Advanced Fibre Based Energy Storage

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Declaration of Originality

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Abstract

New energy storage devices are required to enable future technologies. With the rise of wearable consumer and medical devices, a suitable flexible and wearable means of storing electrical energy is required. Fibre-based devices present a possible method of achieving this aim. Fibres are inherently more flexible than their bulk counterparts, and as such can be employed to form the electrodes of flexible batteries and capacitors. They also present a facile possibility for incorporation into many fabrics and clothes, further boosting their potential for use in wearable devices.

Electrically conducting fibres were produced from a dispersion of carbon nanomaterials in a room temperature ionic liquid. Coagulation of this dispersion was achieved through manual injection into aqueous solutions of xanthan gum. The limitations of this method are highlighted by very low ultimate tensile strengths of these fibres, in the order of 3 MPa, with high variation within all of the fibres. Fibres were also produced via scrolling of bicomponent films containing poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and poly(vinyl alcohol) (PVA). Chemical treatments were employed to impart water compatibility to these fibres, and their electrochemical, physical and electrical properties were analysed.

Fibres were wet spun from two PEDOT:PSS sources, in several fibre diameters. The effect of chemical treatments on the fibres were investigated and compared. Short 5 min treatment times with dimethyl sulfoxide (DMSO) on 20 µm fibres produced from Clevios PH1000 were found to produce the best overall treatment. Up to a six-fold increase in electrical conductivity resulted, reaching 800 S cm$^{-1}$, with up to 40% increase in specific capacitance and no loss of mechanical strength (55 F g$^{-1}$ and 150 MPa recorded).

A wet spinning system to produce PEDOT:PSS fibres containing functionalised graphenes and carbon nanotubes, as well as birnessite nanotubes was subsequently developed. Manganese dioxide was also grown electrochemically on the outside of PEDOT:PSS fibres, with polypyrrole and PEDOT:PSS coating protection methods investigated. Electrochemical testing determined that birnessite nanotube-containing fibres presented the most viable option for energy storage device applications. Using the birnessite nanotube-containing fibre, fibre-based supercapacitors were fabricated and investigated. Specific capacitance values of 80 F g$^{-1}$ were obtained, stable for over 1,000 cycles at 0.5 A g$^{-1}$.
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<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>BMIBF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1-methyl-3-butylimidazolium tetrafluoroborate</td>
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<td>CCD</td>
<td>Cyclic charge discharge</td>
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<td>CNT</td>
<td>Carbon nanotube</td>
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<td>FLG</td>
<td>Few layer graphene</td>
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<td>GNP</td>
<td>Graphene nanoplatelets</td>
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<td>MWCNT</td>
<td>Multi-wall carbon nanotube</td>
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<tr>
<td>PAni</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PBS</td>
<td>Phosphate buffered saline</td>
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<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylendioxythiophene) polystyrene sulfonate</td>
</tr>
<tr>
<td>PPy</td>
<td>Poly(pyrrole)</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly(vinyl alcohol)</td>
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<tr>
<td>RSD</td>
<td>Relative standard deviation</td>
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<tr>
<td>RTIL</td>
<td>Room temperature ionic liquid</td>
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<tr>
<td>SDBS</td>
<td>Sodium dodecyl benzene sulfonate</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<td>SWCNT</td>
<td>Single-wall carbon nanotube</td>
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<td>TEM</td>
<td>Transmission electron microscopy</td>
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<td>Abbreviation</td>
<td>Description</td>
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<td>TGA</td>
<td>Thermogravimetric analysis</td>
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1 Introduction

1.1 Context

The ever-growing use of electronics has transformed the way we live our lives. From recreational consumer devices to breakthrough medical devices, all require a power source. The use of such technologies is continually growing; new technologies are continually being developed and produced, with one such example being wearable and flexible personal electronics (1-3). The possible uses for these technologies range from flexible mobile phones, to wearable health-monitoring sensors (4); these devices have the potential to make a huge impact on our daily lives.

For flexible electronic devices to be realised, there is a need to develop flexible power sources, such as batteries and/or supercapacitors. Currently electrical energy storage devices, such as lithium-ion batteries, are typically bulky and rigid, restricting their use in flexible and/wearable applications. One possible development may be through the use of fibre-based energy storage (5). In such a device, fibres would be employed as the electrodes of a capacitor or battery. These fibres can conduct charge through the system, as well as acting as (or as part of) the energy storage system.

It is envisioned that these devices could be employed as energy storage systems in wearable medical devices, such as heart rate monitors or fitness tracking devices, or in consumer devices incorporated within clothing. As such, the fibres will need to be robust enough to allow them to be incorporated within these systems. They will also need to be highly flexible, with limited or no degradation occurring through repeated bending movements.

Such devices would require a base fibre which is electrically conductive, while also incorporating materials enabling the storage of electrical energy through either capacitive or battery-based mechanisms. This may consist of an intrinsically conducting polymer material such as polypyrrole or poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS), or the use of nanomaterials such as carbon nanotubes (CNT) or graphenes, as well as the addition of energy storage materials, including manganese dioxide. There exists a wide range of materials and processes which may be suitable for producing such devices, several of which are detailed and investigated within this work.
1.2 Energy Storage System Comparison

Multiple energy storage technologies exist for powering portable electronics. Two of the most common of these are battery and capacitor-based systems. Each of these systems can be produced in several variants, each with their own inherent advantages and disadvantages (6). As such, multiple properties of the device to be employed must be considered, including the total energy required to be stored, the power requirements of the desired load, the device lifetime, and the physical requirements placed on the device (e.g. temperature, size, flexibility). Careful selection of the correct device to meet the specific needs of the use is required. A Ragone plot, as shown in Figure 1, is commonly used to visually demonstrate the differences in achievable energy and power density of such devices (7-8). Power density is defined as the amount of power (rate of energy transferable per second) per unit weight of the device, while the energy density is defined as the total amount of energy stored in the device per unit weight (6). It can be seen that capacitors offer the highest power density, due to their rapid charge and discharge ability, but store the lowest amount of total energy per weight. Supercapacitors bridge the gap between traditional capacitors and batteries, offering higher energy densities than capacitors, but at lower deliverable power densities. Batteries offer high levels of energy density, making them more suitable for systems with a lower, more sustained power requirement, but for longer amounts of times. Fuel cells offer higher levels of energy density again, but at further decreased rates of power delivery.

For wearable applications, it is likely to be necessary to store larger amounts of energy than what is currently achievable using traditional capacitors, and as such, batteries and more recently supercapacitors present the best potential method for powering wearable electronics (9-10). This work will focus on understanding and furthering the development of fibre-based supercapacitor energy storage devices.
1.3 Energy Storage Through Capacitance

Capacitance, measured in Farads, is defined as amount of charge a system can store, per unit voltage. The capacitance of a two-plate capacitor may be calculated by dividing the charge stored (in Coulombs) by the voltage applied (in Volts) between the plates, as shown in Equation 1, Where q is calculated as the current (in Amps) multiplied by time (in s) (11).

$$C = \frac{Q}{V} = \frac{(I \ast T)}{\Delta V}$$

*Equation 1 – Calculation of capacitance (11-12).*

The plates of a capacitor may take many forms; from simple metal sheets separated by an insulating layer, to complex composite materials with vastly increased surface areas, employing tailored dielectric separators. Capacitance is often reported as mass specific capacitance, obtained by dividing the total capacitance by the mass of the materials employed. The energy stored in such a device can be calculated by relating the mass specific capacitance to the voltage at which the device is charged to, given in Equation 2. It can be seen that the energy stored is proportional to the square of the voltage, thus
highlighting that devices which can operate at higher voltages are able to store exponentially higher levels of energy (13).

\[ E = \frac{1}{8} C_s V^2 \]

Equation 2 – Determination of energy stored in a capacitor (13).

Two main mechanisms of energy storage occur in capacitors and supercapacitors; electric double-layer capacitance, and pseudocapacitance. These two forms, however, arise from different mechanisms (6). Electric double-layer capacitors employ the electric double-layer effect. In this, a voltage is applied between two conductive electrodes (plates) separated with a liquid electrolyte or another such insulating dielectric layer. The application of this voltage causes the formation of a layer of charged ions on each electrode, corresponding to the opposite charge to the plate, as demonstrated in Figure 2. When a load is placed on the device, the opposite movement occurs, transferring electrons through the load, and depleting the double layer, thus returning the system to the original, normally-distrusted arrangement of ions.

![Figure 2](image1.png)

Figure 2 – Illustration of electric double-layer effect in capacitor devices (14).

Pseudocapacitance, as shown in Figure 3, differs from double-layer capacitance in that it occurs through a faradaic charge transfer between the electrolyte and the electrodes of the capacitor (15). Electron transfer occurs, balanced with electrosorption and intercalation of
charged species on and within the structure of the electrodes. It is important to note that no chemical bonds are broken or formed during pseudocapacitive mechanisms. Pseudocapacitance often occurs in tandem with double-layer capacitance, further boosting the overall capacitance of the material employed.

![Simplified schematic of pseudocapacitance charge storage. Showing charge transfer between electrolyte and manganese dioxide active material. Reproduced from (16).](image)

Pseudocapacitance can occur along with electric double-layer capacitance to produce materials with greatly enhanced capacitance values (15). Such materials can be added to a system to increase the overall capacitance of the material (17).

## 1.4 Materials of Interest

The choice of material is important to convey the necessary electrical and electrochemical properties required for energy storage. An electrical conductivity of the order of 100 S cm\(^{-1}\) may be adequate for this application, although this may be re-assessed throughout this work. The fibres will also need to be robust enough able to withstand being manipulated, and attached to other surfaces. Potentially the most crucial fibre property is their ability to store charge, their specific capacitance. This value is desired to be as high as possible, without compromising other aspects of the fibres.
1.4.1 Graphene

Graphene has been an area of intense research in the previous decade; its unique and notable properties have seen it used in a broad range of areas, applications and devices (18). It has received much attention from the scientific community, stemming from Novoselov and Geim’s Nobel Prize winning research (19), with a large amount of interest in future materials and devices using or being produced from graphene (20).

Graphene consists of two dimensional hexagonal patterns of sp² bonded carbons. Its properties of interest include extremely high electrical and thermal conductivities of $6.4 \times 10^6$ S cm$^{-1}$ and $5 \times 10^3$ W m$^{-1}$ K$^{-1}$ respectively, and high physical and mechanical strengths, with a Young’s modulus in the order of 1,100 GPa (21). Graphene’s two-dimensional structure, also yields useful properties; such as a massive surface area of theoretically up to 2,630 m² g$^{-1}$ (21). Many forms of graphene can be produced, depending on the number of layers required, as shown in Figure 4 below.

![Figure 4 – Illustration of single (SL), few (FL), and multi-layer (ML) graphene sheets on the atomic scale (21).](image)

Graphene is a key material of interest in this work as it has the potential to increase electrical conductivity, surface area, and increased charge storage in a composite (22-23). This requires the graphene to be incorporated efficiently, for example dispersed uniformly within a fibre, increasing the electrical conductivity through percolation of the nano particles dispersed within the fibre. Pristine graphene is difficult to process, including dispersing within aqueous solutions, due to strong inter-sheet forces (24). Due to this, a suitable procedure, for exfoliation and dispersion, will need to be used to allow efficient use and incorporation of the material (24-25).
1.4.2 Carbon Nanotubes (CNT)

One of the most well-known and highly used of all nanomaterials, carbon nanotubes (CNTs) consist of a cylindrical structure of carbon sheets. Single wall carbon nanotubes (SWCNTs) consist of a single sheet of graphene wrapped around to form a cylinder, while multiwall carbon nanotubes (MWCNTs) have multiple cylinders each wrapped around the previous cylinder. Similar to graphene, both of these nanotube types possess excellent electrical conductivity up to $10^6$ S cm$^{-1}$ (26), and physical properties, such as a Young’s Modulus of 900 GPa (27). Thermal conductivities are believed to be up to 5,800 W m$^{-1}$ K$^{-1}$ for SWCNTs and up to 10,000 W m$^{-1}$ K$^{-1}$ for MWCNTs (28).

![Figure 5 – Single walled carbon nanotube structure (29).](image)

CNTS may be used in a similar way to graphene, increasing many desired properties, such as electrical conductivity and specific capacitance, of the CNT-containing materials/composites (30). As with graphene sheets, CNTs are difficult to process and disperse, due to powerful van der Waals interactions arising from their large surface area (31). As such will they require adequate processing such as surfactant or polymer stabilised dispersion.

1.4.3 Manganese Oxides

Many forms of manganese compounds are routinely used in a wide range of energy storage systems, such as in batteries (32) and capacitors (33). Due to manganese’s ability to move between a range of oxidation states, it can be employed to store and release electrical energy in secondary batteries, or to generate electrical energy when employed within primary batteries (34-35).

Manganese oxides can be used in both primary (36) and secondary batteries (37), as well as in supercapacitor applications (38). Many production methods of manganese oxides exist, producing multiple different forms and variants of the material. Manganese dioxide prepared for energy storage applications is commonly produced electrolytically (39-40). Such a process typically involves calcining manganese-containing ores, into solutions
containing sulfuric acid. The solution is filtered and electrolysed to produce electrolytic manganese dioxide (40). Alternative forms, such as birnessite, can be produced through hydrothermal processes (41), involving the use of potassium permanganate with potassium hydroxide at elevated temperature for several days.

Birnessite is a layered form of manganese dioxide, and consists of edge-shared \( \text{MnO}_6 \) octahedra, with water molecules and cations in the interlayer sites (42-43). A large surface area arises from the layered nature of the structure, and also allows for the cations to transport between the interlayer regions. These properties have allowed birnessite to be used in energy storage applications in a range of areas (44-45).

![Figure 6 - Birnessite Structure (43).](image)

The incorporation of different forms of manganese oxides should allow for additional electrochemical energy storage to be incorporated into the fibres, thus increasing the total amount of energy stored by the system (46).

### 1.4.4 Conducting Polymers

Conducting polymers are polymeric materials which are electrically conductive, allowing them to be used for electrical applications. These materials have been produced from many structures, including, amongst others, polyacetylene, polypyrrole, polyaniline (PAni), and polythiophene. Conducting polymers have found use in a wide range of applications, including solar cells (47) and biosensors (48).

One of the first reported conducting polymers was produced through the oxidation of polyacetylene with halogen ions, producing a nine order of magnitude increase in its electrical conductivity, relative to polyacetylene itself (49). Continual investigation and progress into conducting polymers has been carried out since, and the area has grown into
a hugely successful field, with Professors Heeger, MacDiarmid, and Shirakawa being awarded the 2000 Nobel Prize for their initial discovery. Conductivities of conducting polymers have steadily increased, with materials possessing conductivities up to and beyond $10^5 \text{ S cm}^{-1}$ (50), similar to that of metallic copper ($6 \times 10^5 \text{ S cm}^{-1}$) (51). Conductivities ranging between 0.1 and 500 S cm$^{-1}$ have been commonly reported for many conducting polymers (52).

The mechanism of conductivity within conducting polymers arises from the doping of the polymer’s conjugated double bond system. When extra electrons are added, labelled n-type doping, or electrons are removed, labelled p-type doping, a conductive pathway through the polymer is formed (53). This doping has been shown to produce multiple orders of magnitude higher conductivity than the undoped polymer (49). Once these missing electrons, called holes, or extra electrons are present, they are able to move throughout the polymer chains, thus conducting charge through the material (54).

![Molecular structure of poly(acetylene) (trans form shown).](image)

Figure 7 shows the structure of trans-poly(acetylene) where the conjugated double bond system can be seen. Other conducting polymers possess various structures, often incorporating heteroatoms, but all maintaining the conjugation system. Figure 8 shows the molecular structure of poly(3,4-ethylenedioxythiophene) (PEDOT) (55), formed of a pair of bicyclic rings, connected through conjugated double bonds, along with polypyrrole which is conjugated through a single connecting ring system (56).
Figure 8 - Molecular structure of poly(3,4-ethylenedioxythiophene) (left, (55)) and polypyrrole (right, (56)).

While conducting polymers possess interesting electrical properties, the doping to achieve high electrical conductivity may require harmful or hazardous chemicals, and the polymers may be difficult to process or handle. Polyacetylene, for example, is highly unstable in air (57), and poly(3,4-ethylenedioxythiophene) (PEDOT) is water insoluble, making processing difficult. In the case of PEDOT, a polymer dopant in the form of polystyrene sulfonate (PSS) is added to aid water solubility (58). However, this greatly decreases the electrical conductivity; PEDOT:PSS has an electrical conductivity below 1 S cm\(^{-1}\) (59-60), while PEDOT formed through vapour phase polymerisation can have conductivities of and above 1,500 S cm\(^{-1}\) (61). Various treatments have been shown to increase the electrical conductivity of PEDOT:PSS by several orders of magnitude (59-60). For example, thin films treatment with sulfuric acid in combination with temperature treatments produced conductivities in excess of 3,000 S cm\(^{-1}\) (60). Similar treatments have been demonstrated using organic acids (59), methanol (59), and ethylene glycol (62), amongst others (63).

Increasing the electrical conductivity of the polymer is a key step in the optimisation of the efficiency of any electrical/energy storage device. Conducting polymers also possess high specific capacitance values, due to their ability to store charge through pseudocapacitance (64). For example, PEDOT:PSS has a theoretical maximum specific capacitance of 210 F g\(^{-1}\) (65-66), while PANi can reach values of up to 750 F g\(^{-1}\) (67-68).

A large amount of research has been conducted looking at understanding and optimising the preparation conditions of PEDOT:PSS films, specifically looking at the sizes of PEDOT nanocrystals formed within the films (69). Takano et al. found that PEDOT grows as a nano-sized crystal within the bulk film, being surrounded by PSS molecules.
The structure of PEDOT:PSS has been shown to consist of positively charged PEDOT chains, coupled with negatively charged PSS counter ions, as shown in Figure 9 left. The solid form of PEDOT:PSS is believed to be formed of electrically conductive nanocrystals of PEDOT, surrounded by insulating PSS spheres, as shown in Figure 9 right. PEDOT chains are shown in red and blue, within green spheres representing PSS regions.

![Molecular (left) and solid form (right) structure of PEDOT:PSS (58).](image)

Preparation and treatment steps which can alter the size of the crystals formed have a dramatic effect on the electrical conductivity of the film produced. For example, it was shown that water, ethanol and ethylene glycol treatments all produced films with smaller PEDOT crystal sizes, with increasing electrical conductivity as crystal size decreased (69).

The combination of electrical conductivity, charge storage capacitance, and ability to be processed into flexible electronics all make conducting polymers a possible material from which to produce fibre-based energy storage devices.
1.5 Discussion of Fibre Production Methods

1.5.1 Wet spinning

Wet spinning of fibres is the solidification of a liquid or gel phase solution/ dispersion to produce a gel-state or solid fibre (70). This liquid, called the spinning solution, may contain a dissolved polymer which will be solidified, or a dispersion of particles which may be agglomerated and precipitated into fibre form. The composition of the spinning solution determines how the fibre will form, and the conditions required. To produce fibres, the solution is injected through a small opening (such as a needle) called a spinneret, into a coagulation bath which induces solidification. Solidification typically occurs through a change in solubility, using a non-solvent in the coagulation bath, but can also occur using a polymer to solidify a dispersion. Other factors, such as pH (71), or salt content and temperature (72) can trigger the solidification process. As the solution is injected, solidification occurs at the interface between the spinning and coagulation solutions. Rotation of the coagulation bath removes solid fibre, allowing fresh solution at the interface. Matching this rotational speed to the speed of fibre injection is required, to prevent fibre breakage. Another option is to attach the end of a fibre to a bobbin, placed outside of the coagulation bath (62). The bobbin is rotated at the required speed, to collect the fibre as it is injected and solidified, providing continuous injection, solidification, and collection. A simplified diagram is shown in Figure 10. Careful consideration and choice of the materials, solutions, and spinning parameters used is critical in obtaining a successful fibre production system.

Figure 10 - Example of wet spinning apparatus – Including syringe pump, spinning solution, coagulation bath, and optional hot-drawing equipment (heating plates and rotating collecting roller) (62).
Wet spinning is one of, if not the simplest method of manufacturing fibres suitable to this work (70). While it is limited in terms of production speed, and cannot produce fibres with diameters as small as those achieved through methods such as electrospinning and centrifugal spinning (73), it is more versatile and can be used with a wide range of materials. Wet spinning techniques allow control over many of the properties of the fibres produced by varying specific parameters. For example, by changing the size of the opening in the spinneret, thicker or thinner diameter fibres can be produced as desired. The use of different coagulation solutions affects the rate at which fibres solidify, and has been shown to change their diameters, as well as their micro-structure (74). Post-treatment steps can also be employed, to further tailor and improve the properties of the fibres (74). Steps such as hot drawing, where fibres are stretched while being heated, can aid in aligning polymer chains within the fibres, giving rise to improved properties such as strength and electrical conductivity (62). The careful selection and optimisation of these steps can all be employed to produce a fibre tailored and optimised to a specific application. Fibre properties such as diameter, density, length, outer shape, and electrical conductivity can all be controlled in this manner.

It is also possible to incorporate extra materials, such as nanomaterials (75) or additional polymers (76) within fibres via wet spinning. This requires a spinning solution containing a homogeneous dispersion/solution of the desired materials, which will then be contained within the precipitated fibre.

Wet spinning has been employed to produce fibres from multiple different materials, such as insulating (77) and conducting polymers (78), as well as nanomaterials (79), using a vast range of conditions and parameters, for hugely varied applications. Fibres produced via wet spinning have been used in energy applications (80), medical fields (81), as well as in applications with high-strength requirements (82), as a few examples.

1.5.2 Dry and Melt Spinning

Dry spinning is a similar technique to that of wet spinning, in that a solution of dissolved polymer(s) is processed. Whereas wet spinning involves injection into a coagulation bath, dry spinning employs evaporation of the solvent to produce a solid fibre (83). As the solution is extruded through the spinneret(s), a stream of air or intern gas is blown over the
stream, causing rapid evaporation of the solvent, and the solidification of the fibre, as shown in Figure 11 (84). The produced fibres are then collected and processed as desired. Fibres from materials including acetate, acrylic, spandex, and polyvinylchloride are produced using this method (84).

