrode (Fig. 4.5d) for the same reason as with the auxiliary electrode. The working electrode is a well-polished steel plunger with a section removed from the side to allow the silver pseudo-reference electrode access to the electrolyte (Fig. 4.5e). The screw of the plunger has been coupled to the free moving working electrode contact that is placed off-centre. This prevents the movement of the steel current collector electrode that would lead to misalignment relative to the working electrode and electrolyte material. To maintain a constant and reproducible pressure a brass nut was added to the top of cell, which was then turned using a torque wrench (Fig. 4.5f).

The cell was tested over a week, checking for leakage of water or other solvents on standing and during electrochemical cycling. No such problems were encountered. The steel collector electrodes and contacts were cleaned regularly using 1200 grade wet/dry paper (CPC / Farnell) and finished in an aqueous ultrasonic bath; this procedure effectively removed any pock marks or other abrasions.
After pressing, the supercapacitor MEAs were cut from excess Nafion®, rehydrated in deionised water for 3 h and then placed in the cell. A torque wrench was then used to apply a constant pressure of 0.5 N m.

CV tests of the MEA cells incorporating electrodes with polymer coatings based on polypyrrole (Ppy) or poly(N-methylpyrrole) (Pmpy) were carried out using an analogue EG&G / Princeton model 173 potentiostat / galvanostat equipped with a model 179 electrometer. The potentiostat was driven via Sycopel PCI-100 digital interface and ramp generator, which allowed full digital control via a computer and associated software. CVs were recorded within various potential windows at three different scan rates (100, 10 and 1 mV s⁻¹ unless otherwise stated) against the silver quasi-reference electrode. This allowed comparison of peak positions and reversibility as a function of scan rate.

4.4.4 Results and discussions of cyclic voltammetry from capacitor test cells.

Cyclic voltammograms (CV) for the device are given after the discussion (Fig. 4.6 to 4.18) and are plotted as current per unit mass of the MEA vs potential. Three colours are used on each CV, representing each of the three scan rates studied: black for 100 mV s⁻¹, red for 10 mV s⁻¹, blue for 1 mV s⁻¹. Studies were within the potential –1000 and 1000 mV versus the silver quasi-reference electrode.

Cyclic voltammetry data for the three electrode cells gave insight into the expected capacitances and properties of the doped polymer electrodes within the cell. The cyclic voltammetry for the capacitor test cell gave different profiles from the work carried out in
Chapter 3 (studies of single polymer coated electrodes). Observations are discussed as follows:

1) The use of Nafion® (even when Nafion® milk was used) resulted in the reduction in electrolyte / electrode interface contact and so an increase in the resistance. Contact is better in the liquid acid, which penetrates the pores giving enhanced electron transfer and lower resistance, resulting in better reversibility (Chapter 3).

2) A reduction in the scan rate of devices incorporating electrodes of polypyrrole doped with heteropolyacids gave an increase in the reversibility. This was accompanied by better resolution of the peaks relating to the heteropoly anions and polypyrrole. Due to overlap, the peak positions could not be individually assigned with any accuracy. The quasi-reversibility of the system was a result of the diffusion properties of the thickly polymer coated carbon support. This caused a slower electron transfer reaction in the system; the same phenomenon is seen in Chapter 3.

3) Irreversible CVs were obtained from the poly(N-methylpyrrole) based devices, with electrodes electrochemically grown with sodium dodecylbenzene sulfonate and with those chemically grown with 14-vanadophosphate and iron(III) chloride. A decrease in the scan rate led to increased irreversibility. This was similar to observations in Chapter 3.

4) Cells with electrodes coated with poly(N-methylpyrrole) doped with 12-molybdophosphoric acid, 12-molybdosilicic acid or 10-molybdo-2-vanadophosphoric acid showed an increase in reversibility on a decrease in scan rate. This was
accompanied by a more enhanced peak profile, better than that of the polypyrrole based devices; this was also seen previously in Chapter 3. These peaks were associated with the heteropolyacids (as previously discussed) and poly(N-methylpyrrole). 12-Molybdophosphoric acid and poly(N-methylpyrrole) gave particularly well defined peaks, three of which are associated with the hetero anion and one associated with the polymer ($\approx -250$ mV on oxidation and $\approx 500$ mV on reduction) (Fig 4.12). 10-Molybdovanadophosphoric gave the least reversible system.

Capacitance results were not calculated from these CVs as peaks (and reversibility) were not distinct enough. Charge / discharge were used to assess capacitance and other properties and in some cases related to observations made using a.c. impedance and cyclic voltammetry measurements (Chapter 5).

**Fig 4.6. CV of the MEA. Carbon paper electrodes with solid Nafion® membrane electrolyte.**
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Fig 4.7. CV of the MEA. Electrode coating: Ppy + sodium dodecylbenzene sulfonate.

Fig 4.8. CV of the MEA. Electrode coating: Pmpy + sodium dodecylbenzene sulfonate.

Fig 4.9. CV of the MEA. Electrode coating: Ppy + iron(III) chloride
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Fig 4.10. CV of the MEA. Electrode coating: Pmpy + iron(III) chloride

Fig 4.11. CV of the MEA. Electrode coating: Ppy + 12-molybdophosphoric acid.

Fig 4.12. CV of the MEA. Electrode coating: Pmpy + 12-molybdophosphoric acid.
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Fig 4.13. CV of the MEA. Electrode coating: Ppy + 12-molybosilicic acid.

Fig 4.14. CV of the MEA. Electrode coating: Pmpy + 12-molybdosilicic acid.

Fig 4.15. CV of the MEA. Electrode coating: Ppy + 10-molybdo-2-vanadophosphoric acid.
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**Fig 4.16.** CV of the MEA. Electrode coating: Pmpy + 10-molybdo-2-vanadophosphoric acid.

**Fig 4.17.** CV of the MEA. Electrode coating: Ppy + 14-vanadophosphate.

**Fig 4.18.** CV of the MEA. Electrode coating: Pmpy + 14-vanadophosphate.
4.4.5 The design of the two-electrode test cells suitable for a.c. impedance and galvanic cycling.

A two-electrode cell was designed for studying the charge / discharge characteristics of the supercapacitor cell (Fig 4.19). The cell was additionally used for a.c. impedance studies of the complete supercapacitor unit.

The two-electrode test cell was a simplification of the three-electrode cell and shared the following features:

- The cell was designed with an adjustable cell thickness by the use of a screw thread plunger and a Teflon bore for leak sealing, coupled (Fig. 4.19b) with a nut allowing a consistent known torque (Fig 4.19h).

- The stainless steel plunger rotates independently of the current collector electrode preventing damage to the supercapacitor MEA (Fig. 4.19f).

- Accessible contacts on the complete cell for the attachment of leads (Fig 4.19a and e).

- PTFE washers and main body (Fig. 4.19c and d), preventing the cell from leaking and adsorbing exterior impurities and secured by brass nuts (Fig. 4.19g).

- PTFE washers around bottom and top current collector electrodes, which prevent contact by the electrolyte.
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4.4.6 a.c. Impedance analysis.\textsuperscript{43,44}

The following section briefly introduces the area of a.c. impedance analysis and provides discussion on some of the basic principles, as well as giving examples of uses and circuit fitting. This is followed by results and discussion of the impedance analysis carried out on the studied capacitor cells. The a.c. impedance plots are given after the discussion (Fig. 4.26 to 4.43).

Fig 4.19. Schematic diagram and photograph of two-electrode cell: (a) screw for the attachment of a contact clip; (b) PTFE screw seal; (c) PTFE O-ring; (d) PTFE cell body; (e) screw-in stainless steel rod for the attachment of contact; (f) stainless steel plunger held together with screws and moving vertically in the PTFE barrel when (a) is rotated; (g) brass nut and cap clamping the cell together; (h) brass nut for application of known torque. Electrodes were 1.30 cm in diameter and 1.32 cm\textsuperscript{2} in area.
Impedance spectroscopy is useful to this project as a quality control procedure and for the interpretation of fundamental electrochemical and electronic processes. These include the resistance and conductance of a material or cell assembly.\(^{45}\)

A set voltage at a single frequency \(\omega\) is applied to a material in a cell (using an impedance analyser) and the resulting steady state current \(i(t) = I_m \sin(\omega t + \theta)\) is measured. \(\theta\) is the phase difference between the voltage and the current, and is zero for purely resistive behaviour. The electrical stimulation gives a large number of microscopic responses of which the major three are:-

1. The flow rate of electricity through electrode and electrolyte materials corresponds to ohmic resistance.

2. Transfer of electrons at the electrode / electrolyte interface. This can happen from charged or uncharged materials in the cell and may be influenced by the surrounding environment.

3. The flow of atoms or other species caused by defects in the electrolyte.

When the frequency is swept from low to high values at fixed voltage, the resulting impedance spectrum can be determined. This gives the frequency dependent phase shift and amplitude of real and imaginary components, which combine to give a vector impedance. In an impedance plot the different components \(a\) and \(b\) are related by the complex number \(j\) and these are related \textit{via} the equation \(Z = a + jb\), where \(j = \sqrt{-1} = \exp(j\pi/2)\), and corresponds to anti-clockwise rotation relative to the x-axis. Thus the real part of \(Z\), \(a\), is in
the direction of the x-axis and $b$, the imaginary part, is along the y-axis. This is re-written as $Z = Z' + jZ''$, and the locus of $Z$ as a function of frequency defines the impedance plot (Fig 4.20). The plot can give information on two sets of parameters:

1. Information about the material itself such as conductivity, dielectric constant, mobility of charges, equilibrium concentrations of charged species and bulk generation-recombination rate of electrons.

2. Information about the electrode-material interface, such as adsorption, reaction rates, capacitances of the interface, diffusion coefficients for neutral species on the electrode itself.

\[ Z/\text{ohm} \]
\[ R_i \]

\[ \omega_p \]

Fig 4.20. Example of a complex impedance plot with frequency increasing in the direction of the arrow.
Equivalent Circuits.

It is sometimes easier to manipulate and represent an experimental impedance plot by using an equivalent circuit (EC). An exact mathematical model can be used, but this is a more complex approach. An EC is made up of the ideal components or elements, each with an assigned constant value. Elements include resistors, capacitors, and inductors. The elements when combined in parallel and/or series give an EC, the impedance characteristics of which can be plotted and related to the experimental plot (Fig 4.21). The elements in the EC are related to the microscopic responses in the system and so can monitor the processes that occur when a current is passed through the material or cell. Using the model EC impedance, $Z_{EC}(\omega)$, fitting the experimental data to a model can be done using a least squares fit.

Procedure for use of the equivalent circuit method:

1. Fabrication of the material or cell system.
3. Model of equivalent circuit impedance $Z_{EC}(\omega)$.
4. Curve fitting using least squares fitting via computer software.
5. Characterisation of the resulting EC, giving information on the electrical properties of the system being studied (for a physically realistic model).

A pure resistor has a frequency independent impedance, a single resistance value $R_i$ on the x-axis (Fig 4.21a). The impedance of a pure capacitor $C_i$ is a line of points on the y-axis that increase in frequency moving towards the origin (Fig 4.21b); the admittance response is related to the capacitance impedance by $Z = 1/\omega C_i$. Generally the EC approach requires a more complex combination of elements to represent data. When a resistor is placed in series
with a capacitor, a vertical line of points off-set from the y-axis by the value of the resistance is observed (Fig 4.21c).