Melt spinning is similar to the previous methods, but differs by employing molten liquid polymers that are turned into fibres. Solid, pre-prepared polymer pellets are melted and extruded through the spinneret(s). As the melt leaves the spinneret it cools and solidifies, forming a solid fibre, as shown in Figure 11 (84). While simple, this method is limited in that it can only be used for polymers which are suitable for melting. Fibres such as nylon are produced in this way (85).

![Diagram of melt and dry spinning equipment](image)

*Figure 11 – Diagrams of melt (left) and dry (right) spinning equipment (84).*

### 1.5.3 Film Scrolling

A less commonly used method of fibre production involves turning films into fibres. In this procedure films of the desired material are produced, which are then typically cut into strips of various sizes, lengths, and shapes, before being twisted into fibres (86). A
rotational force is applied to one end of the fibre, while the other end is held in position. This rotation turns the fibre over itself, forming a scrolled fibre (87).

Several examples of fibres produced this way have been made; one such example produced films of graphene oxide and scrolled them in to fibres. Figure 12 shows this process, on the left the film is attached to a base and the rotational force applied on the right.

![Figure 12 - A graphene oxide film being mechanically scrolled to produce a fibre (86).](image)

This procedure requires a film which is suitably flexible and elastic, to enable it to be tightly coiled, and remain so, based on the interaction with itself produced from the scrolling process. It is often necessary to use a softening agent to give the film the required flexibility to avoid tearing or breakage while being twisted. Fibres produced using this method have the possibility to incorporate a range of additional materials, as they could be added to the film prior to scrolling.

Another method for producing fibres through scrolling involves drawing and twisting fibres from carbon nanotube forests. In this procedure, carbon nanotube forests are grown on a substrate, typically silicon, before being pulled and twisted to create a carbon nanotube yarn (88-89). During pulling and twisting, the nanotubes entangle sufficiently to bind together forming a solid, stable fibre, as shown in Figure 13. Yarns produced through this method were found to have an electrical conductivity of 300 S cm$^{-1}$. 
Figure 13 – Production of carbon nanotube yarns through drawing of carbon nanotube forests (89).

1.6 Fibres for Energy Applications in Literature

1.6.1 Conducting Polymer Fibres

Advanced fibres, that function as flexible electrodes, could allow them to be used in ways not accessible by typical battery technology. Many different materials have been used to produce such fibres, including conducting polymers. Their inherent conductivity and capacitive charge storage properties make them perfect candidates for these applications. Many different conducting polymers have been spun into fibres, including PANi, polypyrrole and polythiophene. One well studied example is the use of PEDOT:PSS, first carried out by Okuzaki and Ishihara (78). In their work a PEDOT:PSS water suspension, purchased from Bayer Co Ltd., was wet spun using an acetone coagulation bath. Fibres were produced using a range of spinnerets, with inner diameters between 180 and 410 µm, allowing for the production of fibres between 5 and 15 µm in diameter. These fibres were found to have electronic conductivities and ultimate tensile strengths of 0.1 S cm⁻¹ and 17.2 MPa respectively. These fibres were found to be have a very smooth surface structure, as shown in the SEM image in Figure 14.

Figure 14 – A wet spun PEDOT:PSS fibre produced by Okuzaki et al. (78).
Further progress towards improving the electrical properties of the fibres was undertaken; one such example was reported by Jalili et al. (74). PEDOT:PSS was sourced in pellet form (Orgacon), and dispersed in water. Investigations into different coagulation baths found that both acetone and isopropanol successfully solidified fibres, with acetone consistently producing larger fibres than isopropanol, due to the quicker solidification rate. The mechanical strengths of the fibres were measured, with fibres spun from isopropanol producing the highest mechanical strengths of 125 MPa, and conductivity values of 9 S cm⁻¹. Post-treatment of these fibres was performed using ethylene glycol and low molecular weight polyethylene glycol. Fibres were soaked in the solvent, before being oven dried at 120 °C for 30 min. Ethylene glycol increased the conductivity to 223 S cm⁻¹, compared to 185 S cm⁻¹ measured with fibres that underwent the polyethylene glycol treatment. To contrast this, the addition of ethylene glycol and polyethylene glycol individually to the spinning solution was measured; ethylene glycol showed no improvement in conductivity, however polyethylene glycol produced fibres with a conductivity of 264 S cm⁻¹. Raman analysis of the fibres found that the Cα=Cβ peak arising from the backbone of the thiophene rings, occurring at 1426 cm⁻¹ in the untreated fibre, was shifted lower by 7 cm⁻¹ in the treated fibres. As this peak arises from the symmetrical stretching of the thiophene rings, the change in wavenumber is attributed to a change in the resonance structure of the benzoid form of the polymer.

Building upon this, record high conductivities of 2,800 S cm⁻¹ were obtained by Thoroddsen et al. (62). PEDOT:PSS was sourced under the Clevios PH1000 brand, and evaporated to form a 2.2 wt.% spinning solution. A coagulation bath consisting of an equal mixture of acetone and isopropanol was used. Four varieties of fibres were produced; all formed using wet spinning followed by a hot drawing process where the as-formed fibres were passed between two hot plates. The stretching of these fibres further increased the properties of the fibres, such as the electrical conductivity. Fibres were formed with no doping treatment, a pre-doping treatment (by the addition of ethylene glycol to the spinning solution), a post-doping treatment by immersion of the fibres in ethylene glycol, and a pre-post-treatment combining both treatments. Electrical conductivity values for these fibres are shown in Table 1. It can be seen that post-treatment has a greater effect than pre-treatment alone, but that the combination of both treatments is required to obtain the highest conductivities.
<table>
<thead>
<tr>
<th>Fibre and Treatment Variant</th>
<th>Electrical Conductivity (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As spun</td>
<td>188</td>
</tr>
<tr>
<td>With hot drawing</td>
<td>368</td>
</tr>
<tr>
<td>With pre-treatment with ethylene glycol</td>
<td>607</td>
</tr>
<tr>
<td>With post-treatment with ethylene glycol</td>
<td>1,304</td>
</tr>
<tr>
<td>With pre and post-treatment with ethylene glycol</td>
<td>2,804</td>
</tr>
</tbody>
</table>

*Table 1 – Conductivity values for PEDOT:PSS fibres wet spun, hot drawn, and treated with various ethylene glycol procedures. Reproduced from (62).*

Figure 15 shows atomic force microscopy (AFM) images detailing the phase separation between PEDOT regions and PSS. In these images the dark regions represent areas of PSS, while the lighter, yellow regions are for PEDOT. The left hand image represents an untreated as-spun fibre, while the right image is for a fibre pre-treated with ethylene glycol. A clear difference in the boundaries and separations can be seen, with the treated fibre having far less dark area, corresponding to an increased interaction between the PEDOT regions, thus increasing the conductivity.

![Atomic force microscopy images](image)

*Figure 15 – Atomic force microscopy images of an untreated as-spun PEDOT:PSS fibre (left), and an ethylene glycol pre-treated fibre (right) (62).*

The hot-drawing process serves to better align the molecular chains within the polymer, aiding the electrical pathways throughout the structure. This process also decreased the diameter of the fibres; from 25 µm to 10 µm. Young’s Modulus values were also found to increase after ethylene glycol treatment, increasing from the as-spun value of 242 MPa to
410 MPa for treated fibres. These treatment steps present a method for improving a number of fibre properties, namely electrical conductivity and mechanical strengths, both essential properties for fibres to be used in wearable and flexible energy storage devices.

Another commonly used conducting polymer is polypyrrole, which was wet spun into fibres by Wallace et al. (90). Polypyrrole was chemically synthesised, before being ground and dissolved in dichlorophenylacetic acid at 12 wt.%. A coagulation bath containing 40 % volume dimethylformamide in water was used. It was necessary to keep the fibre in the coagulation bath for 30 min after injection, followed by a further 4 h in a water bath. The fibres were then removed and dried in air. Mechanical analysis of the fibres determined their ultimate tensile strength to be 25 MPa, and their electrical conductivity found to be of the order of 3 S cm$^{-1}$. Other research featuring polypyrrole, published by Foroughi et al. (91), used high molecular weight polypyrrole and the dopant di(2-ethylhexyl)sulfosuccinate. A conductivity of 3 S cm$^{-1}$ was found for these fibres after wet spinning, with mechanical strengths of 27 MPa. The effect of changing the polypyrrole polymerisation temperature was studied, and it was found that decreasing the temperature increased the tensile strength to 65 MPa and more than tripled the breaking strain to almost 8 %, due to the formation of higher molecular weight polypyrrole and a higher degree of molecular ordering occurring within the fibres. This result, and that shown previously for PEDOT and PSS region size changes after treatment, show the importance of optimising the conducting polymer to best exploit the desired properties of the material(s).

Fibres of PANi have also been prepared by wet spinning by Zhang et al. who demonstrated the production of PANi fibres using a large range of coagulation solvents (92). Through the use of these solvents, it was possible to produce fibres which did not require post-spinning doping treatments to produce electrical conductivity. Fibre spinning using coagulating baths containing aqueous solutions of small anions, such as carbonate and sulfate, produced very short fibres that were unsuitable for use. Small cationic molecules, such as propylamine hydrochloride and hexadecyltrimethylammonium bromide, also produced short fibres. Spinning into coagulation solutions containing polycations, including poly(allylamine hydrochloride) or poly(diallyldimethylammonium chloride) produced longer fibres, but still of low quality. Spinning using coagulation solutions containing poly(styrene sulfonic acid) (PSS) was found to produce longer, higher quality fibres. Increasing the concentration of PSS was found to increase the length at which fibres could
be produced, with concentrations at or above 10 % volume found to produce fibres in infinite length, with a smooth cylindrical profile, shown in Figure 16. The highest conductivities of $35 – 37 \text{ S cm}^{-1}$ were obtained from low (2.5 to 5.0 %) concentrations of PSS, decreasing to $23 \text{ S cm}^{-1}$ for solutions produced from 20.0 % PSS coagulation baths.

![Figure 16 - Fibres spun using coagulation baths containing 1.5 % (A), 5.0 % (B), 15.0 % (C) PSS (92).]

Conducting polymers have also been used by growing the polymer itself directly on to a surface or fibre. Leary et al. (93) grew PAni on carbon fibre fabric to produce pseudocapacitor electrodes. The fabrics were mounted to a steel electrode and immersed in a solution containing aniline, with sodium sulfate as the counter ion. The applied electropolymerisation voltage, deposition time, and aniline concentration were all varied to determine the optimum conditions for polymer growth. The PAni coated fibres produced were compared by measuring their specific capacitance at a constant current of 0.5 mA. It was found that longer deposition times for 0.01 and 0.10 mol dm$^{-3}$ concentrations of aniline both increased the specific capacitance produced (Table 2). A maximum capacitance of $311 \text{ F g}^{-1}$ was obtained from a 5 min deposition from 0.50 mol dm$^{-3}$ aniline; longer times than this began to decrease the capacitance obtained. A voltage of 0.78 V vs. the Ag/AgCl reference electrode was found to be optimal. Again, this work shows that careful choice of the preparation and/or treatment conditions involved in the processing of conducting polymers is essential to best optimising their properties.
Aniline Concentration (mol dm\(^{-3}\)) | Deposition Time (min) | Specific Capacitance (F g\(^{-1}\))
--- | --- | ---
0.01 | 10.0 | 4.2
 | 20.0 | 45
0.10 | 1.0 | 20
 | 5.0 | 166
 | 10.0 | 155
 | 20.0 | 276
0.50 | 5.0 | 311
 | 10.0 | 234
 | 20.0 | 220

*Table 2 – Specific capacitance values for PAni grown in carbon fibre fabrics for different deposition times and aniline concentrations. Reproduced from (93).*

### 1.6.2 Fibres Incorporating Carbon Nanomaterials

While conducting polymers have been shown to exhibit impressive and useful properties on their own, combining them with other materials can greatly increase many desirable properties of the composites produced (94). One such avenue for exploration is the addition of nanomaterials within the fibres, with the aim of exploiting the enhanced properties possessed by many nanomaterials. For example, the addition of graphene and CNTs can be used to increase the electrical (30), electrochemical (30) and physical (75) properties of the fibres.

One of the earliest examples imparting electrical conductivity to a composite fibre involved the injection of a dispersion of SWNCT into a solution of PVA (95). The resulting precipitation produced PVA-SWCNT ribbons and fibres. The electrical conductivity of these dried fibres was measured and found to be 10 S cm\(^{-1}\). Higher electrical conductivities of up to 186 S cm\(^{-1}\) were achieved for chitosan fibres, spun into solutions of chitosan instead of PVA, containing SWCNTs dispersed with hyaluronic acid (HA) (96). SWCNTs were dispersed in an aqueous solution of HA, before being injected into a rotation coagulation bath containing acetone. The resultant fibres were then extracted and dried, after which they were observed to have a ribbon-like structure. A
similar procedure, employing chitosan instead of HA was also performed, producing fibres with electrical conductivities of 23 S cm\(^{-1}\). This method presented a facile technique for incorporating such nanomaterials in to polymeric fibres, and demonstrated that the fibres are imbued with the properties of the SWCNTs.

While the addition of nanomaterials to polymers has been demonstrated to enhance their electrical conductivity, this conductivity is limited due to the amounts of insulating material still present within the fibres. Using a conducting polymer instead presents a method to further increase the levels of electrical and electrochemical properties possible, by reducing the amount of insulating material. An example by Wallace et al. added SWCNTs to PEDOT:PSS fibres in a wet spinning process (30). Solutions of SWCNT with sodium dodecyl sulfate surfactant were prepared using sonication and centrifuging. Water soluble Orgacon PEDOT:PSS pellets were then added to specific volumes of these dispersions to produce PEDOT:PSS-SWCNT dispersions at a range of concentrations corresponding to volume fractions between 0.00 and 0.02 SWCNT. It was found that increasing amounts of SWCNT in the fibres produced a near linear increase in the ultimate tensile strength, from a value of 130 MPa up to a value approaching 200 MPa for a fibre containing a 0.02 volume fraction of SWCNT, as shown in Figure 17.

![Figure 17 – Effect of increasing the amount of SWCNT in a PEDOT:PSS-SWCNT composite fibre on ultimate tensile strength (top) and strain (bottom) (30).](image)

An increase in the fibres’ electrical conductivity was also observed, increasing from a value of 200 S cm\(^{-1}\) for a pure PEDOT:PSS fibre, to a value near 450 S cm\(^{-1}\) for a 0.02
SWCNT volume fraction fibre. Again a near linear increase in conductivity is seen up to this point, suggesting that further increases may have been possible at higher SWCNT loading levels, until saturation occurs. Similar increases are also found for the fibres’ electrochemical properties, with specific currents in cyclic voltammetry increasing by roughly one order of magnitude. Comparing specific capacitance values for the fibres gives a value of 15 F g$^{-1}$ for a pure PEDOT:PSS fibre, which increased to 67 F g$^{-1}$ for a 0.02 SWCNT volume fraction fibre. This work shows that mechanical and electrical/electrochemical properties can all be increased simultaneously by the addition of CNTs to a conducting polymer fibre.

A second published work by Jalili et al. looked at the incorporation of pre-functionalised SWCNTs within a PEDOT:PSS fibre (75). This helps to avoid the use of additional surfactant(s) which can detract from the properties of the fibres produced due to being insulating, and disrupting contact between the nanomaterials within the polymer fibre. Polyethylene glycol functionalised SWCNTs were dispersed in water and Orgacon PEDOT:PSS pellets were added in the required amounts to produce fibres with volume fractions of functionalised SWCNTS of up to 0.12. Fibres were spun via injection in to an isopropanol coagulation bath through a 20 gauge needle. Measurements of tensile strength were performed, and it was found that strengths increased from roughly 125 MPa for a fibre with no nanotube content, up to 250 MPa for a fibre with 0.12 volume fraction functionalised-SWCNT. A larger increase is seen at the lower levels of nanotube content than is observed at higher contents, showing a reduction in the effectiveness of higher levels of nanotube loadings. An increase in electrical conductivity from 10 S cm$^{-1}$ to 35 S cm$^{-1}$ when moving from pure PEDOT:PSS fibres to a 0.12 volume fraction fibre was observed. Treatment with ethylene glycol showed a further improvement in conductivity, increasing to 400 S cm$^{-1}$ at 0.016 volume fraction, and decreasing at higher loadings. The paper attributes this decrease to limited possibility for polymer reordering, due to the increased modulus seen in higher loading fibres. Another possibility is that the functionalised nanotubes, at higher loadings, begin to inhibit conductivity between PEDOT regions of the fibre, due to their reduced conductivity when compared with pristine nanotubes.
1.6.3 Fibres Incorporating Manganese Oxide(s)

While fibres produced using conducting polymers are able to store charge through pseudocapacitive mechanisms, the addition of materials such as manganese dioxide has been used to greatly boost the total amount of charge that can be stored.

Very little work has been reported for directly incorporating manganese oxides within fibres, especially within conducting polymers. One method of producing manganese dioxide within PEDOT was achieved by Lee et al., through immersion of a PEDOT nanowire in a solution of potassium permanganate (97). In this work PEDOT nanowires were electrochemically synthesised potentiostatically from a solution containing 100 mmol dm$^{-3}$ of the 3,4-ethylenedioxythiophene monomer, with 100 mmol dm$^{-3}$ lithium perchlorate at 1.2 V. The PEDOT produced was then immersed in solutions of potassium permanganate of concentration between 5 and 50 mmol dm$^{-3}$, for durations of up to 10 min. There is the possibility of adapting this method to produce manganese dioxide within PEDOT:PSS fibres by direct immersion of the fibres within potassium permanganate solutions.

Electrochemical measurements were performed on the PEDOT-MnO$_2$ composites via cyclic voltammetry and galvanostatic charge discharge techniques. After a 10 min immersion in 10 mmol dm$^{-3}$ potassium permanganate, a quadrupling of the voltammetry current was observed, as well as an increase of over 500 % in the discharge duration. Square voltammetry profiles were observed at scan rates of up to 500 mV s$^{-1}$, and the charge discharge capacitance was calculated to be 250 F g$^{-1}$ at a current density of 5 mA cm$^{-2}$, performed between 0 and 1 V in 1 mol dm$^{-3}$ aqueous lithium perchlorate solution. Increasing the current density from 5 to 25 mA cm$^{-2}$ yielded only a 20 % reduction in specific capacitance, decreasing from 250 to 200 F g$^{-1}$.

![TEM and EDS maps of a PEDOT-MnO$_2$ composite nanowire (97).](image_url)
The presence of manganese was confirmed using TEM and EDS mapping techniques (Figure 18). This analysis confirmed that manganese was successfully incorporated into the nanowires, and distributed throughout their diameter.

Similar methods for the direct growth of manganese dioxide via dipping of fibres in to potassium permanganate solutions have been used for a range of fibre applications. These include carbon fibre cloths (98-99), PAni (100), and freestanding carbon nanofibres (101). Hence this is a versatile method for incorporating manganese dioxide into fibre materials.

A more common method for incorporating manganese oxides is through the use of electrodepositions. This typically involves a solution containing manganese ions. When the fibre is employed as the working electrode, manganese oxides can be electrodeposited on the fibre. Through tailoring the solutions and concentrations used, the voltage/current employed, and the deposition time, control over the oxides produced can be achieved. However, as an electrochemical technique, this method requires a conducting fibre to be used as the working electrode, to form the oxides on it. One such example is the work of Zhang et al., who produced MnO$_2$ on commercially available carbon fibre yarns (102). The electrodeposition was controlled using a constant current deposition, with durations dependant on the mass of yarn used. The electrodeposition solution consisted of manganese acetate and ammonium acetate. Increasing the electrodeposition duration yielded fibres with increasing amounts of galvanostatic charge discharge capacitance based on volume specific capacitance; however, when analysed as mass specific capacitance, a decrease in capacitance was observed with longer deposition times. As shown in Figure 19, a maximum mass specific capacitance was reported for fibres with 100 s deposition times, decreasing with longer deposition durations (shorter durations were not reported). This decrease shows the importance of choosing the optimal conditions at which to perform electrodeposition. Parameters such as the deposition voltage or current used, as well as the deposition duration are critical to producing materials with the highest possible properties.
Another example of electrodeposition is reported by Chen et al. describing the inclusion of MnO\(_2\) nanostructures into graphene fibres (103). In this work, a graphene fibre was produced through hydrothermal reduction of graphene oxide (104); this had a diameter of 35 µm and conductivity in the region of 10 S cm\(^{-1}\). Additional graphene was then added to this fibre by the electrolysis of an aqueous solution of graphene oxide. Finally, MnO\(_2\) nanomaterial was added to the fibre via electrodeposition from a solution of sodium sulfate and manganese sulfate. A constant current was employed, maintaining 400 µA cm\(^{-2}\) for a duration of 5 to 40 min. Various deposition times were analysed, and the resulting products analysed via SEM images, to monitor the growth, shown below in Figure 20.

Figure 20 - MnO\(_2\) deposition at (a) 5 min, (c) 10 min, (d) 20 min, (e) 40 min (103).
The resulting fibres were analysed using cyclic voltammetry at a range of scan rates, between 10 and 100 mV s\(^{-1}\). It was found that fibres with shorter deposition times presented voltammograms closer to that of an ideal capacitive rectangle, with longer times deviating from this shape slightly. Higher currents were also observed with each increasing deposition time, showing a higher level of charge storage being produced.

### 1.6.4 Fibre-Based Energy Storage Devices

Devices have been produced and reported where fibre electrodes have been successfully paired and employed to produce fibre-based supercapacitor devices. These devices can in theory be produced from any flexible, fibre shaped material capable of conducting an electrical current. However, as with traditional capacitors, the capacity of these devices would be low, due to the lack of surface area or pseudocapacitive materials to store charge. As such, conducting polymers, carbon nanomaterials, and manganese oxides present excellent choices as materials from which to produce such devices.

Looking again at the previously discussed work by Chen et al., on the inclusion of MnO\(_2\) nanostructures into graphene fibres (103); two fibres each with a 40 min deposition time were twisted together and a gel electrolyte of H\(_2\)SO\(_4\)-PVA was used to form a supercapacitor system. Electrochemical testing of the symmetric capacitor determined the mass specific capacitance to be between 34 and 36 F g\(^{-1}\), higher than many other fibre-based supercapacitors (105-106). This team also attempted the formation of a second, asymmetric supercapacitor system where one fibre did not contain MnO\(_2\). This system was found to have only 16 % of the capacitance of the symmetric device, highlighting that the MnO\(_2\) nanomaterial is key in achieving higher capacitances. This also demonstrates the need for both fibre electrodes to possess high levels of capacitance. Bend testing of the fibres found that the capacitor retained all of its capacitance even after 1,000 bending cycles.

In another example of a fibre supercapacitor device, Cai et al. produced fibre-based microcapacitors using MWCNTs (107). MWCNTs were produced via standard chemical vapour deposition, and fibres were produced via drawing and twisting of the aligned forests. These fibres were found to have electrical conductivity in the region of 10\(^3\) S cm\(^{-1}\), and a tensile strength of between 10\(^2\) and 10\(^3\) MPa. PANi was then deposited onto the surface of the fibre electrochemically. To fabricate the microcapacitor, two fibres were
aligned and coated in an electrolyte solution (H$_3$PO$_4$–poly(vinyl alcohol)), as illustrated in Figure 21 below. Values for the specific capacitance of the system are reported in Table 3 where a current density of 2 A g$^{-1}$ was used for all weights.

![Figure 21 – Schematic of a microcapacitor containing twisted fibres within an electrolyte coat (a), SEM image of twisted CNT fibres (b) (107).](image)

<table>
<thead>
<tr>
<th>Poly(aniline) Weight (%)</th>
<th>Specific Capacitance (F g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>4.5</td>
</tr>
<tr>
<td>7.4</td>
<td>78</td>
</tr>
<tr>
<td>19</td>
<td>114</td>
</tr>
<tr>
<td>29</td>
<td>117</td>
</tr>
<tr>
<td>48</td>
<td>274</td>
</tr>
</tbody>
</table>

*Table 3 - Specific capacitance values (at 2 A g$^{-1}$) for varying weights of PAni (107).*

It is believed that the increase in specific capacitance with PAni is due to pseudocapacitance arising from the PAni coating. This could present options for extracting greater capacitance from other fibre based systems compatible with a PAni coating (or other suitable conducting polymer). The supercapacitors response to bending/flexing was also measured. The supercapacitor was found to retain over 97 % of its original capacitance after 50 full bending cycles. While there is some decrease in capacitance, suggesting that some damage is being done to the structure, it is a relatively low amount. Further testing above 50 cycles would be desirable, to determine if the capacitance degradation continued with successive bending cycles, or reached a plateau value after a certain point.

Supercapacitor devices have also recently been produced from PEDOT:PSS fibres. Work by Wang *et al.* involved the wet spinning of PEDOT:PSS fibres, before producing twisted fibre yarns to be employed as electrodes (108). PEDOT:PSS fibres were wet spun from a
solution of 1 wt.% PEDOT:PSS dispersed from dry pellets, using a coagulation bath containing 75% volume ethanol and 25 % water, with 3 wt.% CaCl₂ added to aid solidification. Sets of three fibres were braided together, before being aligned together to produce the supercapacitor device. The device was found to exhibit a volumetric capacitance of 20.9 F cm⁻³ at a current density of 50 µA cm⁻². The device was found to retain 93 % of its initial capacity after 5,000 cycles, and no decrease in capacitance was produced after 2,000 bending/straightening cycles. This work shows the potential for producing fibre supercapacitor devices from PEDOT:PSS. The addition of other materials, such as manganese dioxide or carbon nanomaterials may present an opportunity to further enhance the properties of the devices produced.
1.7 Aim and Objectives

The aim of this work was to develop optimised fibre-based electrodes that were suitable for energy storage applications.

The objectives to achieve this were to:

- Develop electrically conducting fibres from suitable materials such as insulating and conducting polymers.
- Produce fibres via several fibre-production systems, including wet spinning.
- Investigate the inclusion of carbon nanomaterials, specifically CNTs and graphenes within fibres, to enhance desirable properties such as electrical conductivity, charge storage, and mechanical strength.
- Incorporate energy storage materials, such as manganese dioxide to enhance the charge storage capability of the fibres produced.
- Characterise the materials and fibres produced, to allow optimisation in order to achieve the highest performance possible. The main properties of interest included the specific capacitance of the fibres, as well as the electrical conductivity and mechanical tensile strength.
2 Instrumentation and Methodology

2.1 Instrumentation Analysis Details and Parameters

2.1.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is a versatile and commonly employed electrochemical technique allowing investigation of the material’s electrochemical properties and response to a range of conditions. CV builds on linear sweep voltammetry by adding a return sweep, as such the voltage is swept between a start and end value (relative to the reference electrode used), at a controlled rate. This allows a full range of voltages to be analysed, in both voltage sweep directions. This scan can be repeated for a chosen number of cycles, allowing additional information to be obtained analysing performance over a given time frame. The electrolyte solution employed can be stirred, or used unstirred, allowing further tuning of the operating parameters and conditions. Through tailoring the use of voltage ranges, sweep rates, as well as the choice of electrolyte (especially if a redox probe is employed), a vast range of properties can be determined and investigated. Properties including capacitance, reaction kinetics, reaction reversibility, and reaction potentials can all be measured through CV.

CV has been widely employed to measure fibres for use in energy storage devices, and as such was a key analysis technique for the work in this thesis. The electroactivity of polypyrrole fibres was measured by Foroughi et al. allowing comparison of their production method with other polypyrrole methods (91). Functional fibre supercapacitor devices have also been analysed using CV, for example Ren et al. produced a fibre supercapacitor (and fibre battery) employing carbon nanotube fibres with and without manganese dioxide, and compared their performance at different scan rates (109). Xu et al. compared the properties of a range of conducting polymer composites were compared through CV, allowing comparison of their capacitance at a range of scan rates (110).

In this work, CV was predominately employed to analyse the capacitive effects of the fibres produced. This provides insight in to how different preparation methods, materials, and treatments may affect the charge storage ability of the fibres, in addition to charge discharge experiments.
CV measurements were performed on a Gamry Reference 600 potentiostat and an eDAQ EA163 potentiostat with e-corder 410. A standard three-electrode system was used, consisting of a platinum mesh counter electrode, a silver silver/chloride reference electrode (containing NaCl (3.0 mol dm$^{-3}$)), and the fibre to be tested connected as the working electrode. 1.0 mol dm$^{-3}$ sodium sulfate was used as an electrolyte, unless otherwise stated. To standardise comparison between different fibres, a known mass of fibre was employed. Typically, a 1 cm length of fibre was used for all experiments, unless explicitly stated otherwise. Scan rates between 1 and 200 mV s$^{-1}$ were employed, with voltage ranges typically between 0.0 and 0.8 V vs. Ag/AgCl used. As the fibres were not typically destroyed during analysis (excluding testing to specifically determine voltage limits, which may damage the samples), the testing was deemed non-destructive, and the fibres could be reused, for example for charge/discharge cycling.

For CV analysis employing a redox couple, 10.0 mmol dm$^{-3}$ potassium ferricyanide in 0.1 mol dm$^{-3}$ potassium chloride was used. Voltammetry was performed at various scan rates between 10 and 200 mV s$^{-1}$, and voltage windows between -1.0 and 1.0 V vs. Ag/AgCl. Through analysis of peak data, the accessible electrochemical surface area of each fibre was determined, using the Randles-Sevcik equation shown in Equation 3.

$$i_p = 0.4463nFAC\left(\frac{nFvD}{RT}\right)^{\frac{1}{2}}$$

*Equation 3 – Randles-Sevcik equation.*

The following values were used for calculations:

- $n =$ Number of electrons = 1 for this system
- $F =$ Faraday Constant = 96,485 C mol$^{-1}$
- $A =$ Electrochemical surface area in cm$^2$
- $C =$ Concentration of ferricyanide = $1 \times 10^{-5}$ mol cm$^{-3}$
- $v =$ Scan rate in v s$^{-1}$
- $D =$ Diffusion coefficient = $7.6 \times 10^{-6}$ cm$^2$ s$^{-1}$
- $R =$ Gas constant = 8.314 J K$^{-1}$ mol$^{-1}$
- $T =$ Temperature in K
2.1.2 Charge Discharge Experiments

Measuring the charge an electrode can store is essential to determine the effectiveness of a given fibre to function as a capacitor. While CV experiments apply a changing voltage to the fibre, charge discharge measurements apply a current to the fibre, and measure the voltage produced relative to the reference electrode employed. This current can be varied, and is chosen based on the mass of the fibre employed, and the desired current density. The voltage limits can be tailored, to examine the usable voltage window of the materials used, as well as the electrolyte chosen. In this work, a constant current was applied to the system until a desired voltage was reached. After this point, the same current was drawn from the system, and the decrease in voltage recorded. Once the voltage reached the set minimum, the cycle was finished. This charge/discharge process was then repeated as many times as chosen. As with CV, this testing was non-destructive, allowing the fibres to be reused.

Charge/discharge cycling measurements are commonly used to characterise capacitor energy storage devices, and this technique has as such been widely employed on fibre-based devices and their materials. For example, the fibres produced by Ren et al. employing carbon nanotube fibres for capacitor and battery applications were also measured using charge/discharge cycling, alongside their analysis through CV to further explore their capacitive properties (109). A carbon nanotube fibre supercapacitor mounted on a polymer substrate was produced and measured by Xi et al., exploring the device’s performance at a range of current densities (111). Xi et al. also demonstrated connecting and measuring such devices connected in series and in parallel, allowing further analysis as to device performance and functionality.
In the work in this thesis, charge discharge experiments were performed using a Gamry Reference 600 potentiostat. For all charge discharge measurements in this work, the same three electrode system was used as per CV: a platinum mesh counter electrode, Ag/AgCl reference electrode (containing 3 mol dm$^{-3}$ NaCl), and a fibre as the working electrode immersed in 1.0 mol dm$^{-3}$ sodium sulfate. Fibres were analysed using a voltage range between 0.0 and 0.8 V, unless otherwise specifically stated. To allow direct comparison between fibres, a known weight of fibre was used, and currents adjusted accordingly to maintain a chosen current density.

The amount of charge stored during each cycle was calculated using Equation 4:

$$C_s = \frac{I \cdot \Delta t}{\Delta V \cdot m}$$

*Equation 4 – Specific capacitance for an electric double layer capacitor.*

Where $C_s$ represents the specific capacitance of the fibre, given in F g$^{-1}$, $t$ the discharge time in s, $I$ the current density in A g$^{-1}$, and $\Delta V$ the voltage window used in Volts. $\Delta t$ is determined by measuring the gradient of the discharge curve in the upper 50 % voltage range, within which supercapacitors are most commonly charged/discharged (11).

For initial capacitance measurements, the first cycle was used to calculate the capacitance. Repeated cycling was also employed for select fibres, up to 1,000 cycles, using the same parameters (e.g. voltage window, current density) for each successive cycle, and the
retention of the fibre’s capacity plotted as a percentage of the initial value obtained vs. increasing cycle count.

2.1.3 Four-Point Electrical Conductivity

The ability of a material to transport current with minimal resistance is essential, to minimise energy losses from heat generated through ohmic heating. For this purpose, it is necessary to design, produce, and measure fibres which have the highest possible electrical conductivity. It is necessary to accurately determine the resistance of individual fibres, used to determine their conductivity as a bulk property of the material. To do this, fibres were mounted using silver paint across four electrical pins of equal spacing of 2 mm apart. A constant current, typically 10 µA, was applied across the two outer pins using an eDAQ e-corder 410 with attached eDAQ EA163 potentiostat. The resultant voltage across the inner two pins was measured using a Keithley 2001 multimeter.

From knowing the current applied, the voltage induced, and all distances involved (the length between pins, as well as the diameter of the fibre, measured using an optical microscope at multiple points along the fibre axis) it is possible to work out the resistance, resistivity, and conductivity of the fibres.

The resistance of each fibre is given by the following equation:

\[
R = \frac{V}{I}
\]

*Equation 5 - Calculation of resistance from voltage and current.*

where \( R \) is the resistance in \( \Omega \), \( V \) is the voltage measured in V, and \( I \) is the current applied in A. The resistivity (\( \rho \)) of each was calculated by taking into account the distances involved:

\[
\rho = \frac{R \times A}{l}
\]

*Equation 6 - Calculation of resistivity from resistance, area, and length.*

where \( A \) is the cross-sectional area in cm\(^2\), and \( l \) is the length between the points at which the voltage is measured in cm. Conductivity (\( \sigma \)) in S cm\(^{-1}\) was calculated as the inverse of resistivity.
While electrical conductivity measurements can provide information about how a fibre may perform, it alone cannot be used to determine the energy storage performance of a fibre. However, it can be a useful tool when comparing different fibres produced using similar techniques and/or components. The effect of different materials, processes, and treatments, for example, on conductivity can all be quickly determined, and used alongside other testing results to guide further development. Due to the need to glue fibres for attachment prior to measurement, this testing was destructive in nature.

Electrical conductivity measurements have been routinely and widely used in materials analysis, including on fibre materials (112-115). Conductivity differences occurring through the use of different materials, proportions, or treatments are all measurable through this technique.

### 2.1.4 Impedance Spectroscopy

Impedance spectroscopy provides a more complex and in-depth analysis of the electrical properties of a material. By taking into account more complex properties and phenomenon than are typically accounted for in electrical resistance understanding such as Ohm’s law, far more information about the material being analysed can be revealed. Impedance measurements are frequently performed by applying a voltage to the material, which is varied by a specified perturbation voltage, typically far lower than the voltage applied. This voltage perturbation is applied at a varying range of frequencies, and the effect recorded. A small perturbation voltage is required, so as to produce a linear, or pseudo-linear current response in the system. The phase shifts in the signal induced, relative to the applied voltage, is used to determine the impedance of the system, presented as a real and imaginary component in Ohms. In this work, Nyquist plots were produced from these components, and used to determine the capacitance of the system.

Impedance measurements were performed on a Gamry Reference 600 potentiostat. Measurements were taken at the open cell potential for each fibre system, using a perturbation voltage of 10 mV amplitude, and a frequency range of 0.01 – 100,000 Hz. A three-electrode setup was used for all measurements employing a platinum mesh counter.
electrode, Ag/AgCl reference electrode (containing 3 mol dm$^{-3}$ NaCl), and the fibre as the working electrode, all immersed in 1.0 mol dm$^{-3}$ sodium sulfate. Impedance measurements of this sort were non-destructive.

Specific capacitances were calculated from Nyquist plots, taking data from above the ‘knee’ frequency in the plot, where pseudocapacitive mechanisms occur. The capacitance was calculated using Equation 8, and mass specific capacitances were obtained by dividing the result by the mass of the fibre used. $C$ represents the capacitance, $f$ the frequency of the data point, and $Z''$ the imaginary impedance component.

$$C = \frac{1}{2\pi f Z''}$$

Equation 8 - Calculation of capacitance from impedance data.

Figure 23 shows example Nyquist plots, in which the ‘knee’ frequency is indicated (116).

![Figure 23 - Example Nyquist plots generated from electrical impedance spectroscopy data of polypyrrole/cellulose films. The ‘knee’ frequency is indicated on both plots (116).](image)

2.1.5 Raman Spectroscopy

Raman spectroscopy can provide information on the chemical bonds present in a sample that are able to undergo a change in polarisability. In such an experiment, laser light of a specific wavelength is shone on to a sample. This light interacts in the sample in a number of ways, including Rayleigh scattering, as well as Stokes and anti-Stokes Raman
scattering. Rayleigh scattering is an elastic scattering, where the emitted photons have the same energy as the incident photons. However, when the photons interact with the molecule, a small number (typically one in multiple tens of millions) will be Raman scattered. This process involves an absorbed photon causing a transition between vibrational energy levels within an electronic energy level, promoting an electron to a temporary virtual excited state. This photon then drops down from this state, and in doing so emits a photon, returning to a different level than originally. This difference in energy can be positive (anti-stokes scattering), or negative (stokes scattering) depending on if energy was given to, or taken from the molecule. This emitted photon is then measured by the instrument, and used to build the Raman spectrum. A key difference between Rayleigh/Stokes/anti-Stokes scattering and, for example, infrared or fluorescence is in the promotion of the electron to a virtual energy state, rather than a different specific vibrational or electronic excited state. This difference is shown in Figure 24.

Figure 24 – Comparison of the similarities and differences between IR, Rayleigh, Raman (Stokes and anti-Stokes), and fluorescence electron energy levels occurring after excitation (117).

Raman spectroscopy often involves the use of microscopes to expose the sample to the laser, and also to collect the resulting scattered photons. This makes Raman microscopy a technique of great interest to fibre-based research, where the materials produced are often very small, typically on the scale of micrometres. Infrared spectroscopy, for example, would usually require far larger samples, which would be difficult and extremely time consuming to produce for fibre research. The analysis time of Raman spectroscopy is also typically low, on the order of single min for an individual point analysis, allowing rapid analysis of a fibre to be performed. The technique was also non-destructive, allowing
samples to be analysed and then used for other/further testing purposes. Raman spectroscopy has been employed to analyse a wide range of materials. For example, PEDOT materials have been analysed, identifying the optimal production methods, and investigating their effect on the material (118). Nanomaterials, such as graphenes, have also been analysed using Raman spectroscopy, allowing for determination of parameters such as the number of layers, and defect quality of the sheets (119). Raman analysis of manganese oxide materials was able to investigate the structure of the material(s) produced, as well as identify included ions (120).

In this work Raman spectroscopy was used to confirm the presence of materials, as well as to analyse the effects of a range of chemical processes and treatments on these materials. Raman spectra were recorded using a Thermo Scientific DXR Raman Microscope with a 532 nm laser with up to 10 mW power, and 10 x or 50 x objectives. Spectra were obtained using four collections of 15 s each, laser power was tailored to the specific material in question.

2.1.6 Optical Microscopy

Many aspects of the work in this thesis required analysis of the fibres on a level smaller than that obtainable by eye, or required accurate measurement of the fibres’ diameters. For this, optical microscopy images were taken using a Nikon Eclipse LV100 POL microscope equipped with 4 x, 10 x and 20 x objectives. Digital images were captured using a Nikon DS-Fi2 microscope camera. Measurements were taken with an appropriate objective for the size of the material being investigated. To ensure accurate and reliable measurements of fibre diameters, a minimum of 10 measurements along each fibre axis were taken, and an average of these used for calculations. Figure 25 shows an example of such measurements.

![Figure 25 - Example of fibre diameter measurements.](image-url)
2.1.7 Scanning Electron Microscopy

While optical microscopy can provide insight into the properties of the fibres down to sub-millimetre level, it was required to analyse the fibres on the scale of micrometres. For this purpose, scanning electron microscope (SEM) images were collected of the samples. SEM images are typically obtained by scanning a focused beam of electrons across the sample of interest, in an evacuated chamber. This beam is produced using an electron gun, typically employing a tungsten filament. This filament is heated electrically until it emits electrons, which are focussed using magnetic lenses, and is directed to scan over the sample. When the electrons interact with the sample several processes occur, including elastic scattering of the electrons, emission of secondary electrons from the sample, as well the emission of electromagnetic radiation from the sample. The detection of these species allows images and information on the sample to be produced, for example, secondary electrons are typically collected to produce the typical SEM image frequently displayed. A generalised schematic of an SEM is shown in Figure 26.

![Generalised schematic of a scanning electron microscope](image)

**Figure 26** – Generalised schematic of a scanning electron microscope, showing emission, focusing, sample, and detection components (121).

SEM images were obtained using a JEOL USA JSM-7100F Analytical Field Emission electron microscope. Samples were mounted on an alumina-coated sample stub, and gold coated. Two applications of 1.5 nm gold coating were chosen and applied via an argon source gold sputter. Gold coatings were required due to the insulating glue used to attach fibres to the measurement stubs. For EDX analysis, gold coating was not employed, to
allow accurate elemental composition determination, and a direct contact between fibre and stub ensured, to allow conductivity. A typical working distance of 10 mm was employed to allow reliable focusing on the samples required, with an acceleration voltage between 5 and 15 KV. Due to the need to attach fibres to gold stubs, and potentially gold coat the samples, SEM analysis was a destructive technique.

2.1.8 X-ray Photoelectron Spectroscopy

In X-ray photoelectron spectroscopy (XPS), a beam of X-rays is irradiated upon a sample, and the kinetic energy and number of electrons emitted are measured. The electrons used to irradiate the sample are required to be of a fixed, known energy. The resulting kinetic energy of expelled electrons can then be used to determine the binding energy of that electron, and thus reveal information about the origin of the electron in the sample (122-123). XPS typically analyses the surface of a material, and can produce quantitative data on the elemental makeup of the material in question. This enables minor changes in chemical composition of materials to be determined through analysis of the elemental changes occurring. The sample can also be subjected to other treatments, such as surface ablation, fracturing, electromagnetic radiation exposure, etc. and the resulting changes characterised. A simplified example XPS instrument is shown in Figure 27.
XPS has been used as a method for identifying the effect of treatments on materials such as PEDOT:PSS, through quantitative comparison of elements present within the material. For example, the amount of sulfur before and after chemical treatment (for example with sulphuric acid) is measured, and used to understand the effect of the treatment (60) (125).

XPS data was obtained using a ThermoFisher Scientific Theta Probe spectrometer. XPS spectra were acquired using a monochromated Al Kα X-ray source (hv = 1,486.6 eV). An X-ray spot of ~400 μm radius was employed in the acquisition of all spectra. Survey spectra were acquired employing a pass energy of 300 eV. High resolution, core level spectra for S2p were acquired with a pass energy of 50 eV. The manufacturer’s Avantage software was used which incorporates the appropriate sensitivity factors and corrects for the electron energy analyser transmission function.

2.1.9 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) provides information on the mechanical strengths and properties of materials. The testing equipment consists of two metal clamps, into which the sample is fixed. The clamps supply a known force to the sample, through the movement of the lower clamp, thus pulling on the immobilised sample. A range of complex measurements can be performed, such as applying a varying and/or repeating stress to a material, while changing parameters such as the frequency of the force variation, or the temperature of the environment.