![Impedance plots](image)

**Fig 4.21.** *a.c. Impedance plots of the circuit elements, (a) a resistor, (b) a capacitor, (c) both in series.*

The properties of multiple or single capacitor devices and their individual materials, such as electrolyte and electrode, can be analysed, including casing components. Properties such as the equivalent series resistance (e.s.r.) and capacitance can be obtained from the impedance complex plane plots. The e.s.r. gives information on the power handling capabilities of the system, in that the lower the e.s.r in the cell the quicker the transfer of energy to and from the capacitor (leading to a higher power output). Impedance analysis may provide information on the frequency dependence of the system; this becomes important in electronic applications. Within a double layer capacitor (Fig 4.23a) there is a network of circuit elements which make up the complete cell; these are the solution resistance ($R_s$) which relates to the electrolyte, interfacial resistance, and a double layer capacitance ($C_{dl}$) which is in parallel with the interfacial resistance ($R_f$). This is dependent on the charge transfer resistance of the cell resulting in the faradaic impedance $Z_f$ of the cell. The $R_f$ becomes smaller as the kinetic reversibility of the system increases and as the system lowers in electrode resistance. A semicircle is usually accompanied by a Warburg impedance in series.
with $R_f$, which gives Randle’s circuit (Fig 4.23b).\textsuperscript{46} This is due to the diffusion properties of the electrode; for instance, carbon is often of high surface area and porosity causes more diffusion throughout its network of fibres, leading to the inclusion of extra ohmic pathways.

For a capacitor involving pseudo-capacitance the cell incorporates a capacitance ($C_p$), which (i) is placed in series with $R_f$, (ii) relates to the electroactive species and (iii) results in a straight line at 90° to the x-axis (Fig 4.23c). A Warburg or a constant phase element (CPE) is added to take account of the deviations. In some cases where pseudo-capacitance is present in a system a second semicircle arises. This is a result of the leaking of pseudo-capacitance caused by the overcharging of the pseudo-capacitance (for example if H$_2$ gas evolved from overpotential deposition in a metal oxide system).

Fig 4.23. The equivalent circuits (top) that can represent the complex-plane impedance plots (bottom) of (a) double layer, (b) double layer with diffusion (Randles circuit) and (c) ideal pseudo-capacitive behaviour.

The results of a.c. impedance studies are found after this discussion (Fig. 4.26 to 4.43). Data are given in two colours, black denoting tests carried out on the MEA under damp conditions
and red representing an MEA stored at RH = 100%. ‘Damp conditions’ are where the MEA has been hydrated in deionised water and remains wet during tests. All a.c. impedance tests were carried out after charge / discharge cycling 200 times.

It is important to note that the accurate equivalent circuit modelling of the capacitors in this project is not possible. These are complex multiple charge transfer systems, which involve the properties of both conductive polymers and heteropoly anions. However, the results with the MEA systems will be discussed.

4.4.7 Results and discussion of a.c. impedance analysis.

1) The shape of the complex plane plots associated with polypyrrole systems (except those doped with 14-vanadophosphate) are similar to many found in the literature, for example supercapacitors incorporating various electrolytes with polypyrrole and polythiophene.\(^{47}\) The resultant plots showed a solution resistance \((R_s, \text{ resistance of the electrolyte and electrolyte / electrode interface})\) in the high frequency range, a faradaic leakage resistance \((R_f)\) in mid-range frequency and a tail associated with the electrodes in the low frequency range.

2) In all cases \(R_s\) and the electrode diffusion resistance (tail on the semicircle) had both increased after 200 galvanic cycles (Fig. 4.24). These observations have been previously reported for a symmetrical capacitor incorporating polyaniline electrodes.\(^{48}\) It was proposed that the electronic and ionic resistances of the polymer electrode increase, resulting in lower capacitance. It was also observed that the polymer films became more
compact at nanoscopic levels, leading to the higher resistances linked to the decrease in the phase angle. The degradation of the polymer is a factor resulting in the higher solution resistance \((R_s)\) caused by increasingly poor electrode / electrolyte contact. This represented an increase in the e.s.r and therefore reduced power handling capabilities.

3) There was a general increase in the electrolyte and interface resistance \((R_e)\) for all MEAs on going from damp to RH = 100%, indicating the dehydration of the Nafion® electrolyte accompanied by fewer charge carriers in the polymer electrode pores (Fig. 4.25).

4) The faradaic leakage resistance \((R_f)\) (associated with the reactions between polymer, water and Nafion®) in most cases increases on decreasing humidity, indicating the effect of water on the reversibility of the electrode reactions.

5) The impedance plots have a line at less than the ideal 90° to the x-axis for a pseudo-capacitor, this being associated with diffusion within the bulk and pores of the electrode system. (Fig 4.24 and 4.25)

6) All of the plots exhibited depressed curves caused by diffusion within the electrodes; as seen in the cyclic voltammetry the operation of the electrodes is very much diffusion controlled. The complexity of the electrode material may also cause the depression of the circle.
Fig. 4.24. Impedance spectra of MEA incorporating electrodes with polypyrrole doped with 12-molybdosilic acid. Before charge/discharge (black), after 200 charge/discharge cycles (red).

Fig. 4.25. Impedance spectra of the MEA incorporating electrodes with poly(N-methylpyrrole) doped with 10-molybdo-2-vanadophosphoric acid.

Under damp conditions (black), and at RH = 100% (red).

7) Nearly all of the capacitors constructed incorporating poly(N-methylpyrrole) show two semicircles, which was not characterised with the “polypyrrole systems” (apart from 14-vanadophosphate doped polypyrrole, which has several curves) (Fig 4.41). The first semicircle arises from the double layer capacitance in parallel with an ohmic resistance.
There are two possibilities for the second semicircle; the first is it may be associated with the pseudo-capacitive part, with some form of desorption which is very high in resistance; the second could be the shear complexity of the electrode material’s diffusion properties (resulting in the addition of several constant phase elements leading to several semicircles). Both the polypyrrole and poly(N-methylpyrrole) show complex capacitance and resistance responses (for example depressed curves, extra semicircles, non-ideal bulk diffusion), which have been described by others as a transmission line circuit made up of electronic and ionic resistances and capacitor components in parallel across the electrode film.\textsuperscript{49, 50} In this model the double layer and pseudo-capacitance are distributed evenly so that they become indistinguishable from each other.\textsuperscript{51}

**Presentation of a.c. impedace plots of the MEAs containing electrodes with polymer coatings and Nafion\textsuperscript{®} electrolyte (see over).**

a.c. Impedance plots (Fig. 4.26 to 4.43) were taken from hot-pressed membrane electrode assemblies, incorporating Nafion\textsuperscript{®} 115 as an electrolyte. Electrodes were carbon papers coated with electrochemically or chemically grown polymers doped with various materials. Measurements were performed in two electrode test cells on a Solartron 1260 impedance analyser coupled with a 1287 electrochemical interface. Cells run under damp conditions are in black and those after MEA storage at RH = 100% are in red. These results are discussed further in Chapter 5.
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Key to a.c. impedance plot figure numbers.

4.26 MEA incorporating electrodes coated with polypyrrole doped with sodium dodecylbenzene sulfonate.

4.27-28 MEA incorporating electrodes coated with poly(N-methylpyrrole) doped with sodium dodecylbenzene sulfonate.

4.29 MEA incorporating electrodes coated with polypyrrole doped with iron(III) chloride.

4.30-31 MEA incorporating electrodes coated with poly(N-methylpyrrole) doped with iron(III) chloride.

4.32 MEA incorporating electrodes coated with polypyrrole doped with 12-molybdophosphoric acid.

4.33 MEA incorporating electrodes coated with poly(N-methylpyrrole) doped with 12-molybdophosphoric acid.

4.34 MEA incorporating electrodes coated with polypyrrole doped with 12-molybdosilicic acid.

4.35 MEA incorporating electrodes coated with poly(N-methylpyrrole) doped with 12-molybdosilicic acid.

4.36-37 MEA incorporating electrodes coated with polypyrrole doped with 10-molybdo-2-vanadophosphoric acid.


4.40-41 MEA incorporating electrodes coated with polypyrrole doped with 14-vanadophosphate.

4.42-43 MEA incorporating electrodes coated with poly(N-methylpyrrole) doped with 14-vanadophosphate.
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Chapter 4. Fabrication and investigation of single cell supercapacitors.

\begin{center}
\includegraphics[width=0.8\textwidth]{diagram.png}
\end{center}

**Figure 4.42**

**Figure 4.43**
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4.5 Conclusions.

This chapter has covered:

1) The design of two test cells, with attention given to the materials used in fabrication. The first was a three-electrode test cell incorporating a silver quasi-reference electrode used for cyclic voltammetry (CV). The second was a two-electrode design used for ac impedance and galvanic cycling. This was in part due to the PTFE seals, which prevented loss of humidity, and to the polishing of the steel electrodes before each test.

2) Fabrication of MEAs was successfully carried out using the hot-pressing of electrodes onto the Nafion® electrolyte, with Nafion® milk as a contacting agent.

3) a.c. impedance analysis showed the effects of humidity and galvanic cycling on the capacitor’s performance. In general, damp cells performed better, with lower solution / interface resistances ($R_s$), lower faradaic leakage ($R_f$) and lower bulk resistances. This would be an advantage when considering the power output, which is influenced by the equivalent series resistance (e.s.r).

4) Cyclic voltammetry of the devices shows that the electron transfer processes are slow, as was found in the lone electrode experiments in Chapter 3. This was as a result of the thick polymer films, which hindered charge transfer to the electrolyte. In comparison with the lone electrodes, which were immersed in a liquid electrolyte, the electrodes in the capacitor were in poorer contact with the electrolyte, as the Nafion® could not completely penetrate the pores. It might be advantageous in further research (if Nafion®
or a similar membrane electrolyte is to be used) to produce an electrode which is much flatter. This would enhance contact with the membrane resulting in higher capacitance. It may also be an advantage to make thinner films (lower e.s.r.), which will result in higher electron transfer rates, leading to higher power handling, energy density and specific capacitance (capacitance per gram of MEA).
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5. **Galvanic cycling and self-discharge of supercapacitor test cells.**

This Chapter deals with charge / discharge and open circuit studies carried out on the membrane electrode assemblies (MEA) whose fabrication was discussed in Chapter 4. The levels of specific capacitance, energy density and power handling are discussed after 200 galvanic cycles. It is desirable that the MEAs give high specific capacitance, energy density and high power handling which persist as stored charge over a long period of time. Differences between the MEAs in this work are compared with examples found in the literature. Cyclic voltammetry and a.c. impedance are briefly mentioned with reference to the data detailed in Chapter 4.

5.1 **Results from the galvanic cycling and self-discharge tests of MEA test cells.**

In this work charge / discharge profiles are used to calculate the specific capacitance, energy density, power and the stability over a number of cycles. Specific capacitance of the MEAs can be directly calculated from the discharge curve using the formula *(Eqn 5.1)*:

\[
C = \frac{i \times dt}{dV}
\]

*Equation 5.1.*

where \( C \) is the capacitance in farads (F), \( i \) is the current applied on discharge, \( dt \) is the time elapsed for the discharge and \( dV \) is the potential difference on discharge. The power handling *(Eqn 5.2)* and energy density *(Eqn 5.3)* can be calculated using the area under the discharge curve:

\[
P = \int_{t_1}^{t_2} iV(t)dt
\]

*Equation 5.2*

\[
E = \int_{t_1}^{t_2} iV(t)dt
\]

*Equation 5.3*
where $P$ is the power in watts (W) on discharge and $E$ is the energy in joules (J). All values of power handling, energy density and specific capacitance are quoted per unit mass of MEA. All a.c. impedance tests were carried out after charge / discharge cycling 200 times.