DMA was performed to gauge the effect of applying a linearly increasing stress on the fibres, using a TA Instruments Q800 instrument. Analysis was performed using a using 0.1 mN preload force, and an appropriate rate of force increase (between 0.02 and 2 N min⁻¹), chosen to provide sufficient data points for each sample. Stress-strain plots were obtained and analysed to determine ultimate tensile strength, along with yield strain, and Young’s modulus values.

Direct attachment of the fibres to the clamps was not possible, due to limited grip caused by the thin diameter of the fibres produced in this work. To combat this and allow reliable fibre attachment, fibres were glued between two rectangular windows of paper, as shown in Figure 28. This allowed for the fibre to extend across this window. Once clamped in the instrument, each side of the paper was cut, allowing for measurement of only the desired fibre in question. Due to the nature of the test, this method of testing was destructive.
Thermogravimetric Analysis

Thermogravimetric analysis (TGA) involves heating a known mass of sample in a controlled atmosphere, at a predefined temperature range. The system can hold a specific temperature, or increase/decrease the temperature at a desired rate, to allow analysis of the material(s) over a range of temperature changes and ranges. The atmosphere can be changed, for example running in an inert gas atmosphere to avoid combustion of the sample, or in air to better represent standard conditions. TGA can analyse both physical, and chemical changes a material undergoes when subjected to a defined heating/cooling regime. Properties such as the thermal decomposition of a material, or changes in mass due to oxidation can be identified. This can be used to determine the amounts of individual constituents in a composite material, by analysing the mass change at different temperatures.

In this work, TGA was performed on a TA Instruments TGA Q500, with heating runs performed between 20 °C and a maximum of 900 °C at a ramp rate of 10 °C min⁻¹ in air. Samples were cut to an appropriate length (< 4 mm) for the pan being used, before being loaded into the platinum pan, the mass zeroed, and transferred to the furnace for heating. Multiple fibres may be required to reach the minimum mass required for the instrument, typically at least 0.2 milligrams.

2.2 General Wet Spinning Equipment

For all fibres in this work produce by wet spinning, wet spinning was performed by injection of the spinning solution into a non-solvent bath though a needle of chosen size. The rate of injection was controlled using a syringe pump, and collection of the fibres within the coagulation bath was performed using a rotating stage with variable speed. Fibres were then extracted using tweezers, and dried under ambient laboratory conditions, unless otherwise stated.
Control over fibre diameter was possible by varying the diameter of the needle employed, along with changing the injection rate of the spinning solution. Spinning solutions were prepared prior to the spinning process. Details of the specific coagulation baths employed, as well as the spinning solution preparation procedure(s) are given in the respective sections.

2.3 Wet Spinning of Ionic Liquid Dispersion Fibres

Acetone, xanthan gum, 1-ethyl-3-methylimidazolium tetrafluoroborate, and 1-butyl-3-methylimidazolium tetrafluoroborate were purchased from Sigma Aldrich and used as received. Single-wall (Nanocyl 1100, 70+ wt.% carbon) and multi-wall (Nanocyl 3100, 95+ wt.% carbon) CNTs were purchased from Nanocyl. Graphene nano platelets were purchased from XG Sciences (xGnP-M-25, serial number S110911). All chemicals were used as received unless otherwise stated.

CNT and/or GNP nanomaterials were added to the above ionic liquids, in the amounts shown in Table 4 below, and horn sonicated in pulses of 1 sec on/1 sec off for 45 min at 30 % amplitude, using an ice/water bath to control the temperature of the dispersion. Fibres were produced by manual injection of these dispersions into a xanthan gum coagulation bath of the concentrations in Table 4 using a 16 gauge (1.19 mm inner diameter) blunt needle. After injection, fibres were left to coagulate overnight, before being transferred into a water bath for 30 min to remove any excess xanthan gum. Fibres were then placed for 5 min into an acetone bath to help remove excess water, before being hung vertically and allowed to dry under ambient conditions.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>CNT Concentration (wt.%)</th>
<th>GNP Concentration (wt.%)</th>
<th>Coagulation Bath Concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW-A</td>
<td>1.00 - SWCNT</td>
<td>0.00</td>
<td>0.05</td>
</tr>
<tr>
<td>SW-B</td>
<td>0.75 - SWCNT</td>
<td>0.25</td>
<td>0.05</td>
</tr>
<tr>
<td>SW-C</td>
<td>0.50 - SWCNT</td>
<td>0.50</td>
<td>0.05</td>
</tr>
<tr>
<td>MW-A</td>
<td>0.50 - MWCNT</td>
<td>0.00</td>
<td>0.10</td>
</tr>
<tr>
<td>MW-B</td>
<td>0.38 - MWCNT</td>
<td>0.13</td>
<td>0.10</td>
</tr>
<tr>
<td>MW-C</td>
<td>0.25 - MWCNT</td>
<td>0.25</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Table 4 – Nanomaterial weights added to ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium tetrafluoroborate.
2.4 Production of Scrolled Film Fibres

Poly(vinyl alcohol) (PVA) and Orgacon PEDOT:PSS were purchased from Sigma Aldrich and used as received unless otherwise stated. Sulfuric acid (used at 1.5 mol dm$^{-3}$), formic acid (used neat), and DMSO (used neat) were each purchased from Sigma Aldrich.

In chapter 4, aqueous solutions were produced from PEDOT:PSS and PVA with weights of 0.20 g and 0.10 g, dissolved in 20 cm$^3$ deionised water respectively. All films were produced from 20 cm$^3$ aqueous solutions cast in 90 mm plastic petri dishes, before being allowed to dry overnight under ambient conditions. Once completely dried, each film was removed from the petri dish, and cut into strips (90 mm × 2 mm). Filtration-based formation of films was carried out by vacuum filtering a known volume of mixed solution through nitrocellulose-based (NC) filter papers. The paper and formed layer were then dried in an oven at 50 °C to remove residual water. Removal of the filter paper was performed by dissolving the NC filter paper in acetone. The films were then removed and allowed to dry under ambient conditions, before being cut into 2 mm strips and used. A method was developed to allow pre-cut films of polymer-based materials to be scrolled into fibres. In this procedure films were first cut in to strips 2 mm in diameter. One end of this film was attached to a glass petri dish, while a rotational force was applied to the other end. Varying amounts of rotation could be applied, allowing for control of the degree of scrolling in the fibres produced. After scrolling was completed, the free end of the film-fibre was also attached to the glass dish, and left. Fibres were immersed in a solution of 90/10 methanol/water, to soften the polymer to increase elasticity and allow scrolling to occur without tearing or breakage. Once fully dried, the fibres retained their scrolled structure and were easily removed for analysis.

2.4.1 Chemical Treatment of Produced Fibres

Post-scrolling treatment of the fibres was performed using saturated sodium sulfate solutions, as well as 1.5 mol dm$^{-3}$ sulfuric acid, 25.2 mol dm$^{-3}$ formic acid, and neat DMSO. For this, fibres were restrained at each end in Hoffman clamps, before being immersed into the solution, as shown in Figure 29, for 5, 60, or 120 min. The fibres were then removed from solution, and dried in the oven at 140 °C for 60 min to complete the treatment. Once dried, the fibres were removed from the Hoffman clamps. Fibres were
held so as to produce a straight fibre, but without applying tension to the fibre during treatment or drying, so as to observe only the effect of chemical treatment on the fibres.

Chemical cross linking of the PVA alcohol groups (126-127) of the fibres was also attempted via immersion of the fibres in saturated aqueous solutions of sodium sulfate, for up to 48 h. The fibres were removed and washed, before being allowed to dry under tension. Once dry the fibres were removed from the Hoffman clamps.

![Figure 29 - Digital camera photograph of PEDOT:PSS-PVA fibres clamped in Hoffman clamps and immersed in solution for chemical cross-linking.](image)

2.5 Wet Spinning of PEDOT:PSS Fibres

Orgacon PEDOT:PSS (water soluble, dry re-dispersible pellets), acetone, iso-propanol, sulfuric acid, formic acid, dimethyl sulfoxide, and manganese(II) acetate, were all purchased from Sigma Aldrich and used as received. Clevios PH1000 PEDOT:PSS was purchased from Heraeus.

As detailed in chapter 5, two different PEDOT:PSS spinning solutions were prepared, sourced from Orgacon and Clevios PH1000. A dispersion of 2 wt.% Orgacon PEDOT:PSS pellets was produced by dispersing 0.2 g of pellets in to 10 cm³ of distilled water, using magnetic stirring. Clevios PH1000 dispersions were produced by evaporating 20 cm³ of neat 1 wt.% PEDOT:PSS at 50°C to form a 2 wt.% solution. Dispersions were injected through a 16 or 28 gauge (1.19 and 0.18 mm inner diameter) needle at a rate of 0.75 or 0.05 ml h⁻¹ respectively into a coagulation bath (50:50 volume mixture of acetone and iso-
propanol, in a glass bath with a radius of 10 cm) rotating at 10 rpm. Fibres were extracted and hung to dry in air at ambient conditions for several h.

Treatment of wet-spun fibres was performed by immersion of the fibres in solutions of 1.5 mol dm$^{-3}$ sulfuric acid (60), 25.2 mol dm$^{-3}$ formic acid (95 %) (128), and 100 % DMSO (129). Fibres were immersed for 5, 60 and 120 min before being extracted, and hung in a 140 °C oven for 30 min.

2.6 Formation and Protection of Manganese Dioxide Coatings

PEDOT:PSS fibres were prepared from Orgacon and Clevios sources using the methods detailed in chapter 5. These fibres were treated with DMSO as also described in chapter 5. Dip immersion was performed in chapter 6 by immersing a section of the fibre in an aqueous potassium permanganate solution ranging in concentration between 0.1 mol dm$^{-3}$ and 1 µmol dm$^{-3}$ for between 1 min and 1 h. Fibres were then removed and immersed in water to wash.

Electrochemical manganese dioxide and conducting polymer formation was carried out by immersing the required length of fibre in the manganese or monomer solution. In this, the immersed length of fibre was employed as the working electrode. The desired voltage was applied for the chosen time, and the fibre was then removed and washed. For depositions from manganese(II) acetate, a concentration of $20 \times 10^{-3}$ mol dm$^{-3}$ was employed with voltages between 0.7 and 1.2 V tested. An aqueous solution containing $1 \times 10^{-3}$ mol dm$^{-3}$ distilled pyrrole and $1 \times 10^{-3}$ mol dm$^{-3}$ KCl was used for production of polypyrrole. For dip coatings of PEDOT:PSS, Orgacon and Clevios PH1000 sources were used, each at 1 wt.%, with 2 min immersions.

All electrodepositions were performed using a three-electrode system consisting of a platinum mesh counter electrode, Ag/AgCl reference electrode, and the fibre working electrode.

2.7 Addition of Nanomaterials into PEDOT:PSS Fibres

In chapter 7, direct addition of birnessite to PEDOT:PSS was performed by adding 0.0 to 0.2 wt.% of nanomaterial (relative to the total mass) to 1.0 or 2.0 wt.% PH1000 PEDOT:PSS solution, followed by treatment in a 100 W sonication bath. Production of aqueous dispersions of nanomaterials was through the addition of the nanomaterials to
water, at concentrations between 0.01 and 0.50 wt.%, before being sonicated using a 500 W ultrasonic horn and/or 100 W bath. The dispersions produced in each step were analysed using optical microscopy.

Aqueous dispersions of birnessite were produced by adding birnessite powder to water at a concentration of 0.50 wt.%. This dispersion was sonicated using a 500 W horn sonicator at 40 % amplitude for 1 h of sonication time. 1 sec on/1 sec off pulse sonication was employed, with an ice/water bath to control the temperature. Solutions for wet spinning were then produced by adding varying volumes, between 0.5 and 5.0 ml, to 5.0 ml of 2.0 wt.% PH1000 PEDOT:PSS. This solution was stirred, before being used for wet spinning of fibres.

Dispersions of functionalised carbon nanomaterials were produced at concentrations between 0.01 and 0.50 wt.% and subjected to up to 3 h of horn sonication at 40 % amplitude (pulsed 1 sec on/1 sec off) using an ice bath to maintain temperature. These dispersions were added to 5 ml of 1 and 2 wt.% PH1000 PEDOT:PSS at volumes between 0.5 and 2.5 ml, stirred, and used for wet spinning of fibres.

Wet spinning was performed using the same parameters as used for the thin (~ 20 µm) PH1000 PEDOT fibres detailed in chapter 5. Dispersions were injected through a 16 gauge (0.18 mm inner diameter) needle at a rate of 0.05 ml h⁻¹ into a coagulation bath (50:50 mixture of acetone and iso-propanol, in a glass bath with a radius of 10 cm) rotating at 10 rpm. Fibres were extracted and hung to dry in air at ambient conditions for several h.

All testing was also performed as per the parameters previously defined and used, to allow for direct comparison of the properties of PH1000 PEDOT:PSS fibres with and without nanomaterial addition.

2.8 Production of Flexible Fibre-Based Supercapacitor Devices

Devices were produced as symmetrical supercapacitors in chapter 8. A gel electrolyte consisting of 1 wt.% phosphoric acid and PVA was produced by adding both materials to water and heating at 60 °C.

A line of gel electrolyte with a width of 2 mm was deposited on a hydrophobic paper backing, into which two test fibres were placed, each with 1 mm extending at one end to
allow for electrical connection. This was then placed in an oven at 50 °C for 1 h to dry the electrolyte.

Devices were connected as a two-electrode capacitor. Charge discharge measurements were produced using constant-current methods, at current densities between 0.1 and 10.0 A g$^{-1}$, and at voltage windows of up to 1.8 V. CV was performed at scan rates between 1 and 200 mV s$^{-1}$ and at voltage windows of up to 1.8 V.

2.9 Connection of the Fibres to a Potentiostat

A special note is required describing the method for connecting fibres to the potentiostats employed in this work. Due to the small diameters of many fibres produced in this work, typical crocodile clips and even tweezers were not able to successfully attach to the fibre used, causing poor electrical connections and thus highly erratic and noisy data to be obtained.

To solve this issue, fibres were attached to thin-nosed tweezers using silver conductive glue (as per conductivity measurements), and the tweezers were then attached to the potentiostats using standard crocodile clips. This additional glue allowed for a reliable connection between fibre and electrochemical equipment.
3 Ionic Liquid Dispersion Fibres

3.1 Introduction

Room temperature ionic liquids (RTIL) are molten salts which are typically defined as having a melting point below 100 °C, and even at room temperature (130). While some uncertainty surrounds their initial discovery, the first observed RTIL is attributed to Paul Walden (131-132). Ionic liquids occur over a wide temperature range, and are able to be produced by simple means such as heating. However, this use of high temperatures, makes them unsuitable for many applications, while also requiring high energy inputs, also leading to safety/handling requirements. RTILs, on the other hand, have the desired properties of an ionic liquid but in a more easily processable and environmentally friendly temperature range. A large number of RTILs are known, consisting of a wide range of cations, such as pyridinium, methylimidazolium and thiazolium (131), and anions such as halides, tetrafluoroborate, and hexafluorophosphate (131). An example structure of 1-butyl-3-methylimidazolium tetrafluoroborate is shown in Figure 30.

![Figure 30 – Chemical structure of 1-butyl-3-methylimidazolium-tetrafluoroborate (133).](image)

RTILs have been used in varied applications, as solvents for a range of materials. One such use is the extraction of cellulose, allowing for easy processing of the material to produce films (134). It is possible to perform electrochemical reactions within ionic liquids, with (butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide being used as an electrolyte in a magnesium air battery as one example (135). Ionic liquids are also frequently used as green solvents (130) (136), as well as finding use as friction modifiers (137), and even the extraction of plutonium (138). In recent years there have been several papers showing that RTILs are a possible medium for dispersing carbon nanomaterials (139-140), including graphene and CNTs. RTILs have the advantage over other solution based dispersion methods as they may not require the use of an additional dispersant, such as a surfactant or polymer to enable the nanomaterials to be stabilised in solution. This
allows for easier manipulation of the materials, as well as fewer unwanted chemicals in the dispersions and/or products.

This chapter details the investigation of a RTIL system to disperse single and multi-wall CNTs, as well as graphene nano platelets, to allow the production of conducting fibres. It has been shown that RTILs can disperse nanomaterials at levels which may allow for fibre spinning (139-140). Typically, fibres formed via wet spinning of nanomaterial dispersions require the use of surfactants or polymer solutions to successfully disperse the nanomaterials prior to spinning. Being able to disperse nanomaterials directly into the solvent being used could present interesting benefits, due to having less unwanted material to remove from the fibres after formation (for example the surfactant, and/or additional solvents employed).

3.2 Aim

The aim the study described in this chapter was to utilise carbon nanomaterials, such as CNTs and graphene, RTILs to create electrically conductive fibres for use as electrodes in energy storage devices. To produce fibres via wet spinning, the preparation of high quality, homogenous dispersions of nanomaterials within a suitable chosen RTIL is required. This involved the identification of a suitable RTIL, into which nanomaterials can be added. Treatment steps such as sonication were utilised to optimise the dispersions formed. A suitable coagulation system was sought, to allow fibre solidification/precipitation, followed by extraction and drying of the fibres.

The fibres produced were analysed and tested using CV, four-point electrical conductivity, Raman spectroscopy, DMA, and SEM.

3.3 Results – RTIL-Based Fibres

3.3.1 Coagulant Determination (Drop Test)

To determine a method for producing fibres from CNT dispersions in RTILs, various different potential coagulants were analysed via drop testing of the dispersion into a small quantity of each coagulant. Drop testing was a necessary step as a suitable coagulant needed to be found, as to the best of my knowledge, none had been reported previously for dispersion systems such as these. The desired coagulant would dissolve the RTIL but not
disperse the nanomaterials being used. This would allow for the dispersions to precipitate and entangle into solid fibres when injected into the coagulant solution.

1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF₄) have both been demonstrated previously to disperse carbon nanomaterials including graphenes and CNTs (141-142) at levels sufficient to potentially allow the wet spinning of fibres. It was found that 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF₄) was superior at dispersing carbon nanomaterials than EMIBF₄ (141-142). As such, BMIBF₄ (Figure 30) was used as the dispersant for all work in this chapter. A dispersion of GNP in BMIBF₄ was produced at 1.0 wt.%, and a dispersion of SWCNT at 1.0 wt.%, both were found to produce stable dispersions. In total, 27 unique potential coagulation chemicals were tested, in addition to combinations of these chemicals mixed with water. Potential coagulants were chosen so as to include a range of varieties, including hydrophilic/hydrophobic types, options yielding different pHs, various salt concentrations, and organic solvents. Of all the options tested, only aqueous solutions of xanthan gum (XG) showed any promise for precipitating fibres.

3.3.2 Coagulation System Optimisations

The dispersions of 1.0 wt.% GNP and a dispersion of 1.0 wt.% SWCNTs were injected into concentrations of XG ranging between 0.01 and 0.10 wt.%. Dispersions of graphene could not be reliably spun and dried into fibres in any of the concentrations of XG. However, dispersions of 1.0 wt.% SWCNT formed fibres in solutions of XG between 0.01 and 0.50 wt.%, suggesting that the greater entanglement found when using SWCNTs was superior in fibre formation than GNPs. Fibres in this chapter are named after the dispersion from which they are formed, as such the concentrations of materials in the fibres are assumed, and may not be exactly the same as in their respective initial dispersions, due to incomplete dispersion, as well as coagulation/agglomeration occurring during the preparation and spinning stages.

CV was performed on 1.0 wt.% SWCNT fibres produced in various XG concentrations, as shown in Figure 31. Reducing the concentration of the XG from 0.10 wt.% to 0.01 wt.% showed only a slight change in the angle of the voltammogram, with lower concentrations showing higher maximum currents. However, no change in the profile of the voltammograms towards that of the idea rectangle was observed. It was found that 0.01
wt.% XG solutions were not capable of reliably producing fibres, with the majority of fibres breaking during extraction and drying. 0.05 wt.% XG was found to be the lower concentration limit, and was therefore used for all further production of SWCNT fibres in this chapter.

Dispersions of MWCNTs between 0.10 and 1.0 wt.% were also produced, for comparison with SWCNTs. It was found that MWCNTs required higher concentrations of XG to successfully produce fibres. While it would have been preferable to produce and compare both CNT types using the same concentration of XG, this was not possible. Production of MWCNT fibres was tested using XG concentrations ranging from 0.50 wt.% to 0.01 wt.%; and it was found that only concentrations above 0.10 wt.% were able to form fibres.

3.3.3 Fibre Production and Characterisation

The previous studies showed that the optimal concentration of a XG coagulation bath was 0.05 wt.% for SWCNTs, and 0.10 wt.% for MWCNT dispersions. Optimisation of the dispersion concentrations was also necessary in order to produce fibre-based electrodes with the best electrochemical performance. It was found that higher concentrations of CNTs produced more reliable, consistent fibres than lower concentrations. This is believed
to be due to the inclusion of higher amounts of conducting nanomaterials in the fibre, with lower amounts of insulating polymer. The upper concentrations limits of CNT dispersions were investigated and found to be 0.5 wt.% for MWCNTs and 1.0 wt.% for SWCNTs. Concentrations of nanomaterials above these limits no longer produced dispersions, but partially dispersed pastes which were unsuitable for fibre spinning, as shown in Figure 32.

Figure 32 - Optical microscopy of a 2.0 wt.% SWCNT paste in BMIBF₄, showing poor dispersion of SWCNTs within the RTIL.