Before showing and discussing the results, it is prudent to discuss how they are presented as much of the data has been condensed to provide an easier overall view. The charge / discharge tests were carried out on supercapacitor test cells via a computer-driven Sycopel AWE-200 potentiostat / galvanostat. The hot-pressed MEAs were prepared, as explained earlier, and placed in a two-electrode test cell. The MEA test cells were cycled 200 times at +/- 1 mA to allow conditioning so that an equilibrium charge / discharge curve was obtained. Tests were performed between the voltage limits -1000 mV and 1000 mV.

5.2 Self-discharge (open circuit) behaviour of supercapacitors.

Batteries and supercapacitors are devices that commonly show self-discharge behaviour, which is observed using an open circuit experiment. Self-discharge in batteries arises from the decomposition of cathode materials and other corrosion effects caused by electrode / electrolyte interaction. This is influenced by the purity of electrolytes, reagents and storage temperature. The rate at which a battery self-discharges is much lower compared to an electrochemical capacitor, which indicates slower kinetics. An ideal non-leaky device, which is very rare, is one where the electrodes are entirely polarised, giving no available pathways for self-discharge. If in a supercapacitor there are available mechanisms for discharge, the high positive Gibbs free energy of the charged state will tend to move the system towards the lower energy of the discharged level. The rate of the self-discharge diminishes over time, ideally giving an exponentially decreasing plot for potential vs time. This leads to lower
available energy density in the device. The kinetics of the self-discharge are dependent on the discharge mechanism and electrode potential. Pathways include:

1) Ohmic leakage caused by mechanical shorts (electrical shorting usually in a bipolar stack).

2) Self-discharge from diffusion controlled charge leakage mechanisms (shuttle mechanisms involving impurities or redox-couples).

3) The capacitor being overcharged above the decomposition limited potential of the electrolyte. In the case of water this will cause, on open circuit, the spontaneous discharge to the reversible potential limits of O₂ and H₂.

In pseudo-capacitors the self-discharge occurs from the loss of potential from both the double-layer charge and the losses attributed to the active material (for example, involving hydrogen in the case of transition metal oxides). The mixed cathodic and anodic processes which take place are similar to the mechanisms in batteries.² If the potential (V) is plotted vs. log(t) the relationship between losses involving the double-layer and pseudo-capacitance is seen. There is first a rapid decrease in the potential associated with the double-layer. A plateau in the potential is then reached where there is a buffering effect caused by the mixed capacitances. The discharge is then resumed to zero potential. The influence of pseudo-capacitance is mostly observed, with the double-layer showing a significant but small impression. An example of self-discharge in a supercapacitor involving a pseudo-active material is RuO₂; these capacitors work through the diffusion of oxidation states via electron hopping as indicated below:³
Chapter 5. Galvanic cycling and self-discharge of supercapacitor test cells.

\[
\begin{align*}
\text{Ru(III)}_{\text{bulk}} + \text{Ru(II)}_{\text{surface}} & \quad \rightarrow \quad \text{Ru(II)}_{\text{bulk}} + \text{Ru(III)}_{\text{surface}} \\
\text{Ru(IV)}_{\text{bulk}} + \text{Ru(III)}_{\text{surface}} & \quad \rightarrow \quad \text{Ru(III)}_{\text{bulk}} + \text{Ru(IV)}_{\text{surface}}
\end{align*}
\]

The above are coupled with reactions between H\textsubscript{2}O and H\textsubscript{3}O\textsuperscript{+};

\[
\text{OH}_{\text{surface}} + \text{O}_2^{\cdot}_{\text{bulk}} \quad \rightarrow \quad \text{O}_2^{\cdot}_{\text{surface}} + \text{OH}_{\text{bulk}}
\]

\[
\text{O}_2^{\cdot}_{\text{surface}} + \text{H}_3\text{O}^{+}_{\text{solution}} \quad \leftrightarrow \quad \text{OH}_{\text{surface}} + \text{H}_2\text{O}_{\text{solution}}
\]

Stack cells must always be made from reproducible single cells, as underperforming cells in the stack (those with a capacitance significantly lower than that of the other capacitors) will become over-charged or over-discharged. If one of the cells in the stack self-discharges at a quicker rate than the others, this will cause all the other capacitors to act in a similar manner, reducing the usefulness of the device. Care must also be taken to eliminate ohmic leaks, which will cause shorting.

Open circuit (dependence of potential) studies were used here to analyse the decrease in energy density (self-discharge) after cycle-life tests. After 200 charge / discharge cycles the cell was charged to 1 V at 1 mA and then allowed to self-discharge in open circuit mode, monitored using a Sycopel AWE-200 potentiostat / galvanostat. The discharge of the cell was measured over 15 h under damp conditions and also at RH = 100%.

The charge / discharge plots are presented in two colours, representing membrane electrode assemblies (MEA) tested under damp conditions (black) and tested at RH = 100% (red).
term ‘damp conditions’ refers to MEAs which were pre-soaked in deionised water and then run as a wet construction sealed in the two-electrode cell. A RH = 100% was obtained in cells by storing the MEA over water within a sealed desiccator for 24 h.

Three colours are used in energy density, power handling and specific capacitance profiles; black for energy density, red for power handling and blue for specific capacitance. All three sets of data are normalised to the mass (grams) of the damp MEA. These are plotted against charge / discharge cycle number. The power handling data has been curve fitted using a locally weighted least squares fit error method within ‘KaleidaGraph’. This results in a curve, which gives a best fit through the centre of the data. This method is insensitive to outlying points. For some of the MEAs this data cannot be given, as the energy density, power handling and specific capacitance have fallen to such low levels that the plot becomes influenced by background fluctuations.

For self-discharge (open circuit) plots, the colours red and black, again represent damp and RH = 100% respectively. The exception is with MEAs incorporating electrochemically grown polymer electrodes, which are shown with a different legend.

The next section presents and discusses the results obtained from the MEAs tested under charge / discharge conditions.
MEA incorporating Nafion® and Toray carbon paper only.

The charge / discharge of the Nafion® and Toray carbon paper test cell under damp conditions was carried out at a current of 0.1 mA, as a charge of 1 mA proved too high in tests (Fig. 5.1). The profile showed the characteristic of the double-layer type capacitor with almost linear charging and discharging. The specific capacitance, specific energy and specific power calculated from the discharge curve were $2.0 \times 10^{-4}$ F g$^{-1}$, $6.0 \times 10^{-5}$ J g$^{-1}$ and $6.0 \times 10^{-5}$ W g$^{-1}$ respectively. The self-discharge profile shows a fast decrease to 0.05 V in the first hour then a slower decrease to zero (Fig 5.2).

![Figure 5.1](image_url)

**Fig 5.1.** Charge / discharge of an MEA test cell using carbon paper electrodes and a solid Nafion® membrane as an electrolyte. Galvanic cycling was at +/- 0.1 mA.

During the self-discharge the interactions between the double-layer capacitance and pseudo-capacitance loss can be monitored when potential (V) is plotted against log(t) (Fig. 5.3). The profile involving uncoated carbon paper and Nafion® can be seen to initially drop exponentially; this represents the loss occurring due to the pure double-layer capacitance.
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The double-layer in this case loses electrons from the negative electrode to O₂ and H₂O₂, which are created during charging. The curve then reaches a plateau at 0.04 V, representing the mixed capacitances of double-layer and pseudo-capacitance. As already introduced in Chapter 1, all double-layer capacitors have a small amount of pseudo-capacitance. The potential then continues to drop, losing the pseudo-capacitance storage until it reaches 0 V. The carbon paper electrodes that have a coating of an electro-active species act in a much more pseudo-capacitive manner. The MEA fabricated with electrodes coated with polypyrrole doped with 12-molybdophosphoric acid gave an initial small drop representing the double layer capacitance (Fig. 5.4). The potential reaches a plateau of mixed capacitances and then continues to discharge, losing pseudo-capacitance storage. The pseudo-capacitance is seen as the dominant part of the discharge, which are compounded with proton losses attributed to the heteropoly anion.

Fig 5.2. Self-discharge of an MEA test cell using carbon paper electrodes and a solid Nafton® membrane as an electrolyte.
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The heteropoly anion may aid in transferring electrons between the conductive polymer chains, resulting in a faster self-discharge. This phenomenon was seen for single cell capacitors containing polymer coated electrodes and appeared to be independent of the discharge curve taken under galvanic cycling, suggesting a different mechanism. This is because the unforced self-discharge is a result of instabilities within the cell and not due to any controlled discharge through a load.

---

**Fig 5.3.** Conversion of the self-discharge curve (Fig 5.2) of the wet carbon paper / Nafion® MEA.

**Fig 5.4.** Comparison of self-discharge plots (Fig 5.12) of the MEA incorporating carbon paper electrodes with a coating of polypyrrole doped with 12-molybdophosphoric acid.
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**MEA incorporating polypyrrole and poly(N-methylpyrrole) electrodes, electrochemically grown with sodium dodecylbenzene sulfonate (SDBS) dopant.**

Charge / discharge curves for the polymers electrochemically grown with sodium dodecylbenzene sulfonate (SDBS) indicated poor specific capacitance and specific energy. After 200 galvanic cycles the highest values reported in this work were $\approx 7 \text{ F g}^{-1}$, $\approx 3.3 \times 10^{-3}$ W g$^{-1}$ and $\approx 1.8 \text{ J g}^{-1}$ for specific capacitance, specific power and specific energy respectively (for polypyrrole doped with 10-molybdo-2-vanadophosphoric acid). The values of the specific capacitance, specific energy and specific power for polypyrrole (Ppy) doped with SDBS were $\approx 2 \times 10^{-4} \text{ F g}^{-1}$, $\approx 1 \times 10^{-4} \text{ J g}^{-1}$ and $\approx 5 \times 10^{-5} \text{ W g}^{-1}$ respectively. These were the approximate values both for MEAs run damp and at RH = 100%. The values for the poly(N-methylpyrrole) (Pmpy) doped with SDBS gave similar values. The self-discharge test gave a selection of profiles, which appeared to show potential recovery after galvanic cycling. This was caused by a small amount of unbalancing which resulted in the asymmetry of the two electrodes (Fig 5.5). This may originate during the fabrication of the electrodes (see Chapter 3), resulting in poor reproducibility.

![Fig 5.5. Open circuit behaviour of the MEA. Electrode coating: polypyrrole (Ppy) or poly(N-methylpyrrole) (Pmpy) + sodium dodecylbenzene sulfonate.](image-url)
**MEA incorporating electrodes with coatings of polypyrrole chemically grown with iron(III) chloride.**

The charge / discharge curve for the capacitor run in damp conditions shows an initial smooth charging to 1 V and then a discharge to 0 V over \( \approx 40 \) s (Fig 5.6). The cell run at RH = 100% was found to reduce in cycle time due to the increase in the internal resistance. Both galvanic cycle curves show non-linear charge / discharge profiles, which is characteristic of a faradaic process resulting from the pseudo-capacitive polymer electrodes. During the multiple cycling of the damp cell specific capacitance, energy density and power handling stabilised after 100 cycles. The final specific capacitance, specific energy and specific power after 200 cycles were 0.24 F g\(^{-1}\), 0.06 J g\(^{-1}\), 3.4 x 10\(^{-3}\) W g\(^{-1}\) respectively (the values varied only by small amounts and the plot has therefore been omitted for clarity). These values were much higher than for the MEAs containing untreated carbon paper electrodes and electrochemically grown polypyrrole electrodes doped with SDBS (2.0 x 10\(^{-4}\) F g\(^{-1}\), 1 x 10\(^{-4}\) J g\(^{-1}\) and 5 x 10\(^{-5}\) W g\(^{-1}\)). It will, however, become clear, later in this work that the polypyrrole electrodes containing encapsulated heteropoly anions led to much higher values of specific capacitance (0.75 to 7 F g\(^{-1}\)) and specific energy (0.08 to 1.8 W h kg\(^{-1}\)). Self-discharge plots show the damp MEA discharging to 0 V after 15 h (Fig 5.7). The plot of potential (V) vs log(t) shows the characteristic discharge as seen with the MEA incorporating electrodes of polypyrrole doped with 12-molybdophosphoric acid (Fig 5.4). There is a potential gain seen with the MEA run at RH = 100%; this may result from polarisation of the electrodes or possible asymmetry within the cell. This phenomenon was difficult to control and hindered reproducibility of this particular device. The potential gain was seen in various cases for MEAs incorporating electrodes of both the polypyrrole and poly(N-methylpyrrole) grown electrochemically or chemically using iron(III) chloride. It should be noted that ME As
using polymer based electrodes grown chemically with any of the heteropolyacids showed no such phenomena, allowing more predictable and reproducible cells.

**Fig 5.6.** Charge / discharge curves of the MEA. Electrode coating: polypyrrole with iron(III) chloride. Cycled at +/- 1 mA.

**Fig 5.7.** Open circuit behaviour of the MEA. Electrode coating: polypyrrole with iron(III) chloride.

MEA incorporating electrodes with coatings of chemically grown poly(N-methylpyrrole) with iron(III) chloride.

Galvanic cycling showed poor specific capacitance, energy density and power output compared with the polypyrrole derivative (**Fig 5.8**). Charge / discharge after 200 cycles gave specific capacitance, specific energy and specific power as 0.016 F g\(^{-1}\), 7.0 \(\times\) 10\(^{-3}\) J g\(^{-1}\) and 6.0 \(\times\) 10\(^{-3}\) W g\(^{-1}\) respectively (the values varied only by small amounts; the plot has been
omitted for clarity). Self-discharge plots for the MEAs run under damp conditions and at RH = 100%, showed a potential gain towards −0.5 V, caused by asymmetry of the electrodes (Fig 5.9). As with the MEAs with electrodes coated with polypyrrole with iron(III) chloride coatings, the asymmetry may be caused by the method of electrode fabrication; reproducing the electrodes with a smooth surface does not seem possible (Fig 3.6). The systems containing vapour transport grown polymers using iron(III) chloride are therefore unsuitable as electrode materials.

Fig 5.8. Charge / discharge curves of the MEA. Electrode coating: poly(N-methylpyrrole) with iron(III) chloride. Cycled at +/- 1 mA.

Fig 5.9. Open circuit behaviour of the MEA. Electrode coating: poly(N-methylpyrrole) with iron(III) chloride.
**MEA incorporating electrodes with coatings of chemically grown polypyrrole doped with 12-molybdophosphoric acid.**

The shape of the charging curve indicates a faradic charging process, as potential is not proportional to time (Fig. 5.10). There is a large drop in the potential on discharge, which can be attributed to the potential dependence of the electrode and its inability to hold substantial energy above 0.4 V. Again, a faradic transfer of charge is seen in the discharge profile as a plateau forms at 0.3 V. For the device at RH = 100% the charge / discharge cycle becomes more rapid. The time over which the discharge curves drops to \( \approx 0.2 \) V indicates an increase in the IR drop caused by the dehydration of the Nafion\textsuperscript{®} electrolyte. The 12-molybdophosphate anions encapsulated in the film may be restricted in transferring protons to the surface of the electrolyte, as lower humidity would indicate less water in the pores within the polymer. During galvanic cycling the specific capacitance, power handling and energy density drop in a rapid manner, which is expected in the initial conditioning of a pseudo-capacitor (Fig 5.11).\(^3\) There is an initial increase in specific capacitance after the first 15 cycles of the damp MEA to \( \approx 5 \) F g\(^{-1}\). After 200 galvanic cycles the capacitance levels out at \( \approx 4 \) F g\(^{-1}\). This gives the energy density and power handling values of 0.9 J g\(^{-1}\) and 3.35 x 10\(^{-3}\) W g\(^{-1}\) respectively. The specific capacitance and specific energy obtained are the second highest values found in this work (highest was polypyrrole doped with 10-molybdo-2-vanadophosphoric acid at 7 F g\(^{-1}\) and 1.8 J g\(^{-1}\)). The specific power level is similar to that of the MEAs containing iron(III) chloride based electrodes. The self-discharge (open circuit) profiles with both the damp and RH = 100% MEAs drop rapidly in the first hour, with a subsequent slower potential loss which continued beyond 15 h (Fig 5.12). After 15 h the wet MEA decreased to 0.38 V, which was one of the highest long-term values for the MEAs studied in this work. The device studied at RH = 100% decreased to 0.09 V due to the
internal resistance of the cell. When the potential (V) is plotted vs. log(t), the small but characteristic initial loss from double-layer capacitances is seen, followed by a partial plateau of mixed capacitances (at ≈ 0.5 V for the damp MEA) and then the dominant decrease in pseudocapacitance with increasing potential (Fig 5.4).

**Fig 5.10. Charge / discharge curves of the MEA. Electrode coating: polypyrrole doped with 12-molybdophosphoric acid. Cycled at +/- 1 mA.**

**Fig 5.11. Plot showing change in energy, power and capacitance of the MEA. Electrode coating: polypyrrole doped with 12-molybdophosphoric acid.**
Chapter 5. Galvanic cycling and self-discharge of supercapacitor test cells.

**Fig 5.12.** Self-discharge behaviour of the MEA. Electrode coating: polypyrrole doped with 12-molybdophosphoric acid.

MEA incorporating electrodes with coatings of chemically grown poly(N-methylpyrrole) doped with 12-molybdophosphoric acid.

The charge / discharge curve is similar in shape to that given by the MEA containing electrodes of polypyrrole doped with 12-molybdophosphoric acid, which is non-linear due to the polymer electrodes (Fig 5.13). A large drop in potential is seen (falling to 0.4 V), again similar to the polypyrrole derivative and is followed by a hump caused by the electrodes. The discharge curve falls to 0.2 V in the MEA of RH = 100% indicating a larger IR drop caused by lower relative humidity. This results in less efficient charge storage by the MEA.

After 200 cycles the specific capacitance has dropped to 2.2 F g⁻¹, lower than the polypyrrole based MEA (which gives 4 F g⁻¹) (Fig 5.14). The specific power reduced to $3.3 \times 10^{-3}$ W g⁻¹, and the specific energy was 0.5 J g⁻¹. The profiles of specific capacitance, specific power and specific energy all appear to decrease beyond the 200 cycles, with no levelling in the curves. The self-discharge profiles of both the damp and RH = 100% MEAs were similar to
each other, falling rapidly to \( \approx 0.2 \) V after 2 h and then more slowly to \( \approx 0.1 \) V after 15 h (longer than with the polypyrrole related polymer (Fig 5.15).

![Graph showing charge/discharge curves of the MEA. Electrode coating: poly(N-methylpyrrole) doped with 12-molybdophosphoric acid. Cycled at +/- 1 mA.]

**Fig 5.13.** Charge/discharge curves of the MEA. Electrode coating: poly(N-methylpyrrole) doped with 12-molybdophosphoric acid. Cycled at +/- 1 mA.

![Graph showing change in energy, power and capacitance of the MEA. Electrode coating: poly(N-methylpyrrole) doped with 12-molybdophosphoric acid.]

**Fig 5.14.** Plot showing change in energy, power and capacitance of the MEA. Electrode coating: poly(N-methylpyrrole) doped with 12-molybdophosphoric acid.
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Fig 5.15. Self-discharge behaviour of the MEA. Electrode coating: poly(N-methylpyrrole) doped with 12-molybdophosphoric acid.

MEA incorporating electrodes with coatings of chemically grown polypyrrole doped with 12-molybdosilicic acid.

The charge / discharge curve of the damp MEA show a sudden increase in the potential after 0.6 V to 1 V; this behaviour is almost mirrored in the discharge curve (Fig. 5.16), which, as with the MEA incorporating electrodes of 12-molybdophosphoric acid doped polypyrrole, drops rapidly to \( \approx 0.4 \) V. The charge / discharge curves of the RH = 100% MEA are much briefer, dropping to below 0.2 V at \( \approx 60 \) s. The specific capacitance reached a steady 3.5 F g\(^{-1}\) after 200 cycles, specific energy and specific power were 0.8 J g\(^{-1}\) and \( 3.7 \times 10^{-3} \) W g\(^{-1}\) respectively (Fig. 5.17). These results were similar, but actually a little lower, compared to the polypyrrole and 12-molybdophosphoric acid MEA (for which the values are 4 F g\(^{-1}\) and 0.9 J g\(^{-1}\)). Self-discharge falls to 0.2 V after 15 h for the damp cell (Fig. 5.18) which gives a pseudo-capacitance dominated plot of potential (V) vs log(t), similar to that of the MEA containing electrodes incorporating polypyrrole doped with the 12-molybdophosphoric acid. The MEA kept under RH = 100% self-discharged quickly to below 0.1 V and after 15 h reached 0.05 V, which was much lower than the damp MEA.
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**Fig 5.16.** Charge / discharge of the MEA. Electrode coating: polypyrrole with 12-molybdosilicic acid. Cycled at +/- 1 mA.

**Fig 5.17.** Plot showing change in energy, power and capacitance of the MEA. Electrode coating: polypyrrole doped with 12-molybdosilicic acid.

**Fig 5.18.** Self-discharge behaviour of the MEA. Electrode coating: polypyrrole doped with 12-molybdosilicic acid.
MEA incorporating electrodes with coatings of chemically grown poly(N-methylpyrrole) doped with 12-molybdosilicic acid.

The charge / discharge curve of the damp run cell shows faradaic charging, but poor energy density caused the discharge curve to drop to zero potential after only 30 s (Fig 5.19). The charge / discharge curve for the cell stored at RH = 100% is similar in shape but the discharge falls to zero after just 10 s. The specific capacitance, specific power and specific energy profiles drop rapidly to low levels after 200 galvanic cycles. Specific capacitance is $\approx 0.4 \text{ F g}^{-1}$, specific energy is a low $0.08 \text{ W h kg}^{-1}$ and specific power is $1.1 \text{ W kg}^{-1}$ (Fig 5.20). These values were much lower than those found with MEAs made with poly(N-methylpyrrole) electrodes doped with 12-molybdophosphoric acid (for which the values were $2.2 \text{ F g}^{-1}$, $0.5 \text{ J g}^{-1}$ and $3.3 \times 10^{-3} \text{ W g}^{-1}$). Self-discharge of the damp MEA results in a decrease to 0.17 V after 15 h and for the cell at RH = 100% it decreased to 0.05 V (Fig 5.21). A plateau is formed in the plot after 5 h, caused by the pseudo-capacitive nature of the electrodes. The nature of the pseudo-capacitance is again seen using the plot of potential (V) vs log(t).

Fig 5.19. Charge / discharge curves of the MEA. Electrode coating: poly(N-methylpyrrole) doped with 12-molybdosilicic acid. Cycled at +/- 1 mA.
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**Fig 5.20.** Plot showing change in energy, power and capacitance of the MEA. Electrode coating: poly(N-methylpyrrole) doped with 12-molybdosilicic acid.