To investigate the potential synergistic effects of the additional inclusion of GNPs in the fibres, CNT dispersions that included additional GNPs were also produced, (Table 5). Nanomaterial weights and ratios were tailored to keep total dispersion concentrations at 1.0 wt.% and 0.5 wt.% for SWCNT and MWCNT based dispersions respectively. Fibres were successfully spun for all dispersions listed in Table 5, using 0.05 wt.% XG coagulation baths for SWCNT dispersions, and 0.10 wt.% baths for MWCNT dispersions.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>CNT Concentration (wt.%)</th>
<th>GNP Concentration (wt.%)</th>
<th>Coagulation Bath Concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW-A</td>
<td>1.00 - SWCNT</td>
<td>0.00</td>
<td>0.05</td>
</tr>
<tr>
<td>SW-B</td>
<td>0.75 - SWCNT</td>
<td>0.25</td>
<td>0.05</td>
</tr>
<tr>
<td>SW-C</td>
<td>0.50 - SWCNT</td>
<td>0.50</td>
<td>0.05</td>
</tr>
<tr>
<td>MW-A</td>
<td>0.50 - MWCNT</td>
<td>0.00</td>
<td>0.10</td>
</tr>
<tr>
<td>MW-B</td>
<td>0.38 - MWCNT</td>
<td>0.13</td>
<td>0.10</td>
</tr>
<tr>
<td>MW-C</td>
<td>0.25 - MWCNT</td>
<td>0.25</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Table 5 - Summary of concentrations of RTIL-CNT+GNP dispersions and coagulation baths employed.
3.4 Fibre Electrical Conductivity

Electrical conductivity measurements, shown in Table 6, reveal that all fibres exhibit conductivities within the same order of magnitude, ranging between 10 - 40 S cm\(^{-1}\) with high variation (RSDs ranging from 14 – 53 %). These conductivities compare well with many similar polymer-containing fibres previously reported: fibres formed from SWCNTs with alginate were reported to have a maximum conductivity of 3.2 S cm\(^{-1}\) (112). Fibres from chitosan, carrageenan and CNTs were reported with a maximum conductivity of 31.7 S cm\(^{-1}\) (143).

<table>
<thead>
<tr>
<th>Fibre Type</th>
<th>Average Conductivity (S cm(^{-1}))</th>
<th>Relative Standard Deviation (RSD) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW-A</td>
<td>22 ± 4.5</td>
<td>20</td>
</tr>
<tr>
<td>SW-B</td>
<td>20 ± 5.7</td>
<td>29</td>
</tr>
<tr>
<td>SW-C</td>
<td>18 ± 2.5</td>
<td>14</td>
</tr>
<tr>
<td>MW-A</td>
<td>22 ± 12</td>
<td>53</td>
</tr>
<tr>
<td>MW-B</td>
<td>20 ± 6.5</td>
<td>32</td>
</tr>
<tr>
<td>MW-C</td>
<td>31 ± 9.9</td>
<td>32</td>
</tr>
</tbody>
</table>

*Table 6 – Four-point electrical conductivity measurements for RTIL produced fibres SW-A, SW-B, SW-C, MW-A, MW-B, and MW-C. Error represents one standard deviation for repeat measurements with \(n \geq 5\) fibre replicates.*

3.5 Fibre Electrochemical Properties - Cyclic Voltammetry

CV on fibres produced from the dispersions listed in Table 6 was carried out using 0.01 mol dm\(^{-3}\) PBS electrolyte and a scan rate of 100 mV s\(^{-1}\). Figure 33 shows CV of the three different variants of both SWCNT and MWCNT fibres.

*Figure 33 – CV of fibres SWCNT-based fibres (left), and MWCNT-based fibres (right). Measured at 100 mVs\(^{-1}\) vs. Ag/AgCl reference in 0.01 mol dm\(^{-3}\) PBS.*
A difference in voltammogram profile is observed between SWCNT and MWCNT-based fibres, with MWCNT fibres showing a profile closer to an ideal capacitive rectangle. Table 7 shows averaged currents for each SWCNT and MWCNT fibre type at 0.4 V as well as the RSDs. Higher currents at 0.4 V were seen for all MWCNT-based fibres than for SWCNT-based; this may partly be a product of the more rectangular profile of the voltammograms for MWCNT-based fibres. It can also be attributed to the higher carbon purity of the MWCNTs used, at 95% relative to 70+ % for SWCNTs used. As MWCNTs could be used at a much lower concentration, the dispersion may be of higher quality, yielding more homogenous fibres, as seen in the lower RSDs observed for MWCNT fibres. However, due to the level of variation for each fibre, no definitive conclusions between fibres within each CNT variant can be drawn from this testing alone.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Current at 0.4 V (A g⁻¹)</th>
<th>Current RSD at 0.4 V (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW-A</td>
<td>0.34 ± 0.12</td>
<td>35</td>
</tr>
<tr>
<td>SW-B</td>
<td>0.20 ± 0.12</td>
<td>61</td>
</tr>
<tr>
<td>SW-C</td>
<td>0.20 ± 0.11</td>
<td>57</td>
</tr>
<tr>
<td>MW-A</td>
<td>0.70 ± 0.12</td>
<td>30</td>
</tr>
<tr>
<td>MW-B</td>
<td>0.63 ± 0.06</td>
<td>10</td>
</tr>
<tr>
<td>MW-C</td>
<td>0.58 ± 0.09</td>
<td>19</td>
</tr>
</tbody>
</table>

Table 7 – Summary of SWCNT and MWCNT fibre currents at 0.4 V with relative standard deviations. Error represents one standard deviation for repeat measurements with n ≥ 5 fibre replicates. The RSDs measured are high but may be explained by the fact that these fibres were produced via manual injection. Variation can occur due to inconsistencies in the formation of the fibres, in particular the rate of injection into the coagulation bath. Moving to a more automated system using a syringe pump and controllable rotating coagulation bath would allow for a higher level of control, however this proved not to be possible due to the high viscosity of the dispersions used, coupled with the highly fragile nature of the fibres in their gel state.

CV using potassium ferricyanide as a redox couple was also performed, to allow further investigation of the fibres’ performance as electrodes, (Figure 34). Potassium ferricyanide was chosen for use in this analysis due to being a well-studied redox probe (144), giving
many possible prior systems to compare with. The use of this will allow comparison of the fibres with other electrodes, and with that of an ideal electrode surface.

![Voltammograms of SWCNT and MWCNT-based fibres with potassium ferricyanide redox couple.](image)

Figure 34 – Voltammograms of SWCNT and MWCNT-based fibres with potassium ferricyanide redox couple. Performed at 50 mV s⁻¹ vs. Ag/AgCl reference in 0.1 mol dm⁻³ KCl with 10 mmol dm⁻³ potassium ferricyanide.

It can be seen that for SWCNT-based fibres only the SW-A fibre shows notable redox peaks, and these are broad and not well-defined. For the SW-A fibre $\Delta E_p$ was found to be 0.288 V, with an $\frac{i_{pa}}{i_{pc}}$ value of 0.99, shown in Table 8. The ideal $\Delta E_p$ for this one electron system would be 0.059 V, showing that this electrode strays from ideal performance, although this is to be expected given the less than perfect nature of the fibre as an electrode already observed. An $\frac{i_{pa}}{i_{pc}}$ value of 0.99 shows good chemical reversibility in the system. It appears that the inclusion of GNP is detrimental to the performance of SWCNT fibres as an electrode. Figure 34 shows that all three MWCNT-based fibres display similar currents, although MW-A has the best redox peak definition and lowest peak separation, shown in Table 8. Peak separation is similar for SW-A and MW-A, while fibres MW-B and MW-C both show greater peak separation. From these results, it can be seen that the addition of graphene platelets into SWCNT and MWCNT dispersions produced fibres with poorer performance as electrodes. The values obtained are similar to those found in comparable fibres (96) (145).
Due to the similarity between fibre types, combined with the levels of error seen throughout the results obtained, differences in the electrochemical properties cannot be attributed to any change in electrical conductivities. The differences observed in voltammograms between MWCNT and SWCNT fibres may be attributed to the higher carbon content purity of the MWCNTs used (70 % + carbon for SWCNT, and 95 % + for MWCNT). This may reduce mass transport issues arising from non-carbon material within the fibre. This difference in voltammetry may also be due to more homogeneous and effective dispersion of MWCNTs due to the lower concentration used compared to SWCNTs.

### 3.6 Fibre Raman Spectroscopy

The Raman spectra presented in Figure 35 and Figure 36 show that all SWCNT-based fibres present similar spectra, and all MWCNT-based fibres again produce spectra with no visible differences. This is expected, as CNT and GNP materials both generate many of the same peaks in Raman spectroscopy due to the nature of the carbon sp² backbone that makes up both nanomaterials. Additional peaks (150 – 300 cm⁻¹) are observed in SWCNT-containing fibres, attributed to radial breathing modes, which were not observed in MWCNT fibres.
Figure 35 – Raman spectra of RTIL fibres SW-A, SW-B, and SW-C.

Figure 36 – Raman spectra of RTIL fibres MW-A, MW-B, and MW-C.
Table 9 shows a summary of the Raman peak data for all six fibre types.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>G-Band (cm(^{-1}))</th>
<th>G’-Band (cm(^{-1}))</th>
<th>D-Band (cm(^{-1}))</th>
<th>Radial Breathing Modes (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW-A</td>
<td>1573</td>
<td>2640</td>
<td>1328</td>
<td>150 - 300</td>
</tr>
<tr>
<td>SW-B</td>
<td>1586</td>
<td>2669</td>
<td>1338</td>
<td>150 - 300</td>
</tr>
<tr>
<td>SW-C</td>
<td>1569</td>
<td>2649</td>
<td>1331</td>
<td>150 - 300</td>
</tr>
<tr>
<td>MW-A</td>
<td>1574</td>
<td>2674</td>
<td>1338</td>
<td>-</td>
</tr>
<tr>
<td>MW-B</td>
<td>1574</td>
<td>2672</td>
<td>1318</td>
<td>-</td>
</tr>
<tr>
<td>MW-C</td>
<td>1576</td>
<td>2712</td>
<td>1341</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 9 – Summary of Raman spectra peaks for SWCNT, MWCNT and CNT/GNP mixed fibres.

All fibres show the G-band, arising from the presence of sp\(^2\) hybridised carbon in the fibre, as well as the G’-band and D-band, both arising from defects in the nanotubes/graphene layers. Radial breathing modes are seen only in the SWCNT fibres. Understandably, all fibres exhibit similar spectra; however, the ratio of G/D band peaks is higher in the SWCNT fibres, indicative of fewer defects in the SWCNT nanotubes. Addition of GNP to MWCNT fibres decreases the ratio of G/D band peaks, best observed for MW-C fibres, suggesting fewer defects present within the GNP added, relative to MWCNTs.

3.7 Scanning Electron Microscopy

SEM images of each fibre, presented in Figure 37, show large differences in their surface structure. It can be seen that as GNP is added to the fibres, the surface takes on a rougher profile, with aggregates of graphene platelets clearly visible on the surface.
Cross-sectional images of the fibres show the presence of GNP as well as CNTs throughout the fibres.

Figure 38A shows the cross sectional image of a fibre of SW-B; both nanoplatelets and nanotube bundles can be seen. These SEM images of the cross section show there are clear areas of bundled CNTs, adjacent to areas of the fibre core which appear more rich in GNP concentration. This suggests ineffective dispersion of SWCNTs within the RTIL, producing non-homogenous fibres. Figure 38B shows a magnified area of the same fibre, showing the nanotube bundles and graphene nanoplatelets.
Figure 38 – SEM images of SW-B fibre showing (A) fibre core and (B) magnified section. Red insert signifies section magnified for image (B).

Figure 39A shows a MW-A fibre, in which the presence of CNTs can be seen; bundles can clearly be seen within the entire cross section of the fibre core, magnified in Figure 39B. MWCNTs appear to be well-dispersed throughout the fibre, in agreement with the lower RSDs obtained for MWCNT fibres relative to SWCNT fibres.

Figure 40A shows the presence of GNP and CNTs in a MW-C fibre, again it can be seen that both GNP and CNTs are distributed throughout the core of the fibre. Figure 40B shows visible carbon nanotube bundles along the cross section of a core of a SW-A fibre. Ideal dispersion would produce fibres with highly exfoliated graphene platelets, and untangled nanotubes. However, it is observed in these images that bundles of nanotubes are present in the fibres, with some areas consisting of GNPs with little or no visible CNTs present. This is suggestive of incomplete dispersion during sonication, again in agreement with the high levels of error observed.
3.8 Fibre Mechanical Properties

Table 10 shows averaged ultimate tensile strength measurements for all six fibre types. Overall the fibres show extremely low tensile strengths, with results from DMA typically of the order of single MPa. This may be explained by low concentrations of polymer being incorporated into the fibre structures, or poor interaction between the nanomaterials and polymer present. Incomplete exfoliation of the CNT and GNP, as suggested by SEM images, means that the full potential strength and conductive properties of the nanomaterials are not being fully exploited in the fibres formed due to large bundles still being present.

In general, these values compare poorly with other similar fibres previously reported. In one example fibres formed using chitosan with polyhedral oligomeric silsesquioxane and SWCNT (77) reported maximum values ranging between 30 MPa and 60 MPa for SWCNT concentrations between 0 % and 9 %. For fibre-based wearable applications a higher level of tensile strength than what has been produced in these fibres is required, while still maintaining the electrical and electrochemical properties observed. The Young’s modulus for each fibre type was determined from the gradient of the stress-strain plots, also shown in Table 10. Large error is seen, with relative standard deviations reaching 100 %. This is indicative of the poor homogeneity within the fibres, producing fibres with a large range of ultimate tensile strengths and Young’s modulus values. This makes possible comparison between different fibres and materials very limited. Overall, the values obtained are low, as per the low ultimate tensile strengths. Almost all of the values are in the MPa range, rather than GPa often measured for fibres incorporating CNTs (146-
147). Higher values are observed for fibres containing only CNTs, decreasing upon the addition of graphene into the fibres, suggesting a poor interaction between the two nanomaterial variants.

<table>
<thead>
<tr>
<th>Fibre Type</th>
<th>Average Ultimate Tensile Strength (MPa)</th>
<th>Young’s Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW-A</td>
<td>7 ± 5</td>
<td>1000 ± 1000</td>
</tr>
<tr>
<td>SW-B</td>
<td>1 ± 1</td>
<td>30 ± 30</td>
</tr>
<tr>
<td>SW-C</td>
<td>1 ± 1</td>
<td>60 ± 60</td>
</tr>
<tr>
<td>MW-A</td>
<td>3 ± 3</td>
<td>200 ± 200</td>
</tr>
<tr>
<td>MW-B</td>
<td>1 ± 1</td>
<td>40 ± 40</td>
</tr>
<tr>
<td>MW-C</td>
<td>1 ± 1</td>
<td>30 ± 10</td>
</tr>
</tbody>
</table>

*Table 10 - DMA results for CNT and CNT/GNP mixture fibres. Error represents one standard deviation for repeat measurements with n ≥ 5 fibre replicates.*

### 3.9 Summary

This chapter has focused on spinning dispersions of carbon nanotubes and graphene nano platelets in ionic liquids to produce novel fibres. RSD values approaching 100% were found in some of the results obtained, which are predominantly attributed to poor dispersion quality, and manual fibre production. CV has shown that all of the fibres tested show similar current values, while MW-A fibres showed the best electrode performance using a potassium ferricyanide redox couple. The addition of GNP to both CNT types reduced their electrode performance. Conductivity measurements showed that the fibres analysed have conductivities in the range of 10 – 40 S cm⁻¹, with RSDs between 20 and 50%, similar to those found through voltammetry. Although fibres produced from SWCNTs and MWCNTs both display large amounts of error in all measurements, it was shown that MWCNT-based fibres displayed superior properties to SWCNT fibres, and that no benefit was found from the addition of GNP to the fibres.

While the results presented in this chapter have shown it is possible to spin fibres from CNT dispersions in ionic liquids, it is believed that better fibre properties can be achieved replacing insulating polymers, such as xanthan gum with conducting polymers in the fibres; this will be investigated in later chapters of this thesis.
4 Production of Scrolled Film Fibres Incorporating Conducting Polymers

4.1 Introduction

A wide range of fibre production methods exist, such as wet, dry, and melt spinning, each with advantages and disadvantages relative to other production methods (148-150). New and innovative methods to produce fibres are constantly being developed (151), and it has been demonstrated in literature that it is possible to produce fibres by scrolling/twisting thin films, to form the fibre structure. It is noted that no literature of scrolled film-fibres which performed characterisation using wet electrochemical methods was found.

4.2 Aims and Objectives

This chapter aims to develop films incorporating conducting polymer(s), which can be scrolled to produce fibres. This will require the production of homogenous films suitable for scrolling. Chemical post-treatment will be investigated to improve the fibres, and aid in retention of the scrolled form.

4.3 Incorporation of PEDOT:PSS into PVA Films

PEDOT:PSS was chosen as the conducting polymer, due to its ability to produce high conductivities, as well as being water soluble, making it suitable for producing films. PVA was added to PEDOT:PSS prior to film production to aid physical strength, as well as to provide elasticity.

The films produced via evaporation were found to be homogenous, without areas of thinness, or clumping occurring from the drying process. The production of films via filtering through nitrocellulose filer papers was also investigated, but was found to be inferior to petri dish casting. Not all polymeric material was captured by the filter paper, evidenced by the colour remaining in the solution in the filter vessel. The filtered films varied in thickness, whereas films produced through evaporative methods were found to be uniform in thickness, due to the slow evaporation allowing for equal distribution of material across the entire petri dish.

Fibres produced from scrolling of films could be bent repeatedly without breaking. They also maintained their scrolled structure, without any visible unravelling. It was noted however, that these fibres unravelled when placed in solution. To combat this, sodium
sulfate was employed as a chemical cross linking agent for PVA (152). After extended treatments of 48 h immersion, the fibres still unravelled when placed in to solution after being dried and removed from the clamps. Alternative chemical treatments were also considered, including the treatment of the films with sulfuric acid, formic acid, and DMSO.

To investigate the effects of these chemical treatments employed on PEDOT:PSS-PVA fibres, scrolled PEDOT:PSS-PVA fibres were immersed in each of the three treatments for 5, 60, and 120 min each. Fibres were assigned the codes “FCXX” with ‘F’ representing fibres produced from films, with the following ‘C’ being the treatment variation, and ‘XX’ stating the time for which the treatment immersion was performed (min). These codes are shown in Table 11. The proportion of PEDOT:PSS and PVA in each fibre is assumed, based on the relative amounts of each component added to the original solutions. Deviation from these proportions may be present in the fibres produced, due to inhomogeneity during drying, and from dissolution of each/both component during treatment(s).

<table>
<thead>
<tr>
<th>Treatment Type</th>
<th>5 min Treatment</th>
<th>60 min Treatment</th>
<th>120 min Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated fibre</td>
<td></td>
<td></td>
<td>FU</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1.5 mol dm(^{-3}))</td>
<td>FS5</td>
<td>FS60</td>
<td>FS120</td>
</tr>
<tr>
<td>Formic acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(25 mol dm(^{-3}))</td>
<td>FF5</td>
<td>FF60</td>
<td>FF120</td>
</tr>
<tr>
<td>DMSO</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 11 – Fibre name codes for treatment types and times for all fibres prepared from PEDOT:PSS-PVA films.*

4.3.1 Fibre Basic Properties

It was found that fibres immersed in formic acid unravelled and broke within moments of being immersed due to the twisting tension within them. This effect was similarly observed with the DMSO immersed fibres to a lesser extent; a small amount of short (~ 1 cm) fibres were salvaged for analysis. It was found that only sulfuric acid treatments reliably produced fibres, without breakage during immersion or drying.
Treated fibres were more brittle than untreated fibres. It was not possible to bend treated fibres in the same way as untreated fibres. Averaged fibre diameters are presented in Figure 41. Relative standard deviations of 15% were observed for all fibre types, and no change in diameter was observed after any of the treatment types or times. Formic acid treated fibres are omitted from the graph due to their consistent breaking during treatment.

![Graph showing fibre diameters for fibres scrolled from PEDOT:PSS-PVA films before and after chemical treatments. Error bars represent one standard deviation for repeat measurements with n ≥ 10 fibre replicates.](image)

SEM images of the fibres were obtained, and are shown in Figure 42 - Figure 44. Images of the lengths of the fibre are shown on the left of the figures, while the right images show core views of the respective fibres. Images of the fibre cross-section show the fibre to be mostly solid, with a void area formed during the twisting procedure, which is seen as the darker area in the centre of the right hand image in Figure 42.
As with the untreated fibre, FS120 fibres show a straight length profile. A rippled surface profile is observed, this difference to fibre FU is attributed to the manual nature of the fibre scrolling. A slight difference in fibre cross-section morphology is seen, relative to the untreated FU fibre. This is attributed to the increased brittleness of the fibres post-
treatment, causing a cleaner break in the fibre when compared with the FU fibre core. This change in core structure could also be produced during the treatment procedures, as it is seen in all treated fibres. The treatments have the potential to soften and partially dissolve both polymers, merging the scrolled layers, before being re-solidified during the drying procedure. Fibres treated with DMSO, shown in Figure 44, presented similar images to those treated with sulfuric acid. They again still display a straight profile, and a core which appears more consistently solid than that of untreated FU fibres.

After treatment, it is noticed that fibres do not swell when placed into solution, whereas untreated fibres do. It is this difference in water uptake that is key in producing fibres which do not unravel when wet. This difference is attributed to chemical cross-linking of the PVA alcohol groups by sulfonate ions from the sulfuric acid (126-127). Figure 45 shows an example of two fibres, one pre-treatment and the other post-treatment. Both fibres had the same original diameter before immersion; a dramatic difference in diameter is observed after immersion. This difference is caused by the treated fibre no longer absorbing water, which stops it unravelling, the beginnings of which are seen for the untreated fibre. Over the course of several h, the untreated fibres unravel back into a film.

![Figure 45 – Digital camera photograph of the sulfuric acid treated (top) and untreated (bottom) fibres after immersion in water.](image)

### 4.3.2 Fibre Electrochemical Properties – Cyclic Voltammetry

CV of fibres treated for 2 h with sulfuric acid (FS120), and DMSO (FD120) are presented in Figure 46, to examine the maximum effect of each treatment. It is apparent that these fibres display poorer voltammogram shapes than would be expected for a conducting-
polymer only fibres (30), as can be seen later in Figure 57 in Chapter 5. This is due to the inclusion of the insulating PVA in the fibre hindering the electrochemical response.

An additional consideration when analysing the voltammograms is that of the difference in water take up between untreated and treated PEDOT:PSS-PVA fibres. As shown in Figure 45 the treated fibres take up dramatically less water than untreated PEDOT:PSS-PVA fibres. This can limit electrochemical access to the core of the fibre, creating additional mass transport issues and lower currents, due to limited electrolyte permeation of the fibre core structure. Voltammetry for untreated fibres was not possible, due to the fibres unravelling when immersed in solution.

4.3.3 Fibre Electrochemical Properties – Charge Discharge Cycling

Charge discharge analysis was performed on fibres treated with sulfuric acid and with DMSO for all three treatment durations. Discharge times were determined from the gradient of the discharge curve in the upper 50 % voltage range, within which supercapacitors are most commonly charged/discharged (11).
Data could not be obtained for untreated fibres or formic acid fibres due to unravelling of the fibres when immersed in both electrolyte and treatment solutions, as such a full comparison was not possible.

Figure 47 – Charge discharge profiles for scrolled fibres treated with sulfuric acid (1.5 mol dm$^{-3}$): FS5, FS60, and FS120. Measured at 0.5 A g$^{-1}$ vs. Ag/AgCl electrode in 1 mol dm$^{-3}$ sodium sulfate.

Figure 47 shows charge discharge profiles for fibres FS5, FS60, and FS120, and Figure 48 shows profiles for fibres FD5, FD60, and FD120. It is apparent that the voltage shows large jumps when charging and discharging. This is likely partly due to the non-conductive PVA hindering the conductivity of the fibres, allowing for less efficient distribution of the charge throughout the fibre. As the fibres no longer swell and absorb water, this may give rise to mass transport issues along and within the fibre, limiting electrolyte access to the fibres, both contributing to an increased internal resistance for the system.
Averaged charge discharge cycling capacitance values are presented in Figure 49, and detailed in Table 12. It can be seen that there is a large amount of variation within each treatment type. This is attributed to the error generated when fibres are manually scrolled; slight variations in the amount of twisting applied to each fibre can have a large effect on the structure of the fibre, altering the electrochemically accessible surface area. While the fibre contained two thirds Orgacon PEDOT:PSS, and one third PVA, values of only $\sim 2 \text{ F g}^{-1}$ are obtained, far lower than values obtained for wet spun Orgacon fibres shown in chapter 5 of this thesis. The inclusion of PVA negatively affects the electrochemical properties due to the lower proportion of PEDOT:PSS present in the fibre, thus reducing the capacitance of the fibre.
Figure 49 – Averaged charge discharge capacitances for fibres FS5, FS60, FS120, FD5, FD60, and FD120. Measured at 0.5 A g\(^{-1}\) vs. Ag/AgCl electrode in 1 mol dm\(^{-3}\) sodium sulfate. Error bars represent one standard deviation for repeat measurements with \(n \geq 5\) fibre replicates.

<table>
<thead>
<tr>
<th>Treatment Time</th>
<th>Sulfuric Acid</th>
<th>Formic Acid</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>Measurement not possible due to unravelling of untreated fibres</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 min</td>
<td>1.3 ± 0.2</td>
<td>Measurement not possible due to fibre breakage during treatment</td>
<td>2.2 ± 0.2</td>
</tr>
<tr>
<td>60 min</td>
<td>2.5 ± 0.3</td>
<td>1.9 ± 0.5</td>
<td>1.9 ± 0.5</td>
</tr>
<tr>
<td>120 min</td>
<td>1.5 ± 0.9</td>
<td>2.5 ± 1.7</td>
<td>2.5 ± 1.7</td>
</tr>
</tbody>
</table>

Table 12 – Averaged charge discharge capacitances for fibres FS5, FS60, FS120, FD5, FD60, and FD120 (Measured at 0.5 A g\(^{-1}\) vs. Ag/AgCl electrode in 1 mol dm\(^{-3}\) sodium sulfate). Error bars represent repeat measurements with \(n \geq 5\) fibre replicates.

4.3.4 Fibre Electrical Conductivity

Four-point electrical conductivity measurements were obtained for fibres FU, FS5, FS60, FS120, FD5, FD60, and FD120. The values are compared in Figure 50 and shown in Table 13. Sulfuric acid treated scrolled fibres showed a conductivity increase of between 100 and almost 300 % relative to untreated fibres, while DMSO treated scrolled fibres showed by
far the largest increase, producing values up to ten times higher than for untreated fibres. The higher values obtained for DMSO-treated scrolled fibres rather than for sulfuric acid treated scrolled fibres can be attributed to the higher solubility of PVA in DMSO than in water (153). With higher amounts of PVA being dissolved into the DMSO and removed from the fibres, a higher proportion of the remaining material is PEDOT:PSS, allowing higher conductivities within the treated fibres. This also serves to explain the difference in values observed for FD5 and FD60 fibres, with the latter having lost more PVA, and thus possessing higher conductivity values, although higher levels of variation are observed.

![Figure 50 – Averaged four-point electrical conductivity values for scrolled fibres FU, FS5 FS60, FS120, FD5, FD60, and FD120. Error bars represent one standard deviation for repeat measurements with $n \geq 5$ fibre replicates.](image_url)

<table>
<thead>
<tr>
<th>Treatment Time</th>
<th>Sulfuric Acid</th>
<th>Formic Acid</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>12.8 ± 5.2</td>
<td>26 ± 11</td>
<td>Measurement not possible due to fibre breakage during treatment</td>
</tr>
<tr>
<td>5 min</td>
<td>26 ± 11</td>
<td>Measurement not possible due to fibre breakage during treatment</td>
<td>70 ± 2</td>
</tr>
<tr>
<td>60 min</td>
<td>18 ± 6</td>
<td>Measurement not possible due to fibre breakage during treatment</td>
<td>130 ± 30</td>
</tr>
<tr>
<td>120 min</td>
<td>34 ± 22</td>
<td>Measurement not possible due to fibre breakage during treatment</td>
<td>127 ± 43</td>
</tr>
</tbody>
</table>

Table 13 – Averaged four-point electrical conductivity values for scrolled fibres FU, FS5 FS60, FS120, FD5, FD60, and FD120. Error bars represent repeat measurements with $n \geq 5$ fibre replicates.
4.3.5 Fibre Raman Spectroscopy

Raman spectra for fibres FU, FS120, and FD120 are presented in Figure 51, the three spectra are normalised around the largest peak, observed at 1,550 cm\(^{-1}\). Peaks assigned to the PEDOT:PSS material observed at 440 and 574 cm\(^{-1}\) corresponding to C-OC deformations, 986 cm\(^{-1}\) for oxyethylene ring deformation, 1,290 cm\(^{-1}\) for CH\(_2\) bending, 1,430 cm\(^{-1}\) for C=C symmetric stretching, and 1,550 cm\(^{-1}\) for C=C antisymmetric stretching (154-155). Broad peaks assigned to C-H in the PVA component are present in the region at approximately 2,900 cm\(^{-1}\) (156). No shift in peak position was observed, as has been reported previously for PEDOT:PSS materials treated with ethylene glycol (74), attributed to changes between the benzoïd and quinoid structure of PEDOT:PSS. The widespread use of X-ray photoelectron spectroscopy (XPS) to identify chemical changes in PEDOT:PSS post treatment has shown Raman spectroscopy to be of only limited use in identifying such changes.

*Figure 51 – Raman spectra for scrolled film fibres FU, FS120, and FD120. Insert shows structure of PEDOT:PSS.*
4.3.6 Fibre Mechanical Properties

Ultimate tensile strength values are reported for fibres FU, FS5, FS60, and FS120 only. Values could not be obtained for formic acid treated fibres due to breaking during treatment. DMSO treated fibres could not be produced in the lengths required for DMA analysis. While shorter fibres could be used for conductivity and electrochemical testing, it was not possible to subject them to mechanical analysis. It is believed that the additional dissolution of PVA into DMSO during the treatment causes a weakening of the scrolled film fibres while in solution, leading to their high breakage rate.

The mechanical properties of treated and un-treated scrolled fibres are listed in Table 14 and shown in Figure 52. The ultimate tensile strength values obtained for untreated fibres are similar to those obtained for other wet spun Orgacon PEDOT:PSS fibres (30). The addition of PVA, which has a far higher tensile strength than PEDOT:PSS contributes to the enhanced tensile strengths observed here. A large decrease in strength is observed after sulfuric acid treatment. This may be due to removal of some amount of PVA during the treatment process, but also likely due to the cross-linking of the PVA occurring during the treatment.

![Figure 52 – Averaged ultimate tensile strength values for fibres FU, FS5, FS60, and FS120. Error bars represent one standard deviation for repeat measurements with n ≥ 3 fibre replicates.](image)

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Analysis of the Young’s Modulus values presented in Table 14 show no discernible difference between untreated fibres and any of the sulfuric acid-treated fibres. The values obtained are each within the error of each other, showing no trend based on treatment time. Mechanical analysis shows that all treatments have a negative effect on the strength of the fibres, with formic acid and DMSO treatments destroying the fibres during treatment, and sulfuric acid treatments greatly weakening the fibres. The large difference observed is attributed to the different behaviour of the scrolled fibres before and after treatment. Before treatment, the fibres are able to undergo elastic stretching through unwinding of the scrolled twists, whereas after treatments, due to the cross-linking occurring, the fibres are not able to undergo this same stretching, producing much lower failure strain values.

<table>
<thead>
<tr>
<th>Fibre Type</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>Young’s Modulus (GPa)</th>
<th>Failure Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FU</td>
<td>103 ± 34</td>
<td>1.4 ± 0.3</td>
<td>47 ± 16</td>
</tr>
<tr>
<td>FS5</td>
<td>42 ± 15</td>
<td>2.1 ± 0.7</td>
<td>5.2 ± 4.3</td>
</tr>
<tr>
<td>FS60</td>
<td>312 ± 19</td>
<td>1.5 ± 0.6</td>
<td>2.1 ± 1.2</td>
</tr>
<tr>
<td>FS120</td>
<td>29 ± 17</td>
<td>1.7 ± 0.4</td>
<td>3.1 ± 1.8</td>
</tr>
</tbody>
</table>

*Table 14 – Averaged ultimate tensile strength, Young’s modulus, and failure strain values for fibres FU, FS5, FS60, and FS120. Error bars represent repeat measurements with n ≥ 3 fibre replicates.*

### 4.4 Summary

In this chapter, conducting fibres formed by scrolling films of PEDOT:PSS and PVA were produced and characterised. Electrical conductivity values of up to 130 S cm⁻¹ were measured for DMSO treated scrolled fibres, although production of these was problematic due to breakage occurring during chemical treatment. This limited fibre length to a maximum of 1 cm. More reliable fibres were produced via treatment of scrolled fibres with sulfuric acid, but these yielded lower conductivities (30 S cm⁻¹), and low ultimate tensile strengths (30 MPa). These sulfuric acid-treated fibres could be produced in potentially any desired length, with no breakage or unravelling occurring during treatment. The conductivities obtained are far lower than those obtained through treating PEDOT:PSS fibres with the same chemicals, with values in excess of 1,000 S cm⁻¹ being possible (62). This limited conductivity would be acceptable, if the capacitance of mechanical strengths of the fibres were improved, however the capacitance values obtained are again
dramatically lower than those obtained for PEDOT:PSS-only materials (62) (74), and the mechanical strengths lower than other PVA-containing fibres (82) (157).

Treatment of scrolled PEDOT:PSS-PVA fibres had the added benefit of enabling them to stay scrolled then immersed in solution. This technique presents a novel method of producing fibres from scrolled films which may be of use in a range of applications including such as water purification, amongst others.

Further optimisation of this work by using higher grade PEDOT:PSS sources, such as Clevios PH1000 may yield improved results due to the inherently higher conductivity of the PEDOT:PSS solutions compared with the Orgacon material used in this chapter. A further avenue for investigation is the potential to use lower amounts of PVA, or the use of additional polymers, likely further increasing the electrochemical and electrical properties of the fibres.
5 Wet Spinning and Treatment of PEDOT:PSS Fibres

5.1 Introduction

One of the interesting properties of conducting polymers is their high level of electrical conductivity (56) (59), as well as the ability to store charge through pseudocapacitive mechanisms (64). Several properties of these fibres have been shown to be improved following chemical treatment (60) (129). It was shown that, for example, ethylene glycol improved the properties of PEDOT:PSS fibres (62), and a wider range of chemicals have been used to enhance the properties of PEDOT:PSS films on glass. It was decided to expand the investigation of chemical treatment of PEDOT:PSS fibres beyond ethylene glycol.

Sulfuric acid (60), formic acid (128), and DMSO (129) have all been shown to improve multiple desired properties of these PEDOT:PSS materials, and were therefore chosen for further investigation with respect to fibres. To investigate multiple aspects of the treatments, a range of treatment times was investigated, wet spun with fibres being immersed in each treatment for 5, 60, and 120 min. Different sources of PEDOT:PSS were also studied, to investigate the effect of each treatment on the PEDOT:PSS variants. Two fibre diameters were produced, treated, and compared, to investigate the respective effect of the treatments when varying the surface area to core volume ratio of the fibres. As it has been shown previously that the treatment effect is mainly confined to the surface of the PEDOT:PSS material (128) (158), it is predicted that fibres with a smaller diameter will show a larger increase or decrease in post-treatment properties.

5.2 Results

Fibres were spun from two PEDOT:PSS precursors, Clevios PH1000 and Orgacon pellets. Treatments were then performed on these fibres. Abbreviated codes for each of these fibres are given in Table 15 and Table 22 below. “U” represents an untreated fibre, “SX” a fibre treated with sulfuric acid for X min, with “FX” and “DX” representing the equivalent for formic acid and DMSO, respectively. Codes prefixed with “PH” represent fibres spun from solutions of Clevios PH1000 PEDOT:PSS.
<table>
<thead>
<tr>
<th>Fibre Treatment Method</th>
<th>5 min Treatment</th>
<th>60 min Treatment</th>
<th>120 min Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Orgacon Pellet Fibre</td>
<td>U</td>
<td>S60</td>
<td>S120</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>S5</td>
<td>S60</td>
<td>S120</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>F5</td>
<td>F60</td>
<td>F120</td>
</tr>
<tr>
<td>DMSO</td>
<td>D5</td>
<td>D60</td>
<td>D120</td>
</tr>
</tbody>
</table>

Table 15 – Fibre codes for fibres spun from 2 wt.% PEDOT:PSS (Orgacon) solutions.

5.2.1 Fibres Spun from Orgacon Pellet PEDOT:PSS

5.2.1.1 Fibre Basic Properties

Fibres were successfully produced via wet spinning from 2 wt.% aqueous solutions of Orgacon PEDOT:PSS; spinning from lower concentrations was found to be possible, but produced shorter fibres with higher variation and breakage, attributed to a lack of PEDOT:PSS material to successfully coagulate. Increasing the coagulation bath rotation speed produced fibres with thinner diameters, and vice versa. It was found that for all variants and times tested, no treatment was found to damage or inhibit the fibre in such a way that further testing and characterisation was not possible.

Optical microscopy, shown in Figure 53 revealed that the average diameter of the untreated fibres was 35 µm, (Figure 54). Diameter averages were calculated from a minimum of 11 fibres, with 10 measurements along each fibre axis.

Figure 53 – Optical microscope diameter measurements for a select PEDOT:PSS (Orgacon) wet spun fibre. Wet spun from 2 wt.% Orgacon PEDOT:PSS.
It was found that no statistically significant change in diameter of the fibres was observed after chemical treatments, with the fibres retaining the same range of diameters as the untreated fibres (Figure 54). Some variance within the fibre diameter is observed, regardless of treatment or not; this is attributed to slight variations in the rate of rotation of the coagulation bath, as well as slight fibre shape changes induced during drying of the fibres from their gel state.

![Graph showing average diameters of wet spun PEDOT: PSS (Orgacon) fibres](image)

*Figure 54 – Average diameters of wet spun PEDOT: PSS (Orgacon) fibres. Error bars represent one standard deviation for repeat measurements with n ≥ 10 fibre replicates.*

Electron microscopy was carried out to analyse the surface structure and cross-section of the fibres (Figure 55). The fibres presented a smooth surface, and were found to be flexible, allowing them to be tied by hand into knots when dry (Figure 55 B).

Analysis of the core of untreated and treated fibres showed no apparent difference in morphology from any of the treatments. This result is to be expected, as the effects occurring through treatment affect the fibre on a scale below that which can be observed through electron microscopy. This is in line with previous results by others where analysis using XPS and/or AFM was required to determine the chemical change occurring through treatments (59) (129) (158-159). It has been shown several times that the changes occur due to removal and rearrangement of some of the insulating PSS material (62) (69) (159-
160), as well as beneficial reordering of the polymer chains (62). This effect is seen mainly at the surface of the material (62) (159).

Figure 55 – SEM images of fibre axis U (A), dry knotted fibre U (B), core view of fibre U (C), core view of fibre S120 (D), core view of fibre F120 (E), core view of fibre D120 (F).
5.2.1.2 Fibre Raman Spectroscopy

Raman analysis was performed on all fibre types, with Figure 56 showing the 120 min time for each of the three treatments (S120, F120 and D120), compared to an untreated fibre (U). No notable differences are observed in the spectra. As discussed previously, the treatments have been shown to remove some PSS material, and alter the physical structure of the PEDOT:PSS polymers. This, however, does not change the overall chemical structure of the polymers present, and has not altered the Raman spectra observed after treatment.

Peaks present at 576, 852 and 987 cm\(^{-1}\) are attributed to deformation of the PEDOT oxyethylene ring, 697 cm\(^{-1}\) to the symmetric deformation of the C-S-C bonds, and the broader peaks between 1,090 and 1,120 cm\(^{-1}\) to the C-O-C bond deformation. Peaks at 1,250 cm\(^{-1}\) are attributed to PEDOT C\(_a\)-C\(_a'\) (inter-ring) stretches, while the peak at 1,380 cm\(^{-1}\) is assigned to C\(_\beta\)-C\(_\beta\) stretches, 1,430 cm\(^{-1}\) to symmetrical C\(_a\)=C\(_\beta\)(-O) stretches, and 1,490 cm\(^{-1}\) to asymmetrical C=C stretches. These correspond accordingly with literature spectra of PEDOT materials (161). As with Orgacon fibres presented earlier, no shift in peak position was observed for any peak (74).

![Raman spectra for fibres U, S120, F120, and D120 for wet spun PEDOT:PSS (Orgacon) fibres. Spectra normalised to 1,430 cm\(^{-1}\) peak for visual comparison. Insert shows PEDOT:PSS structure.](image)

83
5.2.1.3 Fibre Electrochemical Properties – Cyclic Voltammetry

CV, shown in Figure 57, reveals a change in the voltammogram observed for all treated fibres, moving towards that of an ideal rectangular capacitive system. There is little change observed in the currents and shapes of voltammograms for all fibre treatments and times. No further improvement is seen with treatment times longer than 5 min, suggesting that all modification of the fibres occurs within the first 5 min. These changes in voltammetry profile could stem from an increase in the electrical conductivity of the fibres. A higher conductivity in the fibre allows for more efficient and quicker transfer of current through the system, thus producing the more rectangular system observed.

![Figure 57 – CV of fibres U, S5, S60, and S120 (Left). CV of fibres U, S120, F120, D120 (Right). Measured at 100 mV s⁻¹ vs. Ag/AgCl electrode in 1 mol dm⁻³ aq. sodium sulfate.](image)

CV using potassium ferricyanide redox probe was also employed to analyse the effect of each treatment on the fibre electrodes. A clear and dramatic difference can be seen in the response observed for untreated and treated fibres, while all three treatments show similar responses. Figure 58 shows these voltammograms for the 5 min treated fibres, from which peak data was extracted and used to generate plots of $\Delta E_p$ (V) vs. scan rate (mV s⁻¹). This also allowed analysis of peak current ratios and determination of the effect of changing scan rate on the peak current.
Figure 58 – CV of fibres U (A), S5 (B), F5 (C), D5 (D). (Measured at varying scan rates. Measured at 100 mV s\(^{-1}\) vs. Ag/AgCl electrode in 10 mmol dm\(^{-3}\) \(K_3[Fe(CN)_6]\) with 0.1 mol dm\(^{-3}\) KCl.

Figure 59 shows \(\Delta E_p\) (V) for all 5 min treatments. Sulfuric acid treatment shows the lowest peak separation, followed by DMSO, with formic acid treatments showing the worst (widest) separation of peaks. It was not possible to obtain data for peaks on untreated fibres at scan rates over 50 mV s\(^{-1}\), due to poor peak definition. When comparing \(\Delta E_p\) vs. scan rate, a linear increase in peak separation is observed with increasing scan rate, suggesting that the system is kinetically limited (162-164).
Table 16 presents the ratios of the peak currents for each fibre at 100 mV s\(^{-1}\). Ratios close to one are observed for all treatments at all measured scan rates, showing that the system is chemically reversible within the timeframe of the experiment (165-167).

<table>
<thead>
<tr>
<th>Fibre</th>
<th>U</th>
<th>S5</th>
<th>F5</th>
<th>D5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(</td>
<td>I_{pc}/I_{pa}</td>
<td>)</td>
<td>0.92</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Table 16 - \(|I_{pc}/I_{pa}|\) peak current ratios for all Orgacon fibres. Measured at 100 mV s\(^{-1}\) vs. Ag/AgCl electrode in 10 mmol dm\(^{-3}\) \(K_3[Fe(CN)_6]\) with 0.1 mol dm\(^{-3}\) KCl.

Figure 60 shows the effect on the peak current by changing the scan rate. Data is shown for each treatment, plotting the peak current against the square root of the scan rate. A straight line is observed in each case, which suggests diffusion controlled system (168-170). This contrasts the previous suggestion from \(\Delta E_p\) values that the system is kinetically limited. This is attributed to the system being a quasi-reversible system, where the voltammetry is governed both by charge transfer, and mass transport limitations (171-173).
Figure 60 – Graphs of peak current vs. square root of scan rate for fibres U (A), S5 (B), F5 (C), D5 (D). Measured at 100 mV s\(^{-1}\) vs. Ag/AgCl electrode in 10 mmol dm\(^{-3}\) K\(_3\)[Fe(CN)\(_6\)] with 0.1 mol dm\(^{-3}\) KCl.

Using the Randles–Sevcik equation given in Equation 3, the accessible electrochemical surface area of each fibre was determined. These values were compared between fibres, and with that of a theoretical cylinder of the same diameter and length as the fibre being measured, shown in Table 17.