**Fig 5.21.** Self-discharge behaviour of MEA. Electrode coating: poly(N-methylpyrrole) doped with 12-molybdosilicic acid.

MEA incorporating electrodes with coatings of chemically grown polypyrrole doped with 10-molybdo-2-vanadophosphoric acid.

The damp MEA with electrodes of polypyrrole and 10-molybdo-2-vanadophosphoric acid gave the most suitable charge / discharge curves (Fig 5.22), which were smooth and showed a shape associated with the pseudo-capacitive influence from the electrodes. The discharge drops to 0.65 V and is followed by a slow discharge to zero, (which takes \( \approx 10 \) min. The
galvanic cycling of the MEA stored at RH = 100% shows a very fast discharge curve, indicating a significant influence on the MEA by the level of humidity. The specific capacitance, power handling and energy density plots increase rapidly in the first few runs and more steadily beyond 200 galvanic cycles (Fig. 5.23). Specific capacitance rises to \( \approx 7 \ \text{F g}^{-1} \) for the damp cell, specific power to \( 3.3 \times 10^3 \ \text{W g}^{-1} \) and \( 1.8 \ \text{J g}^{-1} \) for specific energy. The value for power handling is the same as the MEA incorporating polypyrrole doped with the 12-molybdophosphoric acid. The specific energy and the specific capacitance are however almost twice the magnitude, suggesting that the 10-molybdo-2-vanadophosphoric acid provides a more suitable polymer dopant compared with 12-molybdophosphoric acid.

![Graph showing charge/discharge curves of the MEA.](image)

**Fig 5.22.** Charge / discharge curves of the MEA. Electrode coating: polypyrrole doped with 10-molybdo-2-vanadophosphoric acid. Cycled at +/- 1 mA.
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**Fig 5.23.** Plot showing change in energy, power and capacitance of the MEA. Electrode coating: polypyrrole doped with 10-molybdo-2-vanadophosphoric acid.

**Fig 5.24.** Self-discharge behaviour of the MEA. Electrode coating: polypyrrole doped with 10-molybdo-2-vanadophosphoric acid.

**MEA incorporating electrodes with coatings of chemically grown poly(N-methylpyrrole) with 10-molybdo-2-vanadophosphoric acid.**

The shape of the charge / discharge curves show no similarity to the polypyrrole MEA derivative with the fast discharge becoming a trend with the poly(N-methylpyrrole) derived MEAs (Fig 5.25). The charging is smoothly curved to the 1 V limit and is followed by a fast discharge to zero, taking 50 s. This is reflected in the rapid loss in specific capacitance over the 200 galvanic cycles, with a decrease to \(\approx 0.65 \, \text{F g}^{-1}\) based on the mass of the MEA (Fig
5.26). The specific energy after this decrease is the lowest of the MEA incorporating heteropolyacid doped polymers (at \( \approx 0.1 \) J g\(^{-1}\)); the specific power was \( 1.95 \times 10^{-3} \) W g\(^{-1}\).

The specific capacitance, specific energy and specific power do not settle and all continue to decrease up to 200 cycles, in common with other poly(N-methylpyrrole) based MEA devices. The self-discharge curves drop to 0.24 V and 0.15 V after 15 h for the damp and RH = 100% MEAs respectively (Fig 5.27). These values are lower than those obtained with the polypyrrole derivative (for which the values were 7 F g\(^{-1}\), 1.8 J g\(^{-1}\) and \( 3.3 \times 10^{-3} \) W g\(^{-1}\)); this was again a common trend seen in the poly(N-methylpyrrole) based MEAs.

![Graph](image1.png)

**Fig 5.25.** Charge / discharge curves of the MEA. Electrode coating: poly(N-methylpyrrole) doped with 10-molybdo-2-vanadophosphoric acid. Cycled at +/- 1 mA.

![Graph](image2.png)

**Fig 5.26.** Plot showing change in energy, power and capacitance of the MEA. Electrode coating: poly(N-methylpyrrole) doped with 10-molybdo-2-vanadophosphoric acid.
Chapter 5. Galvanic cycling and self-discharge of supercapacitor test cells.

Fig 5.27. Self-discharge behaviour of the MEA. Electrode coating: poly(N-methylpyrrole) doped with 10-molybdo-2-vanadophosphoric acid.

MEA incorporating electrodes with coatings of chemically grown polypyrrole doped with 14-vanadophosphate.

The shape of the charge / discharge curve from the damp run MEA (Fig 5.28) is similar to the MEA incorporating 10-molybdo-2-vanadophosphoric acid doped poly(N-methylpyrrole) (Fig 5.25). The discharge time of the damp stored device is also similar, as it rapidly decreases to 0.3 V and then to 0 V after 55 s. During the 200 charge / discharge cycles the plot for specific capacitance, power and energy density drop rapidly (Fig 5.29). The specific capacitance fell to 0.75 F g\(^{-1}\), specific energy dropped to 0.08 J g\(^{-1}\) and specific power was 1.5 x 10\(^{-3}\) W g\(^{-1}\) after 200 galvanic cycles. The specific capacitance and specific energy were the lowest of the heteropolyacid + polypyrrole MEA combinations. On self-discharge of the MEA run in damp conditions, discharge was in a pseudo-capacitive manner to 0.3 V after 15 h (Fig 5.30). The cell that was run at RH = 100% decreased to 0 V after 2 h.
Chapter 5. Galvanic cycling and self-discharge of supercapacitor test cells.

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**Fig 5.28.** Charge / discharge curves of the MEA. Electrode coating: polypyrrole doped with 14-vanadophosphate. Cycled at +/- 1 mA.

---

**Fig 5.29.** Plot showing change in energy, power and capacitance of the MEA, polypyrrole doped with 14-vanadophosphate.

---

**Fig 5.30.** Self-discharge behaviour of the MEA. Electrode coating: polypyrrole doped with 14-vanadophosphate.
**MEA incorporating electrodes with coatings of chemically grown poly(N-methylpyrrole) doped with 14-vanadophosphate.**

The charge / discharge curve of the damp MEA is rapid, indicating poor charge storage (*Fig 5.31*). The specific capacitance, specific energy and specific power for the damp MEA are 0.01 F g\(^{-1}\), 5.0 \(\times\) 10\(^{-3}\) J g\(^{-1}\) and 7 \(\times\) 10\(^{-3}\) W g\(^{-1}\) respectively (the plot has been omitted for clarity). The values for specific capacitance and energy density are much lower than for the MEA incorporating the polypyrrole-derived electrodes (for which the values were 0.75 F g\(^{-1}\), 0.08 J g\(^{-1}\)) (*Fig 5.29*). Self-discharge drops to 0.02 V after 15 h for the damp MEA the lowest of all the damp MEAs (*Fig 5.32*).

![Graph](image1)

*Fig 5.31. Charge / discharge curves of the MEA. Electrode coating: poly(N-methylpyrrole) doped with 14-vanadophosphate. Cycled at +/- 1 mA.*

![Graph](image2)

*Fig 5.32. Self-discharge behaviour of the MEA. Electrode coating: poly(N-methylpyrrole) doped with 14-vanadophosphate.*
Comparison of charge / discharge results with a.c. impedance plots from Chapter 4.

1) On dehydration of the MEAs (going from ‘damp’ to RH = 100%) there is in general a large decrease in the discharge time leading to lower specific capacitances and specific energies. Accompanying this there is an increase in the internal resistance, reducing the performance further. Impedance studies provide corroborating data; as the humidity of the MEAs are reduced to RH = 100% the electrolyte / interface resistance ($R_s$) and the Faradaic leakage resistance ($R_f$) increase, resulting in higher IR drop (Fig 4.25).

2) After 200 galvanic cycles for most MEAs there was a decrease in the specific capacitance, specific energy and specific power. Impedance studies indicated that this was related to the increase in the electrolyte / interface resistance ($R_s$) and the increase in the bulk resistance (line after the semicircle, Chapter 4).

5.3 Consideration of the basis for comparison to other work.

The best values obtained from a membrane electrode assembly (MEA) were from the electrodes of polypyrrole coated carbon paper doped with 10-molybdo-2-vanadophosphoric acid run in damp conditions. These were 7 F g$^{-1}$, 1.8 J g$^{-1}$ and 3.3 x10$^{-3}$ W g$^{-1}$ for specific capacitance, specific energy and specific power respectively, based on unit mass of MEA materials (including water). Self-discharge tests indicated that the potential after 15 h was 0.35 V, which was one of the highest persisting values at that time. Values for specific energy and specific power were converted into the forms W h kg$^{-1}$ and W kg$^{-1}$ respectively, which are the most often used in the literature. This resulted in the values 0.5 W h g$^{-1}$ and
3.3 W kg\(^{-1}\) respectively for the 10-molybdo-2-vanadophosphoric acid + polypyrrole-based MEA.

Further assessment of the literature reveals that many research groups scale the values for specific energy and specific power to the unit mass of the active polymer within both the electrodes (*Table 5.2*). This is not necessarily correct, as goals set by the American Department of Energy for electric vehicles are based on packaged devices and not on active polymer content.\(^4\) (The targets are: near term > 5 W h kg\(^{-1}\), 50 kW kg\(^{-1}\) and <100 kg for energy power and package weight respectively; longer term > 15 W h kg\(^{-1}\), 80 kW kg\(^{-1}\) and < 50 kg).\(^4\) However, to provide a form of comparison, values for the devices tested in this work were not only normalised to the unit mass of MEA but also re-expressed in terms of electrodes masses and unit mass of active polymer (from both electrodes) (*Table 5.1*).

On conversion of the specific energy and specific power to per unit mass active polymer, the electrodes doped with a polypyrrole doped 10-molybdo-2-vanadophosphoric acid coating gave 27.6 F g\(^{-1}\), 2.09 W h kg\(^{-1}\) and 13.4 W kg\(^{-1}\). The MEA with electrodes coated in polypyrrole doped with 12-molybdophosphoric acid gave similar magnitudes for specific capacitance and specific power, although the specific energy was lower (22.9 F g\(^{-1}\), 8.87 W kg\(^{-1}\) and 1.44 W h kg\(^{-1}\) respectively). Electrodes coated in polypyrrole doped with 12-molybdosilicic acid gave slightly higher specific capacitance per unit mass of active polymer (33.4 F g\(^{-1}\)), a similar specific energy (2.12 W h kg\(^{-1}\)) and much higher specific power (35.7 W h kg\(^{-1}\)). The specific power for the MEA incorporating polypyrrole grown with iron(III) chloride (49.5 W kg\(^{-1}\)) was higher than the other polypyrrole derived MEAs. With the MEA based on the electrochemically grown polypyrrole the specific capacitance and energy density were much smaller than for other polypyrrole based MEAs. These comparatively
low levels were due to poor contact, as the morphological studies showed in Chapter 3 for the iron(III) chloride based systems and the inability to hot-press the electrochemically grown electrode, as discussed in Chapter 4. The MEAs based on the doped poly(N-methylpyrrole) coating all gave lower specific capacitances and specific energy compared to their polypyrrole derivatives.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Capacitance (F g⁻¹), energy (W h g⁻¹) and power (W kg⁻¹), per unit mass of MEA, electrodes and active polymer.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F g⁻¹</td>
</tr>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>4.0</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>3.5</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>7.0</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>0.75</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>0.24</td>
</tr>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>2.2</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>0.40</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>0.65</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>0.01</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 5.1. Capacitance, energy and power per unit mass of MEA (black), electrodes (red) and active polymer material (blue). Mass of active polymer is the sum for both electrodes.
5.4 **Comparison of the MEAs with the literature.**

Comparisons of the specific capacitance, energy density and power handling can be made with literature values (Table 5.2). Some of the examples give two sets of data; each set refers to a different current density during discharge tests. It can be seen that as the energy density decreases the power handling increases. The electrodes of polyfluorophenylthiophene (PFPT) are dominant in the open literature, with acetonitrile-based electrolytes. As discussed in Chapter 1, PFPT gives a stable n-doped polymer, which can be used in a type III capacitor. This gives higher specific energy and specific power levels compared with symmetrical systems (type I), such as polyaniline, or asymmetrical systems (type II), such as polyaniline with polypyrrole (Table 5.2). Most of the literature systems utilising polymer electrodes are based on acetonitrile electrolytes and a few use gels.

A symmetrical system (type I) of polyaniline found in two of the literature sources gives specific energy of 5 and 3.1 W h kg\(^{-1}\) with respective specific power of 1 and 1.4 kW kg\(^{-1}\) (all values were per unit mass of active polymer) (see Table 5.2 for references); both these systems were based on acetonitrile-based electrolytes. The symmetrical supercapacitor using polypyrrole electrodes with a gel based electrolyte gave specific energy of 3.5 and 2.5 W h kg\(^{-1}\) (depending on the current density) with respective specific power of 0.2 and 1.5 W kg\(^{-1}\).
### Capacitor construction with polymer and electrolyte material

<table>
<thead>
<tr>
<th>Material Description</th>
<th>Specific Energy / Wh kg(^{-1})</th>
<th>Specific Power / kW kg(^{-1})</th>
<th>Ref</th>
</tr>
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<tr>
<td>Polyfluorophenylthiophene (type III) / ACN</td>
<td>47</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Polyaniline (type I) / ACN</td>
<td>26</td>
<td>10</td>
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<tr>
<td>Polypyrrole (type I) / ACN</td>
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<td></td>
</tr>
<tr>
<td>Polypyrrole / polythiophene (type II) / ACN</td>
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<td>N/A</td>
<td>6</td>
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<tr>
<td>Polyfluorophenylthiophene (type III) / ACN</td>
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<td>N/A</td>
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</tr>
<tr>
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<tr>
<td>Polyfluorophenylthiophene (type III) / ACN</td>
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<td>Polyaniline / polypyrrole (type II) / ACN</td>
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<td>1.4</td>
<td>7</td>
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<td></td>
</tr>
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<td>2.2</td>
<td>8</td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>Polyaniline / polypyrrole (type II) / ACN</td>
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<td>0.2</td>
<td>9</td>
</tr>
<tr>
<td>Polyfluorophenylthiophene (type III) / ACN</td>
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<td>0.4</td>
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</tr>
<tr>
<td>Polyfluorophenylthiophene (type III) / ACN</td>
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<td>Polyfluorophenylthiophene (type III) / ACN</td>
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<td>0.25</td>
<td>10</td>
</tr>
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<td></td>
</tr>
<tr>
<td>Poly(3,4-ethylenedioxythiophene) (type III) / ACN</td>
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<td>2.5</td>
<td>11</td>
</tr>
<tr>
<td>Polyfluorophenylthiophene (type III) / Carbon (negative electrode) / gel</td>
<td>38</td>
<td>6.8</td>
<td>12</td>
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<tr>
<td>Polyaniline (type I) / ACN</td>
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<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Polyaniline (type I) / ACN</td>
<td>0.8</td>
<td>3.2</td>
<td></td>
</tr>
</tbody>
</table>

### Table 5.2. Example of supercapacitors incorporating various polymer electrodes with acetonitrile (ACN) and gel based electrolytes. References 5-10 express values per gram of active polymer; reference 11 refers to the mass of the two electrodes; reference 12 refers to the mass of the whole cell.
Chapter 5. Galvanic cycling and self-discharge of supercapacitor test cells.

The highest values found in this work were lower, when compared to the values obtained per unit mass of active polymer or cell, than the systems found in the literature. There are, however, major advantages to the system developed in this work. These are as follows:

1) Acetonitrile-based electrolytes give higher power and specific energy as a result of a larger voltage window of $\approx 3 \text{ V}$ compared to an aqueous system $\approx 1 \text{ V}$ limit (to prevent the decomposition of water). Acetonitrile is, however, both toxic and flammable; this is such a problem that its use in manufacturing and research has been banned in Japan. “Covalent”, a battery company based in the United States of America, has made non-flammable acetonitrile-based electrolytes, but these are very expensive and therefore may not be as commercially viable as other electrolytes. Aqueous systems would be more suited in the manufacture of, for example, toys, computers, cars or any large-scale applications.

2) Fabrication of aqueous systems is much simpler as there are no special precautions to be considered. This contrasts for example with (i) the complete dryness which is necessary for electrolytes such as acetonitrile, (ii) the difficulty of controlling humidity levels of gel electrolyte polymers such as poly(ethyleneoxide), which decomposes if too wet. Neither of these is a problem with Nafion®, as the damp conditions are easily maintained without damage to the membrane (in fact these conditions are essential).

3) The use of a solid electrolyte membrane such as Nafion® overcomes corrosion of supercapacitor materials, such as the casing, which can result from the use of aqueous acids (e.g. $\text{H}_2\text{SO}_4$)
4) Vapour growth of the polymer electrodes onto the aqueous oxidant requires only the energy necessary to maintain a constant temperature. This method overcomes the problems associated with electrochemical growth, which are the large energy usage and, therefore, high cost, low industrial viability and poor environmental impact.

5) Vapour transport growth of the polymer electrodes overcomes the need for the very pure electrolytes and monomers otherwise required for electrochemical growth. If the electrolyte and monomer are not completely pure, the electrochemically grown electrodes have poor cycling lifetimes. By evaporating the monomer (e.g. pyrrole) into the sealed chamber, it is essentially purified. [There are no organic solvent-based electrolytes used].

6) Vapour transport growth enables reproducible fabrication of electrodes when temperature is held constant.
Chapter 5. Galvanic cycling and self-discharge of supercapacitor test cells.

5.5 Conclusions.

Chapter 5 has introduced the development work of MEA test cells. Analytical techniques which were used included galvanic charge / discharge cycling and open circuit (self-discharge) monitoring. There was further discussion of results obtained earlier from a.c. impedance and cyclic voltammetry (results shown in Chapter 4).

1) Capacitor cells incorporating electrochemically grown polymers doped with sodium dodecylbenzene sulfonate (SDBS) and those chemically grown via the vapour transport method using iron(III) chloride were both found to give poor results. The galvanic cycling showed low energy storage and specific capacitance. The electrode balancing was a problem, as fabrication of electrodes showed poor reproducibility and unsatisfactory surfaces for the iron(III) chloride based systems (Plate 3.6). This resulted in a potential gain in the self-discharge curves caused by asymmetry. CVs showed irreversibility and breakdown of the electrode materials. These observations lead to the conclusion that the polymer electrodes made chemically using iron(III) chloride and SDBS are unsuitable for capacitors using a Nafion® electrolyte.

2) Test cells analysed under damp conditions gave higher specific capacitance, energy density, power handling and improved self-discharge characteristics compared with the same polymer MEAs run at RH = 100%. A wet-conditioned MEA is also easier to maintain and so would be more useful in future experiments.

3) The damp polypyrrole-based capacitors held more energy on self-discharge when compared to the equivalent poly(N-methylpyrrole) and polypyrrole electrode constructions run at RH = 100%. The damp polypyrrole-based systems would therefore give better power handling and energy density over a longer period of time.
4) MEAs based on electrodes coated with polypyrrole chemically grown with heteropolyacids showed the highest specific capacitance and energy density values for the MEAs, when compared with those incorporating poly(N-methylpyrrole). Each of these decreased in the following order of specific capacitance and energy density per unit mass of hydrated MEA:

10-molybdoo-2-vanadophosphoric acid > 12-molybdophosphoric acid > 12-molybdosilicic acid >14-vanadophosphate > iron(III) chloride > sodium dodecylbenzene sulfonate.

5) When the mass of the active polymer was taken into account, the specific capacitance and energy density decreased in the following order of specific capacitance and energy density (for energy density 14-vanadophosphate and SDBS are interchangeable) per unit mass of active polymer:

12-molybdosilicic acid > 10-molybdoo-2-vanadophosphoric acid > 12-molybdophosphoric acid >14-vanadophosphate ≡ sodium dodecylbenzene sulfonate

The most promising MEA incorporated the carbon paper electrode with a polypyrrole coating chemically grown via vapour transport using 10-molybdoo-2-vanadophosphoric acid as the oxidant. Galvanic cycling studies of the cell run under damp conditions showed that capacitance, energy and power continued to rise beyond the 200 initial cycles. The most promising results based on the unit mass of active polymer coating were obtained from the 12-molybdosilicic acid doped polypyrrole; the specific capacitance and energy density were then 33.4 F g⁻¹ and 2.12 Wh kg⁻¹, higher than any other polymer in this study. Although the power density (35.7 W kg⁻¹) was not as high as some of the poly(N-methylpyrrole) based systems, it was accompanied by a much larger energy density.
Chapter 5. Galvanic cycling and self-discharge of supercapacitor test cells.

5.6 References.


6. Overall conclusions and future work.

This work has seen development from material evaluation to electrode testing and the final fabrication and evaluation of simple MEAs and capacitors. The main findings of this work are given below.

Chapter 2 evaluated monomer and oxidant combinations, using methods such as direct addition and thin-film growth. The thin-films successfully grown via the vapour transport method showed an unusual morphology, when viewed using SEM and which has not previously been reported. Successful oxidants were 12-molybdophosphoric acid, 12-molybdosilicic acid, 10-molybdo-2-vanadophosphoric acid, 14-vanadophosphate, iron(III) chloride and potassium ferricyanide. The monomers chosen, after various evaluation tests, were pyrrole and N-methylpyrrole. Toray carbon paper was the chosen support.

Chapter 3 evaluated the combinations of monomer and oxidant in producing a satisfactory coating, which could be used within a capacitor membrane electrode assembly (MEA). An electrochemically-grown electrode was introduced, incorporating the surfactant sodium dodecylbenzene sulfonate, for comparison. The multiple coating of the chemically grown polymers onto the carbon paper electrodes gave complete coverage for nearly all of the monomer / oxidant combinations, with the exception of potassium ferricyanide which was disregarded before cyclic voltammetry (CV) tests. Polymers grown with the heteropolyacids after multiple coatings all gave smooth surfaces as observed using SEM. The polymer electrodes doped with the heteropolyacids gave, with exception of the 14-vanadophosphate, three redox events in their CVs (which became more reversible on decreasing scan rate). These peaks were characteristic of the encapsulated heteropolyacid, which was maintained
within the polymer matrix during repeated cyclic tests. The most promising combination used polypyrrole and 10-molybdo-2-vanadophosphoric acid, which gave the highest specific capacitance per gram of active polymer material (Chapter 3). For further comparisons, all combinations of monomer / oxidant were studied further as electrodes within MEAs in capacitors.

Chapter 4 introduced the design of test cells for use in the evaluation of the MEAs. The test cells were a two-electrode design suitable for a.c. impedance studies and galvanic cycling, and a three-electrode cell, suitable for CV. The results of a.c. impedance studies showed that, in general, the electrolyte / interface ($R_e$), faradaic leakage resistance ($R_f$) and the bulk diffusion resistance all increase on reduction in humidity from wet conditions to RH = 100%. The resistances also increase after 200 charge / discharge cycles. These resistances, when combined, are known as the equivalent series resistance (e.s.r.) which when increased result in the reduction in energy density and power handling of the devices. The a.c. impedance plots for the polypyrrole-based systems were similar to those found in the literature (Chapter 5). MEAs containing poly(N-methylpyrrole) gave two semicircles, indicating a more complex process. Both polypyrrole and poly(N-methylpyrrole) MEAs gave behaviour deviating from the ideal capacitor and required the use of a constant phase element (CPE) to take account of the diffusion properties within these polymer systems. The CVs indicated diffusion processes, (also evident in Chapter 3), as a reduced scan rate resulted in increased reversibility for most of the polymer-coated electrodes.