A large increase in accessible electrochemical surface area is observed for all treatments, showing approximately a sevenfold increase. All treatments show similar increases in their electrochemical surface areas, with formic acid exhibiting slightly higher values than the remaining two. Comparisons between the experimentally suggested electrochemical surface area and that of the theoretical cylinder show the treated fibres to have values well in excess of 100 %. This is attributed to the surface of the fibres not being perfectly smooth, as well as electrochemical surface area accessible within the fibre due to swelling of the polymer when placed in solution (174-176).

An increase in the accessible electrochemical surface area is important for the fibres’ usage in electrochemical capacitor applications as it allows greater active surface area in the device, reducing the unused area of the fibre and thus helping to increase the electrochemical efficiency and total charge storage of the device.
### Table 17 – Comparison of electrochemically calculated accessible surface area values for all PEDOT:PSS (Orgacon) fibres.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Cylindrical Surface Area (cm²)</th>
<th>Electrochemical Surface Area (cm²)</th>
<th>% Of Cylindrical</th>
<th>% Of Respective Untreated Fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>0.0112</td>
<td>0.0045</td>
<td>64.4</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>0.0129</td>
<td>0.0311</td>
<td>241</td>
<td>430</td>
</tr>
<tr>
<td>F5</td>
<td>0.0112</td>
<td>0.0334</td>
<td>298</td>
<td>462</td>
</tr>
<tr>
<td>D5</td>
<td>0.0121</td>
<td>0.0319</td>
<td>264</td>
<td>441</td>
</tr>
</tbody>
</table>

5.2.1.4 Fibre Electrochemical Properties – Charge Discharge Cycling

Cyclic charge discharge measurements were performed on each fibre type, at a current density of 0.5 A g⁻¹. Discharge times were again determined by measuring the gradient of the discharge curve in the upper 50 % voltage range, within which supercapacitors are most commonly charged/discharged (11). A clear increase in charge and discharge times
can be seen between untreated and treated fibres. No discernible difference between
different treatments times was observed, with all results exhibiting a typical error of up to
10 % RSD, calculated from multiple fibres of each fibre type. There is also no difference
observed between each treatment type, with each showing the same increase relative to
untreated fibres (Figure 61). These results correspond well with the increases observed in
the CV results presented earlier. It is noted that untreated fibres display an initial voltage
step upon charging, charging from approximately 0.2 V. An initial voltage drop is also
observed in the discharge cycle. This is not observed in the treated fibres, or is observed to
a lesser effect where seen. This suggests that the untreated fibres have a higher resistance
than the treated fibres, thus causing a larger equivalent series resistance for the system
(177). Averaged charge discharge capacitances were calculated; values are shown in
Figure 62 and listed in Table 18.

As expected from the CV results, an increase in capacity is observed for all treatments and
times. A doubling in capacitance is seen on all treatments. No further increase was
observed after 5 min for any treatment. This increase is attributed to removal of some PSS
from the surface of the fibre (60) (128) (159), enabling the electrolyte to interact more
effectively with PEDOT in the fibre. These results show that the charge storage capacity of
the fibres, an essential property of the material for energy storage applications, is doubled
with a simple chemical treatment. This presents a reliable and facile method of improving
the properties of devices formed using these materials.

<table>
<thead>
<tr>
<th>Treatment Time</th>
<th>Sulfuric Acid</th>
<th>Formic Acid</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>10.9 ± 1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 min</td>
<td>24.2 ± 2.2</td>
<td>23.2 ± 1.3</td>
<td>26.4 ± 1.4</td>
</tr>
<tr>
<td>60 min</td>
<td>22.8 ± 1.4</td>
<td>24.1 ± 1.4</td>
<td>27.9 ± 1.4</td>
</tr>
<tr>
<td>120 min</td>
<td>23.9 ± 0.6</td>
<td>22.8 ± 2.0</td>
<td>23.9 ± 1.5</td>
</tr>
</tbody>
</table>

Table 18 – Averaged charge discharge capacitance values for all fibre treatment
types of wet spun PEDOT:PSS (Orgacon) fibres. Measured at 0.5 A g⁻¹ vs.
Ag/AgCl electrode in 1 mol dm⁻³ aq. sodium sulfate vs. Ag/AgCl) Error bars
represent repeat measurements with n ≥ 5 fibre replicates.
Figure 62 – Averaged charge discharge capacitance values for all fibre treatment types of wet spun PEDOT:PSS (Orgacon) fibres. Measured at 0.5 A g$^{-1}$ vs. Ag/AgCl electrode in 1 mol dm$^{-3}$ aq. sodium sulfate vs. Ag/AgCl). Error bars represent one standard deviation for repeat measurements with $n \geq 5$ fibre replicates.

5.2.1.5 Fibre Electrical Conductivity

The electrical conductivity of all fibres was also found to have increased after treatment, and are compared for each fibre type in Figure 63 and listed in Table 19. A tripling of conductivity is observed for all treatments and times. No difference is found between each treatment type, or duration. This is attributed to PSS removal from the fibre, specifically from the surface (60) (128) (159). Reorientation/size change of the PEDOT grain has also been reported previously (59) (158), and is also believed to contribute to the observed improvements in conductivity. A larger increase is seen here for electrical conductivity than was seen for capacitance; however, both are essential properties to increase the efficiency of energy devices.
Figure 63 – Averaged four-point electrical conductivity values for all fibre treatment types of wet spun PEDOT:PSS (Orgacon) fibres. Error bars represent one standard deviation for repeat measurements with $n \geq 5$ fibre replicates.

<table>
<thead>
<tr>
<th>Treatment Time</th>
<th>Sulfuric Acid</th>
<th>Formic Acid</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>31.4 ± 2.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 min</td>
<td>118 ± 13</td>
<td>108 ± 15.0</td>
<td>93 ± 8</td>
</tr>
<tr>
<td>60 min</td>
<td>104 ± 11</td>
<td>108 ± 14</td>
<td>94 ± 10</td>
</tr>
<tr>
<td>120 min</td>
<td>105 ± 12</td>
<td>110 ± 16</td>
<td>99 ± 8</td>
</tr>
</tbody>
</table>

Table 19 – Averaged electrical conductivity values for all fibre treatment types of wet spun PEDOT:PSS (Orgacon) fibres. Errors represent one standard deviation for repeat measurements with $n \geq 5$ fibre replicates.

5.2.1.6 Fibre Mechanical Properties

Ultimate tensile strength values were obtained for all fibres, through DMA testing. Figure 64 shows example stress strain curves for treated fibres, compared with an untreated fibre. A decrease in ultimate tensile strength is observed for all treatment times using sulfuric acid, while formic acid and DMSO appear to show an increase in tensile strength.
Figure 64 – Example stress strain graphs comparing unrelated fibres with sulfuric acid treatments (top left), formic acid treatments (top right), and DMSO treatments (bottom) for 5, 60, and 120 min each.

The variation in tensile strength values for repeated fibres is 30 % RSD. This level of error is higher than seen for other analysis techniques, and is attributed to the physical difference in shapes occurring in fibres. While electrical and electrochemical testing is not affected by a fibre’s shape or physical layout, mechanical testing is, due to potential weakening at areas of non-uniformity.

Averaged tensile strength values for all fibres are compared in Figure 65, and listed in Table 20. Sulfuric acid treatments were found to have lower ultimate tensile strengths. The cause of this weakening is not well studied or understood, but is believed to be due to residual sulfate ions in the fibre. This result will be further investigated in later chapters. Another factor to consider is the relative strength of each acid. Sulfuric acid is a far stronger acid than formic acid, and as such may be capable of degrading the polymer material more than formic acid. Even though the formic acid concentration used was 25.2 mol dm$^{-3}$, and sulfuric acid concentration 1.5 mol dm$^{-3}$, the difference in their respective acid strengths spans multiple orders of magnitude (178-179). Formic acid and DMSO both show increases in average strength compared with untreated fibres. Due to the level of
variance present in these results, no clear differentiation between formic acid and DMSO treatments can be determined.

Figure 65 – Ultimate tensile strengths of all fibre treatments for wet spun PEDOT:PSS (Orgacon) fibres. Error bars represent one standard deviation for repeat measurements with \( n \geq 3 \) fibre replicates.

<table>
<thead>
<tr>
<th>Treatment Time</th>
<th>Sulfuric Acid</th>
<th>Formic Acid</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>54 ± 16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 min</td>
<td>22 ± 8</td>
<td>62 ± 8</td>
<td>82 ± 20</td>
</tr>
<tr>
<td>60 min</td>
<td>18 ± 5</td>
<td>75 ± 2</td>
<td>77 ± 5</td>
</tr>
<tr>
<td>120 min</td>
<td>21 ± 11</td>
<td>72 ± 17</td>
<td>87 ± 3</td>
</tr>
</tbody>
</table>

Table 20 – Averaged ultimate tensile strength values of all fibre treatments for PEDOT:PSS (Orgacon) wet spun fibres. Error represents one standard deviation for repeat measurements with \( n \geq 3 \) fibre replicates.

Although sulfuric acid treatments have been found to weaken the fibres, both formic acid and DMSO treatments did not decrease the ultimate tensile strength relative to untreated fibres. This demonstrates two different chemical treatments which improve the electrical
and electrochemical properties of the fibres, as well as the mechanical strengths of the fibres.

Table 21 shows average Young’s modulus values for all treatment types. As with the ultimate tensile strength values, lower values are observed for sulfuric acid-treated fibres. Formic acid-treated fibres show similar Young’s modulus values, within the level of error to untreated fibres. DMSO-treated fibres show increased values for Young’s modulus, showing a higher level of stiffness than for the other set of treated fibres. No trend is seen for increased treatment times, as per all other characterisation performed on these fibres, reinforcing that a 5 min treatment is sufficient.

<table>
<thead>
<tr>
<th>Treatment Time</th>
<th>Sulfuric Acid</th>
<th>Formic Acid</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>1,300 ± 700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 min</td>
<td>400 ± 300</td>
<td>1,000 ± 500</td>
<td>2,00 ± 20</td>
</tr>
<tr>
<td>60 min</td>
<td>700 ± 300</td>
<td>1,700 ± 600</td>
<td>1,600 ± 800</td>
</tr>
<tr>
<td>120 min</td>
<td>300 ± 80</td>
<td>1,500 ± 600</td>
<td>1,900 ± 600</td>
</tr>
</tbody>
</table>

Table 21 - Averaged Young’s modulus values of all fibre treatments for PEDOT:PSS (Orgacon) wet spun fibres. Performed with 0.1 N min⁻¹ ramp force. Error represents one standard deviation for repeat measurements with n ≥ 5 fibre replicates.
5.2.2 Fibres Spun from Clevios PH1000

5.2.2.1 Fibre Basic Properties

As received Clevios PH1000 PEDOT:PSS solutions (1 wt.%) could not be spun into fibres, due to insufficient polymer material in the solution to enable coagulation. Fibres were successfully spun from 2 wt.% solution, produced as described in section 2.5, and was this used for all further spinning work in this section.

Fibres were produced in two different sizes, controlled by using a different size needle and solution injection rate. Larger diameter fibres were produced using a 16 gauge inner diameter needle with an injection rate of 0.75 ml min\(^{-1}\), while thinner diameter fibres were produced with a 28 gauge inner diameter needle, and an injection rate of 0.05 ml min\(^{-1}\). Both fibre sizes could be produced in any desired length, and were extracted from the coagulation bath and air dried before being treated.

Treatment of these as spun fibres was then performed using the same treatments as described previously, namely 1.5 mol dm\(^{-3}\) sulfuric acid, 25.2 mol dm\(^{-3}\) formic acid, and neat DMSO, to allow comparison with Orgacon fibres. Each treatment was performed for only 5 min, based on the previous findings that times longer than 5 min presented no additional benefit.

Fibres were assigned codes, detailed in Table 22. The prefix “PH” was given to fibres to signify the use of Clevios PH1000 PEDOT:PSS, with thin fibres then having the letter “T”, followed by the code for the treatment, e.g. “S5” for a 5 min sulfuric acid treatment.

<table>
<thead>
<tr>
<th>Fibre Treatment</th>
<th>Thick Diameter Fibre Code</th>
<th>Thin Diameter Fibre Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated as-spun fibre</td>
<td>PHU</td>
<td>PHTU</td>
</tr>
<tr>
<td>5 min sulfuric acid</td>
<td>PHS5</td>
<td>PHTS5</td>
</tr>
<tr>
<td>5 min formic acid</td>
<td>PHF5</td>
<td>PHTF5</td>
</tr>
<tr>
<td>5 min DMSO</td>
<td>PHD5</td>
<td>PHTD5</td>
</tr>
</tbody>
</table>

Table 22 – Name codes for fibres spun from 2 wt.% PEDOT:PSS (PH1000) solutions and treated for 5 min.
Optical microscopy images were obtained to determine the diameters of the fibres produced, and the effect of each treatment on the fibre diameter. Averages of these are compared in Figure 66, and listed in Table 23.

![Figure 66 – Averaged fibre diameters for PHU and PHTU-based Clevios PH1000 PEDOT:PSS fibres. Error bars represent one standard deviation for repeat measurements with \( n \geq 10 \) fibre replicates.](image)

<table>
<thead>
<tr>
<th>Fibre Treatment</th>
<th>PHU-Based</th>
<th>PHTU-Based</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated as-spun fibre</td>
<td>75 ± 13</td>
<td>21 ± 2</td>
</tr>
<tr>
<td>5 min sulfuric acid</td>
<td>98 ± 29</td>
<td>26 ± 2</td>
</tr>
<tr>
<td>5 min formic acid</td>
<td>82 ± 24</td>
<td>20 ± 3</td>
</tr>
<tr>
<td>5 min DMSO</td>
<td>77 ± 7</td>
<td>21 ± 2</td>
</tr>
</tbody>
</table>

*Table 23 – Averaged fibre diameters for PHU and PHTU-based PEDOT:PSS (PH1000) fibres. Error represents one standard deviation for repeat measurements with \( n \geq 10 \) fibre replicates.*

It was found that the larger PHU-based fibres had diameters in the range of 75 - 98 µm; while the thinner PHTU-based fibres ranged from 20 - 26 µm. Sulfuric acid treatment caused a small increase in fibre diameter in both sizes of fibre, while formic acid and
DMSO treatments showed no effect on the diameter of the fibres. This result suggests that there may be some additional effect on the structure of the fibre during sulfuric acid treatment, potentially some residue left within the fibre, thus causing the diameter increase.

Electron microscope images were obtained for each fibre, with images for PHU thicker fibres shown in Figure 67, and images for thinner PHTU fibres shown in Figure 68. The left image of each shows the surface profile of the respective fibres along the fibre axis, with magnified core views of the fibre cross-section presented in the right images. Thinner fibres were found to have a smoother shape. This is attributed to the larger needle diameter and higher injection rate for thicker fibres causing slower coagulation than for the thinner fibres, thus allowing for more variation within the fibres during solidification.

No difference in surface profile, or core structure was observed after any of the treatments, for either set of fibres, as per Orgacon fibres. While the chemical treatments have been shown to remove PSS from the surface, and cause a re-ordering of the polymer, neither effect is visible using SEM.
Figure 67 – SEM images for PHU-based fibres. PHU (A), PHS5 (B), PHF5 (C), PHD5 (D). Fibre surface profiles are shown left, with magnified cross-section images right.
Figure 68 – SEM images for PHTU-based fibres. PHTU (A), PHTS5 (B), PHTF5 (C), PHTD5 (D). Fibre surface profiles are shown left, with magnified cross-section images right.
To confirm the effect of treatments on the fibres, XPS spectra were obtained for PHU and PHD5 fibres, to allow for comparison before and after treatment. Figure 69 shows full survey scans for both fibres. Highly similar spectra are observed for each, and as such, scans of specific elements were required for detailed analysis.

Figure 69 – XP spectra obtained for fibres PHU and PHD5, showing full survey scan emission.

Figure 70 shows XPS results for the 155 – 175 eV range, for PHU and PHD5 fibres. This range shows the emissions from the s2p electrons from sulfur present in the material. Two main peaks are observed, with the peak at 162 – 166 eV corresponding to sulfur present in the PEDOT, while the peak at 166 – 171 eV corresponds to sulfur present in the PSS. The spectra have been normalised to the intensity of the PEDOT sulfur peak, to allow visual comparison of the PSS sulfur before and after treatment with DMSO.
It can be seen that the emission produced by PSS sulfur decreases by 50% after treatment, showing a reduction in the amount of PSS present on the surface of the fibre. This corresponds with the results observed in literature for PEDOT:PSS treated with DMSO (158) (180) and other solvents (60) (159).

5.2.2.2 Fibre Raman Spectroscopy

Raman spectra for wet spun PH1000 PEDOT:PSS fibres are presented in Figure 71. It is observed that the treatments show no dramatic deviation in their Raman spectra for either
set of fibres. A difference can however be observed in the peaks in the region of 1460 to 1570 cm\(^{-1}\), where untreated fibres show higher intensities than treated fibres for all peaks in this region. Peaks in this range correspond to C=C asymmetric and symmetric stretching, as well as CH\(_2\) stretching \((118) (125) (155) (181)\). This decrease may be attributed to removal of PSS from the surface.

5.2.2.3 Fibre Electrochemical Properties – Cyclic Voltammetry

CV was performed on thin and thicker fibre types, using the same parameters and setup as for the Orgacon fibres in section 5.2.1.3. Figure 72 shows the results for all three 5 min treatments for both fibre diameters, as compared with their respective untreated fibre. As with the Orgacon fibres, a clear change in shape moving towards an ideal rectangular capacitor behaviour can be seen. This shows that the treatments are having a beneficial effect on the electrochemical properties and performance of PH1000 PEDOT:PSS fibres as well as Orgacon based fibres. No notable difference is seen between each fibre treatment, with all treatments resulting in similar shapes and currents throughout the voltammetry.

![Figure 72 – CV of fibres PHU, PHS5, PHF5, and PHD5 (left) and PHTU, PHTS5, PHTF5, and PHTD5 (right). Measured at 100 mV s\(^{-1}\) vs. Ag/AgCl electrode in 1 mol dm\(^{-3}\) aq. sodium sulfate vs. Ag/AgCl.](image)

Analysis of fibre performance as an electrode was carried out using CV with a potassium ferricyanide a redox couple, shown in Figure 73 and Figure 74 for PHU-based and PHTU-based fibres respectively.
Figure 73 – Second cycle CV of fibres PHU (A), PHS5 (B), PHF5 (C), PHD5 (D). Measured at varying scan rates vs. Ag/AgCl electrode in 10 mmol dm$^{-3}$ $K_3\text{[Fe(CN)]}_6$ with 0.1 mol dm$^{-3}$ KCl vs. Ag/AgCl.

Figure 74 – Second cycle CV of fibres PHTU (A), PHTS5 (B), PHTF5 (C), PHTD5 (D). Measured at varying scan rates vs. Ag/AgCl electrode in 10 mmol dm$^{-3}$ $K_3\text{[Fe(CN)]}_6$ with 0.1 mol dm$^{-3}$ KCl vs. Ag/AgCl.
All fibres show the expected redox peaks for the ferricyanide redox couple. Analysis of the peak data produced straight line graphs for plots of $\Delta E_p$ (V) vs. scan rate (mV s$^{-1}$). It is observed that peak separation increases linearly with increasing scan rate for all fibres; suggesting the system to be kinetically limited (as was found with Orgacon fibres), hence the greater peak separation effect observed at the highest scan rates. A comparison of $\Delta E_p$ (at 100 mV s$^{-1}$) for each fibre type is shown in Figure 75. Comparing treatments, the lowest peak separations are observed for sulfuric acid treated fibres, 0.07 V lower than formic acid and DMSO treatments. It is observed that the thicker, PHU-based fibres show lower peak separations than their respective PHTU-based fibres with values 0.4 V lower for untreated thick and an average of 0.1 V lower for treated thick fibres.

![Graph showing ΔEp at 100 mV s$^{-1}$ vs. Ag/AgCl electrode for all 5 min treatments of PHU and PHTU-based fibres.](image)

*Figure 75 – ΔEp at 100 mV s$^{-1}$ vs. Ag/AgCl electrode for all 5 min treatments of PHU and PHTU-based fibres.*

Table 24 shows ratios of peak currents for anodic and cathodic peaks for all PHU and PHTU-based fibres. It can be seen that all ratios are close to 1, showing a high level of chemical reversibility for this system within the timeframe of this experiment.
Table 24 – \( \frac{I_{pc}}{I_{pa}} \) peak current ratios for fibres PHU and PHTU-based fibres, (Measured at varying scan rates vs. Ag/AgCl electrode in 10 mmol dm\(^{-3}\) \( K_3[Fe(CN)]_6 \) with 0.1 mol dm\(^{-3}\) KCl vs. Ag/AgCl).

Figure 76 and Figure 77 show the effect of changing scan rate on the peak current. Currents for anodic and cathodic peaks are shown for PHU and PHTU-based fibres respectively. Peak currents were found to increase and decrease linearly vs. the square root of the scan rate used, again indicating a diffusion controlled system. As was found for fibres produced from Orgacon PEDOT:PSS, the system is believed to be quasi-reversible (171-173).

Figure 76 – Graphs of peak current vs. square root of scan rate PHU (A), PHS5 (B), PHF5 (C), PHD5 (D). Measured at varying scan rates vs. Ag/AgCl electrode in 10 mmol dm\(^{-3}\) \( K_3[Fe(CN)]_6 \) in 0.1 mol dm\(^{-3}\) KCl vs. Ag/AgCl.
Figure 77 – Graphs of peak current vs. square root of scan rate PTHU (A), PHTS5 (B), PHTF5 (C), PHTD5 (D). Measured at varying scan rates vs. Ag/AgCl electrode in 10 mmol dm$^{-3}$ K$_3$[Fe(CN)$_6$] in 0.1 mol dm$^{-3}$ KCl vs. Ag/AgCl.