Chapter 5 presented the results and discussions obtained from the study of the galvanic charging and discharging of the capacitors with MEAs under both damp and RH = 100% conditions. The most successful combinations involved polypyrrole and the heteropolyacids
12-molybdophosphoric acid, 12-molybdosilicic acid and 10-molybdo-2-vanadophosphoric acid. Of these, the 10-molybdo-2-vanadophosphoric acid gave the highest values for specific capacitance (7 F g\(^{-1}\)) and energy density (0.5 W h kg\(^{-1}\)) per unit mass of MEA (see Table 5.1 for full data). When the values were compared against the unit mass of the active polymer, polypyrrole doped with 12-molybdosilicic acid gave the highest values for specific capacitance (33.4 F g\(^{-1}\)), energy density (2.12 W h kg\(^{-1}\)) and power handling (35.7 W kg\(^{-1}\)). Although this power handling was lower than some of the other doped polymers, it was accompanied by much higher energy density.

Further study of electrodes would include polypyrrole doped with 12-molybdophosphoric acid, 12-molybdosilicic acid or 10-molybdo-2-vanadophosphoric acid. Particular attention would be given to the 10-molybdo-2-vanadophosphoric acid; although it may not give the highest values per unit mass of active polymer, it is more stable than the other two heteropolyacids.

Development of more reversible electrodes could be achieved with thinner polymer coatings, reducing the diffusion and resistances. This would reduce the equivalent series resistance (e.s.r), giving electrodes with enhanced power handling and energy density.

The vapour transport method of growth would be used in future studies, as it provides pure monomer through evaporation at room temperature. The purity of the reagents is very important when designing polymer electrodes for supercapacitors; impurity contamination is a problem found with the electrochemical growth of electrodes. An impure monomer and electrolyte will result in the fast degradation of the polymer electrode on cycling.
A significant problem in practical terms with electrochemically grown polymers is the quantities of electrical energy needed to produce the thin-film coating. The vapour transport method of growth is potentially more suitable for large-scale applications.
Appendix 1. Infrared analysis, data tables for polypyrrole and poly(N-methylpyrrole) based materials.

Key: Numbers in parentheses ‘(number)’ are wavelength peak positions in cm⁻¹; notation ‘C-C’ for example are the band assignments; notation x/y: x is either s = strong, m = medium or w = weak bands; y is either n = narrow, b = broad and vb = very broad band width, sh = shoulder peak. Notation Mo-O-Mo es = edge sharing and and cs denotes corner sharing. Str = stretch, ben = bend.

<table>
<thead>
<tr>
<th>Oxidant doped in polypyrrole</th>
<th>Infrared detail</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>C-H overlap with Mo-O-Mo es (795) s/b, Mo-O-Mo cs (880) w/b, Mo=O (973), (1104) w/b, C-H overlap with P-O (1062) s/n, C=N (1164) s/b, C-C str (1299) s/b, C=C ben (1467) w/b, C=C str (1543) s/b.</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>C-H overlap with Mo-O-Mo es (800) s/b, Mo-O-Mo cs (876) sh, Si-O (913) s/n, Mo=O (957) w/n, C-H (1060) m/n, (1101) w/b C-N str (1181) s/b, C-C str (1292) m/b, C=C str (1544) s/b.</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>C-H overlap with Mo-O-Mo es (807) s/b, Mo-O-Mo cs (884) w/b, Mo=O (950) m/b; C-H overlap with P-O (1065) s/n, (1101) w/b C=N (1181) s/b, C-N (1327) m/n, C=C ben (1459) w/b, C=C str (1560) s/b.</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>C-H (807) w/b, (877) w/b, C-H overlap with P-O (1057) s/b, (1088) w/n, (1096) w/n, (1104) w/n, C-H (1152) s/b, C-C str (1283) m/b, C=C str (1542) s/b.</td>
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<tr>
<td>Iron(III) chloride</td>
<td>C-H (779) m/n, (835) w/n , (869) w/n, C-N (906) s/b, (960) w/n, C-H (1057) m/b, (1088) m/n, C=N (1170) s/b, C-C str (1277) m/b, C=C str (1545) s/b.</td>
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</tbody>
</table>

Table A1.1. Infrared analysis (KBr disk) of polypyrrole thin-film reaction products.
<table>
<thead>
<tr>
<th>Oxidant doped in polypyrrole</th>
<th>Infrared detail</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>C-H overlap with Mo-O-Mo es (804) s/b, Mo-O-Mo cs (883) sh, C-N (936) s/vb; Mo=O (968) sh, C-H overlap with P-O (1063) s/n, (1093) w/b, C=N (1184) s/b, C-N (1321) s/vb, C-C (1459) m/vb, C=C (1551) s/n.</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>C-H overlap with Mo-O-Mo es (798) s/b, Mo-O-Mo cs (876) sh, Si-O (913) s/n, M=O (958) s/n, C-H (1058) m/n, (1093) w/b, C=N (1175) m/vb, C-N (1305) w/vb, C=C (1542) m/vb.</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>C-H overlap with Mo-O-Mo es (806) s/b, Mo-O-Mo cs (883) w/b, Mo=O (947) s/b, C-H overlap with P-O (1067) m/n, (1096) w/b, C-N (1202) s/vb, C-N (1342) m/vb, C=C (1561) s/vb.</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>C-H overlap with V-O-V es (814) s/b, V=O (949) sh, C-H overlap with P-O (1067) m/vb, C-N (1341) m/vb, C=C (1561) s/b.</td>
</tr>
<tr>
<td>12-Tungstophosphoric acid</td>
<td>(528) s/n, C-H (731) s/b, W-O-W es (792) s/b, W-O-W cs (874) m/n, C-N (920) s/n, W=O (972) s/n, C-N (1016) s/n, P-O (1098) m/n, (1117) w/n, (1287) w/n, C=C (1373) m/n, C=C (1423) m/n, (1457) w/n, C=Cben (1565) m/vb(1668)w/n, C-H (3105) m/b, N-H (3378) m/b, (3557) w/b.</td>
</tr>
<tr>
<td>12-Tungstosilicic acid</td>
<td>(532) s/n, (736) s/b, C-H (736) s/b, W-O-W es (794) s/b, W-O-W cs (883) m/n, Si-O (920) s/n, W=O (972) s/n, C-N (1015)s/n, C-Hben (1098)m/n, (1117) w/n, C-N (1379) w/n, C-C (1423) m/n, C=C (1563) w/n, C=N (1610) m/n, C-H (3134) w/n, N-H (3391) m/n,</td>
</tr>
<tr>
<td>Potassium ferricyanide</td>
<td>C-H (796) s/n, C-N (899) s/b, C-N (965) m/n, C-H (1040) s/n, C-N (1090) m/n, C=N (1168) s/b, C-N (1302) m/b, C-Cben (1456) w/b, C=C str (1539) s/n.</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>C-H (784) w/b, C-N (887) s/vb, C-N (965) m/n, C-H (1053) s/n, C-N (1084) w/n, (1100) w/n, C=N (1161) s/vb, C-N (1298) m/vb, C=C (1542) s/n.</td>
</tr>
</tbody>
</table>

Table A1.2. Infrared analysis (KBr disk) of polypyrrole direct addition reaction products.
Appendix 1. Infrared analysis, data tables for polypyrrole and poly(N-methylpyrrole) based materials.

<table>
<thead>
<tr>
<th>Oxidant doped in poly(N-methylpyrrole)</th>
<th>Infrared detail</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>Mo-O-Mo es (815) s/n, Mo-O-Mo cs (892) m/n, Mo=O (971) s/n, C-H overlap with P-O (1075) s/n, (1135) w/n, C=N (1158) sh, C-N (1302) m/b, C-C (1425) w/vb, C=C (1528) m/vb.</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>C-H overlap with Mo-O-Mo es (810) s/n, Mo-O-Mo cs (866) w/sh, Si-O (918) s/n; Mo=O (965) m/n; C-H (1073) w/vb, (1132) w/n, C-N (1321) m/vb, C-C (1440) w/vb, C=C (1561) m/vb.</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>Mo-O-Mo es (808) s/n, Mo-O-Mo cs (885) m/b, Mo=O (969) s/n, C-H overlap with P-O (1068) m/b, (1132) w/vb, C-N (1341) m/vb, C-C (1439) m/b, C=C (1600) s/vb.</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>V=O (969) s/b, Spread between (1062) – (1158) m/vb, (1330) w/b, C-N (1383) w/n, C-C (1439) m/b, C=C (1618) s/vb.</td>
</tr>
<tr>
<td>12-Tungstophosphoric acid</td>
<td>(512) m/n, (695) m/n, W-O-W es (803) s/n, W-O-W cs (893) s/n, W=O (986) s/n, P-O (1079) s/n, C-N (1363) s/n, (1398) w/n, (1522) w/n, C=C (1627) w/b, (2928) w/n, (3102) w/b.</td>
</tr>
<tr>
<td>12-Tungstosilicic acid</td>
<td>(524) m/n, (730) sh, W-O-W es (796) s/n, W-O-W cs (873) m/n, Si-O (924) s/n, W=O (970) s/n, C-N (1013) m/n, (1095) w/n, (1289) w/n, C-C (1456) m/vb, C=C (1638) m/vb, (2943) w/b, (3102) w/b.</td>
</tr>
<tr>
<td>Potassium ferricyanide</td>
<td>C-H (796) m/n, (912) w/n, C-H (1048) m/b, (1145) w/b, Spread between (1324) and (1697) s/vb.</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>(680) w/b, (723) w/n, C-H (773) w/b, C-H (1058.23) m/b, C-N (1101) w/b, C=N (1148) m/b, C-N (1315) s/vb; C-N (1383) sh, C-C (1448) s/n, C=C (1560) s/vb.</td>
</tr>
</tbody>
</table>

Table A1.3. Infrared analysis (KBr disk) of poly(N-methylpyrrole) direct addition reaction products.
<table>
<thead>
<tr>
<th>Oxidant doped in polypyrrole</th>
<th>Infrared detail</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>C-H (762) w/b, overlap with Mo-O-Mo es (782) w/b, Mo-O-Mo cs (870) w/b, C-N (918) w/b, Mo=O (942) w/b, C-H overlap with P-O (1062) s/n, (1087) w/n, (1098) w/n, C-N (1114) w/n, C=N (1166) s/vb, C-N (1296) m/vb, C=C (1542) s/b.</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>C-H overlap with Mo-O-Mo es (799) s/b, Mo-O-Mo cs (863) sh, Si-O (913) s/b, Mo=O (962) sh, C-H (1061) s/n, (1104) w/n, C=N (1175) s/vb, C-N (1290) m/vb, C=C (1542) s/b, C=C (1561) m/n.</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>C-H overlap with Mo-O-Mo es (798) s/vb, Mo-O-Mo cs (865) w/n, Mo=O (965) m/b, C-H overlap with P-O (1062) s/n, (1104) w/n, C-N (1186) s/vb, C=N (1314) m/vb, C=C (1556) m/vb.</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>V=O (921) s/vb, C-H overlap with P-O (1064) m/n, C=N (1189) m/vb, C-C (1311) w/vb, C=C (1560) m/vb.</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>C-H (776) s/n, C-N (948) s/b, C-H (1056) s/b, C=N (1200) s/b, C-C (1293) m/vb, C=C (1553) s/vb.</td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td>Broad lump up to (891), C-N (976) m/n, C-H (1052) s/b, C-N (1092) m/n, C=N (1161) s/vb, C-C (1292) m/vb, N-H (1460) w/vb, C=C (1541) s/vb.</td>
</tr>
</tbody>
</table>

Table A1.4. Infrared analysis (KBr disk) of Toray carbon papers coated with polypyrrole doped with various oxidants.
<table>
<thead>
<tr>
<th>Oxidant doped in poly(N-methylpyrrole)</th>
<th>Infrared detail</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>C-H overlap with Mo-O-Mo es (813) s/b, Mo-O-Mo cs (894) sh. Mo=O (969) s/n, C-H overlap with P-O (1074) s/n, C-N (1107) m/vb, C=C (1618) m/vb</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>C-H overlap with Mo-O-Mo es (799) s/n, Mo-O-Mo cs (883) sh. Si-O (914) s/n, Mo=O (968) m/n, C-N (1128) w/n.</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>C-H overlap with Mo-O-Mo es (799) s/b, Mo-O-Mo cs (883) m/b, Mo=O (969) s/n, C-H overlap with P-O (1071) m/b, (1333) m/vb, C-N (1383) w/b, C-C (1449) w/b, C=C (1595) m/vb, C=C (1697) w/b.</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>V=O (955) w/vb, C-H (1064) w/n, C-N (1117) w/n, C-N (1382) w/n, C=C (1624) m/vb.</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>C-N (1033) s/vb, C-N (1370) m/vb, C-C (1444) m/vb, C=C (1638) s/vb.</td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td>C-H (667) m/b, large number of overlapping peaks between (1001-1157) s, (1228) w/n, C-N (1301) m/b, C-C (1458) m/b, C=C (1541) s/vb, C=C (1690) m/vb.</td>
</tr>
</tbody>
</table>

Table A1.5. Infrared analysis (KBr disk) of Toray carbon papers coated with poly(N-methylpyrrole) doped with various oxidants.

Appendix 2. TG and DTA data of the heteropolyacids.

Fig A2.1. TG and DTA plot of 10-molybdo-2-vanadophosphoric acid.

Fig A2.2. TG and DTA plot of the 12-molybdoielic acid.
Appendix 2. TG and DTA data of the heteropolyacids.

Fig A2.3. TG and DTA plot of 14-vanadophosphate.

Fig A2.4. TG and DTA plot of the 12-molybdophosphoric acid.
Appendix 3. Peak position and capacitance data tables for cyclic voltammetry tests carried out on carbon paper/polymer coated electrodes.

The following Tables give data relating to the cyclic voltammograms found in Chapter 3. The scan rates 100 mV s\(^{-1}\) (Table A3.1), 10 mV s\(^{-1}\) (Table A3.2) and 1 mV s\(^{-1}\) (Table A3.3) are shown below. The peak position data is given in up to three columns A / A', B / B' and C / C'. These represent the three consecutive electrochemical reactions that occur in some of the polymers containing the heteropolymetallates. For all the other electrodes, which show only one set of reduction and oxidation peaks, C / C' is used (e.g. this was the case for the electrochemically grown polypyrrole doped with the sodium dodecylbenzene sulfonate). Some of the peaks were either not present or not assignable; these have been denoted as such. The black values in the peak position tables represent the oxidation part and the red value is the corresponding reduction curve.

The capacitance has been calculated for the corresponding peak positions (Tables 3.4 to 3.6) using the mean value of the positive and negative peak currents. Capacitance values are converted by taking into account the mass of the active material in the electrode and the geometrical area of the electrode. The scan rates 100 mV s\(^{-1}\) (Table 3.4), 10 mV s\(^{-1}\) (Table 3.5) and 1 mV s\(^{-1}\) (Table 3.6) are shown below. The C / C', B / B' and A / A', again represent the consecutive electrochemical reactions seen in the cyclic voltammograms. Some of the peaks were either not present or not assignable; these have been denoted as not applicable (N/A).
<table>
<thead>
<tr>
<th>Oxidant or dopant</th>
<th>Poly(pyrrrole)</th>
<th>Poly(N-methylpyrrrole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-Molybdophosphoric acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12-Molybdosilic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A3.1. Cyclic voltammogram peak positions of redox-centred polymer electrodes. Scan rate of 100 mV s⁻¹.
Appendix 3. Peak position and capacitance data tables for CV for cyclic voltammetry tests carried out on carbon paper / polymer coated electrodes.

<table>
<thead>
<tr>
<th>Oxidant or dopant</th>
<th>Peak positions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C / C'</td>
</tr>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>196</td>
</tr>
<tr>
<td></td>
<td>99</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>256</td>
</tr>
<tr>
<td></td>
<td>96</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>333</td>
</tr>
<tr>
<td></td>
<td>56</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>455</td>
</tr>
<tr>
<td></td>
<td>255</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>N/A</td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxidant or dopant</th>
<th>Peak positions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C / C'</td>
</tr>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>176</td>
</tr>
<tr>
<td></td>
<td>122</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>133</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>198</td>
</tr>
<tr>
<td></td>
<td>119</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>N/A</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>N/A</td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table A3.2. Cyclic voltammogram peak positions of redox-centred polymer electrodes. Scan rate of 10 mV s⁻¹.
Appendix 3. Peak position and capacitance data tables for CV for cyclic voltammetry tests carried out on carbon paper / polymer coated electrodes.

<table>
<thead>
<tr>
<th>Oxidant or dopant</th>
<th>Peak positions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A /A’</td>
</tr>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td>122</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>249</td>
</tr>
<tr>
<td></td>
<td>149</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>256</td>
</tr>
<tr>
<td></td>
<td>89</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>470</td>
</tr>
<tr>
<td></td>
<td>300</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>437</td>
</tr>
<tr>
<td></td>
<td>210</td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxidant or dopant</th>
<th>Peak positions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A /A’</td>
</tr>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>135</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>186</td>
</tr>
<tr>
<td></td>
<td>151</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>130</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>N/A</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>N/A</td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table A3.3. Cyclic voltammogram peak positions of redox-centred polymer electrodes. Scan rate of 1 mV s⁻¹.
Appendix 3. Peak position and capacitance data tables for CV for cyclic voltammetry tests carried out on carbon paper / polymer coated electrodes.

<table>
<thead>
<tr>
<th>Oxidant or dopant</th>
<th>Capacitance / F g⁻¹</th>
<th>Capacitance / F cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A / A’</td>
<td>B / B’</td>
</tr>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>38</td>
<td>46</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>70</td>
<td>81</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>N/A</td>
<td>68</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>103</td>
<td>103</td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td>3 x 10⁻³</td>
<td>0.02</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>290</td>
<td>290</td>
</tr>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>19</td>
<td>32</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>71</td>
<td>108</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>The reaction was irreversible, no result obtained.</td>
<td></td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td>The reaction was irreversible, no result obtained.</td>
<td></td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>The reaction was irreversible, no result obtained.</td>
<td></td>
</tr>
</tbody>
</table>

Table A3.4. Specific capacitance data of polymer coated lone electrodes doped with various oxidants. Cyclic voltammetry was carried out at scan rate of 100 mV s⁻¹.
Appendix 3. Peak position and capacitance data tables for CV for cyclic voltammetry tests carried out on carbon paper / polymer coated electrodes.

<table>
<thead>
<tr>
<th>Oxidant or dopant</th>
<th>Capacitance / F g⁻¹</th>
<th>Capacitance / F cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A/A'</td>
<td>B/B'</td>
</tr>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>104</td>
<td>128</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>316</td>
<td>421</td>
</tr>
<tr>
<td>12-Molybdosilic acid</td>
<td>179</td>
<td>233</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>153</td>
<td></td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>42</td>
<td>70</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>35</td>
<td>48</td>
</tr>
<tr>
<td>12-Molybdosilic acid</td>
<td>166</td>
<td>230</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A3.5. Specific capacitance data of polymer coated lone electrodes doped with various oxidants. Cyclic voltammetry was carried out at a scan rate of 10 mV s⁻¹.
Appendix 3. Peak position and capacitance data tables for CV for cyclic voltammetry tests carried out on carbon paper / polymer coated electrodes.

<table>
<thead>
<tr>
<th>Oxidant or dopant</th>
<th>Capacitance / F g(^{-1})</th>
<th>Capacitance / F cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A / A'</td>
<td>B / B'</td>
</tr>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>172</td>
<td>240</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>629</td>
<td>776</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>270</td>
<td>315</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td>192</td>
<td>0</td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td>421</td>
<td></td>
</tr>
<tr>
<td>12-Molybdophosphoric acid</td>
<td>83</td>
<td>139</td>
</tr>
<tr>
<td>10-Molybdo-2-vanadophosphoric acid</td>
<td>93</td>
<td>139</td>
</tr>
<tr>
<td>12-Molybdosilicic acid</td>
<td>248</td>
<td>486</td>
</tr>
<tr>
<td>14-Vanadophosphate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium dodecylbenzene sulfonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron(III) chloride</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A3.6. Specific capacitance data of polymer coated lone electrodes doped with various oxidants. Cyclic voltammetry was carried out at a scan rate of 1 mV s\(^{-1}\).

Shown in the following pages are several X-ray microanalysis plots. The analytical method of X-ray microanalysis and results shown here are discussed in more detail in Chapter 3. The following list identifies the spectra by its corresponding letter (nearly all below are chemically grown apart from e. and f. which are obtained through galvanic growth):

a. Untreated Toray carbon paper.

b. Thin-film of polypyrrole doped with 12-molybdophosphoric acid.

c. Thin-film of polypyrrole doped with 12-molybdosilicic acid.

d. Thin-film of polypyrrole doped with 14-vanadophosphate.

e. Carbon paper + polypyrrole coating doped with sodium dodecylbenzene sulfonate

f. Carbon paper + poly(N-methylpyrrole) coating doped with sodium dodecylbenzene sulfonate.

g. Carbon paper + polypyrrole coating doped with 12-molybdophosphoric acid.

h. Carbon paper + poly(N-methylpyrrole) coating doped with 12-molybdophosphoric acid

i. Carbon paper + polypyrrole coating doped with 12-molybdosilicic acid.

j. Carbon paper + poly(N-methylpyrrole) coating doped with 12-molybdosilicic acid

k. Carbon paper + polypyrrole doped with 10-molybdo-2-vanadophosphoric acid.

l. Carbon paper + poly(N-methylpyrrole) coating doped with 10-molybdo-2-vanadophosphoric acid

m. Carbon paper + polypyrrole coating doped with 14-vanadophosphate.

n. Carbon paper + poly(N-methylpyrrole) coating doped with 14-vanadophosphate.

o. Carbon paper with a polypyrrole coating doped with potassium ferricyanide.
Appendix 4. X-ray microanalysis of plain Toray carbon paper, selected thin-films and carbon paper coated with polymers
Appendix 4. X-ray microanalysis of plain Toray carbon paper, selected thin-films and carbon paper coated with polymers
Appendix 4. X-ray microanalysis of plain Toray carbon paper, selected thin-films and carbon paper coated with polymers

Counts

Energy (keV)

Counts

Energy (keV)

Counts

Energy (keV)

Counts

Energy (keV)