Through analysis of the peak current data using the Randles Sevcik equation, the accessible electrochemical surface area of each fibre was determined. Surface area values were calculated, and compared with the values for a theoretical cylinder of the same 20 µm by 1 cm dimensions as the fibres used, presented in Table 25.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Cylindrical Surface Area (cm$^2$)</th>
<th>Electrochemical Surface Area (cm$^2$)</th>
<th>% Of Cylindrical</th>
<th>% Of Respective Untreated Fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHU</td>
<td>0.025</td>
<td>0.077</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>PHS5</td>
<td>0.025</td>
<td>0.095</td>
<td>380</td>
<td>120</td>
</tr>
<tr>
<td>PHF5</td>
<td>0.025</td>
<td>0.095</td>
<td>380</td>
<td>120</td>
</tr>
<tr>
<td>PHD5</td>
<td>0.025</td>
<td>0.096</td>
<td>38</td>
<td>130</td>
</tr>
<tr>
<td>PHTU</td>
<td>0.006</td>
<td>0.019</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>PHTS5</td>
<td>0.006</td>
<td>0.034</td>
<td>540</td>
<td>180</td>
</tr>
<tr>
<td>PHTF5</td>
<td>0.006</td>
<td>0.033</td>
<td>520</td>
<td>180</td>
</tr>
<tr>
<td>PHTD5</td>
<td>0.006</td>
<td>0.032</td>
<td>510</td>
<td>170</td>
</tr>
</tbody>
</table>

Table 25 – Comparison of electrochemically calculated accessible surface area values for all PHU and PHTU-based PEDOT:PSS (PH1000) fibres.
It can be seen that all fibres possess a surface area far greater than that of a theoretical cylinder of the same dimensions. This is attributed to two factors, firstly the rough surface of the fibres, and secondly the ability for the internal surface area of the fibres to be accessed due to small amounts of swelling from water uptake of the fibres when placed into aqueous electrochemistry solutions. The surface area of the fibres increased from 0.077 cm$^2$ to 0.095 - 0.096 cm$^2$ for all treatments of PHU-based fibres, and from 0.019 cm$^2$ to 0.032 – 0.034 cm$^2$ for all treatments of PHTU-based fibres. This correlates well with the other data obtained, showing an increase in electrochemical properties obtained after treatments are performed. No clear discrimination can be made between treatments based on their surface area changes.

While the thicker PHU-based fibres displayed a 23% increase in accessible surface area after treatment, the thinner PHTU-based fibres exhibited an increase of 79%. As with other results obtained for these thinner fibres, the larger surface to core ratio causes the treatments to have a larger effect on the fibres. Again no pronounced difference is observed between the treatments, but all have a highly beneficial effect on the fibres’ electrochemical surface areas.

5.2.2.4 Fibre Electrochemical Properties – Charge Discharge Cycling

Cyclic charge discharge measurements were performed on all PH1000 fibre types, at a current density of 0.5 A g$^{-1}$. As with previous charge discharge measurements, discharge times were determined from the gradient of the discharge curve in the upper 50% voltage range (11). Figure 78 shows example charge discharge times for each fibre type. It can be seen that all PH1000 fibres display longer total times than their Orgacon counterparts (section 5.2.1.4). No Orgacon fibre was found to have a total time longer than 80 s, whereas fibres spun from Clevios PH1000 PEDOT:PSS range between 100 and 130 s before reaching 0 V, thus PH1000 fibres therefore exhibit higher capacitance than Orgacon fibres.

No initial voltage jump or drop is observed upon charging or discharging untreated or treated fibres in this system, unlike previous Orgacon fibres. It is believed that these PH1000 fibres possess a higher electrical conductivity, decreasing the equivalent series resistance in the system.
Figure 78 – Example individual charge discharge plots for PHU and PHTU-based wet spun PEDOT:PSS (PH1000) fibres. Measured at 0.5 A g\(^{-1}\) vs. Ag/AgCl electrode in 1 mol dm\(^{-3}\) sodium sulfate vs. Ag/AgCl.

As shown in the averaged capacitance values in Figure 79 and detailed in Table 26, the values obtained for PHTU-based fibres were found to be on average 30% higher than those obtained previously for the thicker PHU-based fibres. This is likely due to the increased surface to core ratio created by a thinner fibre. This increased ratio means that a greater proportion of the fibre can be accessed by the electrolyte, thus increasing the mass specific capacity.

Figure 79 – Averaged charge discharge capacitance values for all PEDOT:PSS (PH1000) fibres. Measured at 0.5 A g\(^{-1}\) vs. Ag/AgCl electrode in 1 mol dm\(^{-3}\) sodium sulfate vs. Ag/AgCl. Error bars represent one standard deviation from repeat measurements with \(n \geq 5\) fibre replicates.
It can be seen that sulfuric acid treated fibres in fact show a decrease in the charge and discharge time relative to untreated fibres, while formic acid treated fibres show little or no change, and only DMSO treated fibres show an increase in their times, and therefore capacitance. The decrease in capacity observed for both sulfuric acid treated fibres is believed to be attributed to the remaining sulfuric acid residue left within the fibre. This residue increases the diameter and mass of the fibres, without providing additional charge storage capability, therefore reducing the mass specific capacitance of the fibre.

To provide a comparative measurement, fibres PHTU and PHD5 were tested using impedance spectroscopy and the results compared with those obtained through charge discharge cycling. The same exact fibres were employed for each measurement technique, to allow direct comparison of both techniques. Nyquist plots for both fibres are shown in Figure 80. Values were taken above the knee frequency for each fibre, where pseudocapacitive mechanisms are fully possible, and used to calculate the specific capacitance of each fibre. Specific capacitance values of 42.4 and 53.6 F g⁻¹ were obtained for fibres PHTU and PHTD5 respectively, and are compared against the values obtained through charge discharge (at 0.5 A g⁻¹) in Figure 81. It can be seen that similar values are obtained for both fibres, confirming the ability to use impedance spectroscopy to analyse fibres such as these. However, as charge discharge measurements allow for control over parameters such as the full voltage range applied, as well as the current density, they were the method of choice for measurements of capacitance within this work.

Table 26 – Averaged charge discharge capacitance values for all PEDOT:PSS (PH1000) fibres. Measured at 0.5 A g⁻¹ vs. Ag/AgCl electrode in 1 mol dm⁻³ sodium sulfate vs. Ag/AgCl. Error represents one standard deviation from repeat measurements with n ≥ 5 fibre replicates.

<table>
<thead>
<tr>
<th>Fibre Treatment</th>
<th>PHU-Based Fibre</th>
<th>PHTU-Based Fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated as-spun fibre</td>
<td>26.8 ± 3.0</td>
<td>34.5 ± 0.5</td>
</tr>
<tr>
<td>5 min sulfuric acid</td>
<td>18.8 ± 1.6</td>
<td>27.4 ± 2.4</td>
</tr>
<tr>
<td>5 min formic acid</td>
<td>29.1 ± 1.9</td>
<td>37.3 ± 4.1</td>
</tr>
<tr>
<td>5 min DMSO</td>
<td>38.1 ± 8.4</td>
<td>49.7 ± 3.8</td>
</tr>
</tbody>
</table>

Capacitance (F g⁻¹)
Figure 80 – Nyquist plots obtained through impedance spectra for fibres PHTU and PHTD5. Measured between 0.01 and 100,000 Hz, with a perturbation voltage of 10 mV in 1 mol dm$^{-3}$ sodium sulfate vs. Ag/AgCl electrode as a three-electrode system.

Figure 81 – Specific capacitance comparison for PHTU and PHTD5 fibres determined through cyclic charge discharged and impedance techniques. Error bars represent one standard deviation from repeat measurements with n ≥ 5 fibre replicates.
5.2.2.5 Fibre Electrical Conductivity

Figure 82 shows averaged four-point electrical conductivity measurements for all PH1000 PEDOT:PSS fibres, with details given in Table 27. It can be seen that the fibres display higher conductivities than their respective Orgacon counterparts (section 5.2.1.5). Untreated PH1000 fibres displayed conductivities similar to those of treated Orgacon fibres, and treated PH1000 fibres show a large increase upon these. A doubling to tripling of electrical conductivity for PHU-based fibres is observed, and a 6-fold increase is achieved for PHTU-based fibres through chemical treatment alone.

![Figure 82 – Averaged electrical conductivity values for all PEDOT:PSS (PH1000) fibres. Error bars represent one standard deviation from repeat measurements with n ≥ 5 fibre replicates.](image)

<table>
<thead>
<tr>
<th>Fibre Treatment</th>
<th>Conductivity (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PHU-Based Fibre</td>
</tr>
<tr>
<td>Untreated as-spun fibre</td>
<td>130 ± 11</td>
</tr>
<tr>
<td>5 min sulfuric acid</td>
<td>420 ± 50</td>
</tr>
<tr>
<td>5 min formic acid</td>
<td>300 ± 30</td>
</tr>
<tr>
<td>5 min DMSO</td>
<td>320 ± 35</td>
</tr>
</tbody>
</table>

*Table 27 – Averaged electrical conductivity values for all PEDOT:PSS (PH1000) fibres. Error represents one standard deviation from repeat measurements with n ≥ 5 fibre replicates.*
5.2.2.6 Fibre Mechanical Properties

Example stress strain curves obtained through DMA are presented in Figure 83. It can be seen that the ultimate tensile strengths are overall lower than those obtained for Orgacon wet spun fibres presented previously (section 5.2.1.6). Similar levels of breaking strain are seen, with fibres typically extending in the region of 3 to 4 % before breaking.

![Figure 83 – Example stress-strain plots for PHU and PHTU-based PEDOT:PSS (PH1000) wet spun fibre.](image)

Averaged results are given in Figure 84, with ultimate tensile strength and Young’s modulus values presented in Table 28. As with previous mechanical strength measurements, sulfuric acid treated fibres were observed to have the lowest strengths. For these PH1000 fibres it was found that formic acid and DMSO treatments did not reduce the mechanical strengths of the fibres. This result further suggests that the sulfuric acid treated fibres are being affected by residual acid remaining within the fibre, which the other formic acid and DMSO treated fibres do not suffer from, as their treatment chemicals fully evaporate without leaving any residue. It was also observed that thinner fibres display higher ultimate tensile strength values than the thicker PHU-based fibres. It is possible that the slower injection rate used for thinner fibres (0.05 rather than 0.75 ml min⁻¹), coupled with the smaller needle diameter employed (0.159 vs. 1.19 mm inner diameter) allowed for slower coagulation and formation of the fibres, producing greater alignment of the polymer chains within the fibres.

Both thick and thin fibre sets all show a decrease in Young’s modulus for all fibre treatments, compared with untreated fibres. Higher modulus values were obtained for thin PHTU-based fibres than for thick PHU-based fibres, which is in agreement with the higher
values obtained for thin fibres for all other testing observed previously. Sulfuric acid-treated PHU fibres show notably lower modulus values than other PHU-based fibres.

Figure 84 – Averaged mechanical strengths obtained by dynamic mechanical analysis for PHU and PHTU-based PEDOT:PSS (PH1000) wet spun fibres. Error bars represent one standard deviation from repeat measurements with \( n \geq 5 \) fibre replicates.

<table>
<thead>
<tr>
<th>Fibre Treatment</th>
<th>PHU-Based Fibre</th>
<th>PHTU-Based Fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ultimate Tensile Strength (MPa)</td>
<td>Young’s Modulus (MPa)</td>
</tr>
<tr>
<td>Untreated as spun fibre</td>
<td>33 ± 2</td>
<td>1,700 ± 400</td>
</tr>
<tr>
<td>5 min sulfuric acid</td>
<td>10 ± 3</td>
<td>150 ± 80</td>
</tr>
<tr>
<td>5 min formic acid</td>
<td>50 ± 3</td>
<td>690 ± 72</td>
</tr>
<tr>
<td>5 min DMSO</td>
<td>48 ± 8</td>
<td>1,100 ± 500</td>
</tr>
</tbody>
</table>

Table 28 – Averaged mechanical strengths obtained by dynamic mechanical analysis for PHU and PHTU-based PEDOT:PSS (PH1000) wet spun fibres. Error represents one standard deviation from repeat measurements with \( n \geq 5 \) fibre replicates.
5.2.2.7 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was used to investigate the treatment’s effect on thick PHU-based fibres (Figure 85), and thinner PHTU-based fibres (Figure 86). Fibres treated with sulfuric acid, PHS5 and PHTS5, showed a clear difference compared with all other fibres which show minimal difference relative to untreated fibres. Sulfuric acid fibres showed a larger mass drop at low temperatures below 100°C, indicative of higher water content remaining within the fibre. A second mass loss is seen between 100 and 200 °C, which is not observed in any other treatment. This indicates some sulfuric acid residue remaining, agreeing with the reduced strength observed in DMA results. The combination of these results reinforces that sulfuric acid treatments leave residue within the fibre, which is the cause of the dramatically reduced strength, not observed in other fibres.

![TGA plots for thick PHU-based wet spun PEDOT:PSS (PH1000) fibres PHU, PHS5, PHF5, and PHD5 with 10 °C min⁻¹ ramp rate in air.](image-url)
Both sets of fibres show mass drops in the same temperature regions, with all mass lost at a little over 500°C. Although the thinner fibres should show the largest overall change from the treatments, due to their smaller size giving them a larger surface to core ratio, it is still not possible to differentiate between untreated fibres and formic acid or DMSO treated fibres in this manner. This is still not unexpected, as the removal of PSS material is unlikely to generate enough of a change in the burn temperature weight change to be detected through TGA techniques.

5.3 Summary

In this chapter, three variants of PEDOT:PSS fibres treated with sulfuric acid, formic acid, and DMSO have been produced. These include fibres produced from two different sources of PEDOT:PSS, as well as a comparison of two different fibre diameters.

Analysis of the effect of these treatments on PEDOT:PSS fibres has shown the treatments to be effective in modifying many of the properties of the fibres. For Orgacon PEDOT:PSS fibres an increase in all measured properties was observed for formic acid and DMSO treatments, while sulfuric acid showed an increase in all properties apart from tensile strengths. Further analysis of different treatment exposure times showed that 5 min treatments are sufficient, with no further improvement being noted after this time.
Comparison of PEDOT:PSS sources including Orgacon and Clevios branded materials showed Clevios to produce fibres with notably higher electrical conductivities as well as charge storage capacitances. Comparison of differing Clevios fibre diameters shows thinner PEDOT:PSS (20 µm) fibres to possess superior electrochemical, electrical, and mechanical properties when compared with thicker (75 µm) fibres produced from the same material. These thinner diameter fibres also show an increased response to treatments, showing a far larger increase in electrical conductivity, and charge storage capacitance, although a decrease in mechanical strengths were observed. While these results have demonstrated notable increases in multiple properties, they are however still lower than results obtained through other treatments, such as 2,804 S cm\(^{-1}\) obtained through treatment with ethylene glycol (62). As discussed, the treatments are believed to be most effective on the surface of the fibres, which is likely the cause of the greater increases in properties observed in similar treatments on thin films (59) (128) (159). The mechanical properties obtained are competitive with those obtained for other PEDOT:PSS fibres produced through wet spinning (62). Ultimate tensile strength values of up to 140 MPa were obtained from 20 µm Clevios PH1000 fibres, treated with DMSO for 5 min (PHTD5), these similar to other PEDOT:PSS-only fibres, measured at 140 MPa. (74). PEDOT:PSS fibres containing additional SWCNTs were found to have higher values, up to 200 MPa for SWCNTs employing SDS (30), and 250 MPa for PEG-functionalised SWCNTs (75). Capacitance values of up to 50 F g\(^{-1}\) were obtained, also from PHTD5 fibres, higher than PEDOT:PSS fibres containing PEG-functionalised SWCNTs measured at 35 F g\(^{-1}\) (75), but lower than the 69 F g\(^{-1}\) obtained from PEDOT:PSS-SWCNT fibres (30). PEDOT:PSS-Polypyrrole composites were found to have a specific capacitance of 200 F g\(^{-1}\), showing the potential benefits of multi-polymer systems (110). PEDOT/MnO\(_2\)/MWCNT composites were found to have a capacitance of up to 148 F g\(^{-1}\) (182), demonstrating the potential for capacity improvement using materials such as manganese dioxide.

Using these results, it is possible to say that a fibre produced from Clevios PH1000 with a 20 µm diameter, and treated with DMSO will produce the fibre most suited for use in electrochemical capacitor devices. These fibres would possess the highest charge storage capability, with the highest balance of electrical conductivity and mechanical strengths.
6 Formation and Protection of Manganese Dioxide Coatings

6.1 Introduction

Manganese dioxide is a promising material for energy storage devices, seeing widespread use in a range of different devices, such as batteries and capacitors (183-185). Manganese dioxide stores charge through pseudocapacitance (186-187), utilising electron transfer to vary the oxidation state of manganese ions, coupled and balanced with insertion and extraction of cations from the electrolyte into the manganese dioxide structure. A simplified equation to demonstrate this process is given below:

\[ \text{Mn}^{IV}O_2 + xe^- + xH^+ \rightleftharpoons H_x\text{Mn}^{III}_x\text{Mn}^{IV}_{1-x}O_2 \]

*Equation 9 – Simplified equation for manganese dioxide pseudocapacitive energy storage mechanism.*

Through these processes, manganese dioxide is able to store large amounts of charge, resulting in a high capacitance, and thus a high charge density, with a theoretical maximum capacitance in the order of 1,300 F g⁻¹ (186) (188). Multiple forms and structures of manganese oxides are possible with manganese dioxide (Figure 87), alone possessing a variety of forms including α, δ, γ, and β. However, the focus of this work is on producing manganese dioxide incorporated on, or within, fibres, with the aim of increasing their specific capacitance.

*Figure 87 – Example SEM image of an MnO₂ film employed as an electrode (189).*
While manganese dioxide is an excellent choice of material for electrical energy storage, it cannot function and be used alone, due to poor electrical conductivity (in the order of $10^{-5}$ S cm$^{-1}$). A conducting material is therefore required to act as a current collector, to supply and remove electrons from the manganese material during charge storage. In this chapter, PEDOT:PSS fibres are to be employed as this conducting material. Manganese dioxide will be incorporated within, or coated on the fibres with the aim of producing flexible fibre capacitor electrodes with capacitances far exceeding those of PEDOT:PSS conducting fibre electrodes alone.

Formation of manganese dioxide will be investigated using several methods. Chemical reduction of manganese compounds will be carried out by dipping PEDOT:PSS fibres into solutions containing manganese. This method has been shown previously to enable quick and simple production of manganese dioxide on PEDOT:PSS materials (190). Electrochemical deposition from aqueous solutions containing manganese compounds such as manganese acetate (191-193), or manganese sulfate (194-195) will also be carried out. Different concentrations of solution, deposition voltages, and deposition times will be investigated to achieve the highest capacitance in the coated fibres.

These fibres will be characterised and their charge storage capability assessed. Additional layer(s) of conducting polymers will be coated on the outside of fibres, following the addition of manganese dioxide. These conductive coatings will serve a dual purpose, to physically protect the manganese dioxide from being leached into the electrolyte or otherwise removed from the fibre, and also to provide further conductivity to the manganese dioxide coatings. Different coating methods and materials have been investigated, including a combination of multiple layers and multiple materials to achieve the highest initial capacity and capacity retention. Figure 88 below shows a fibre cross sectional diagram of the proposed composite fibres, displaying the core PEDOT:PSS fibre, MnO$_2$ layer, and outer conducting polymer layer(s).
Figure 88 – Cross sectional diagram of multi-component multi-layer fibre. Inner PEDOT:PSS fibre, MnO₂ middle layer, and further conductive polymer layer(s) are shown.

6.2 Results - Chemical Deposition from Solutions of KMnO₄ on Orgacon Fibres

6.2.1 Dip Immersion into KMnO₄

Immersion of PHD5 fibres in solutions of potassium permanganate at concentrations of 10 mmol dm⁻³ was found to quickly destroy the PEDOT:PSS fibres. Immersion in solutions of lower concentration was possible, without destroying the fibres. It was found that fibres immersed in 1 mmol dm⁻³ solutions did not disintegrate during the initial treatment, but were sufficiently weakened to the point where drying and testing of the fibres was not possible, and as such only concentrations lower than 1 mol dm⁻³ were used for further testing.

6.2.2 Cyclic Voltammetry

Figure 89 shows CV results of PHD5 fibres immersed in 100 µmol dm⁻³ potassium permanganate for 1 and 10 min, and for 1 min and 1 h in 10 µmol dm⁻³ potassium permanganate. It can be seen that higher concentrations, and longer immersion times both produce fibres with lower currents, and poorer CV profiles than those for PHD5 fibres without permanganate immersion. The highest capacitance of an immersed fibre was obtained from 1 min 10 µmol dm⁻³ immersion; however, this is still a notably poorer performance than without immersion. Longer immersion times were found to deteriorate fibre performance further. This degradation is attributed to the strong oxidising nature of permanganate, which has been demonstrated to oxidise organic molecules (196), including PEDOT (197), as evident in the fibre destruction and weakening described previously.
Figure 89 – CV of PHD5 PEDOT:PSS (PH1000) fibres after immersion in 
KMnO₄ solutions of various concentrations and durations. Measured at 100 mV 
$s^{-1}$ vs. Ag/AgCl electrode in 1 mol dm$^{-3}$ sodium sulfate.

6.2.3 Charge Discharge Cycling

It was found that no combination of concentration and immersion time produced a 
beneficial effect on the electrochemical properties of the fibres as measured by CV. Charge 
discharge measurements were taken to confirm these results, with all immersed fibres 
storing less charge than fibres before immersion. There is a clear decrease in capacitance 
observed after immersion of the PHD5 fibres into KMnO₄, which is further decreased with 
longer immersion times.

<table>
<thead>
<tr>
<th>Fibre Treatment</th>
<th>Capacitance (F g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHD5</td>
<td>38.1 ± 1.6</td>
</tr>
<tr>
<td>1 min 1 mmol dm$^{-3}$ KMnO₄</td>
<td>13.1 ± 9.2</td>
</tr>
<tr>
<td>10 min 1 mmol dm$^{-3}$ KMnO₄</td>
<td>8.5 ± 3.1</td>
</tr>
</tbody>
</table>

Table 29 – Comparison of charge discharge capacitance values for spun 
PEDOT:PSS (PH1000) fibres before and after KMnO₄ chemical deposition. 
Error represents one standard deviation from repeat measurements with $n \geq 3$ 
fibre replicates.

Following these results, it was decided that chemical formation of manganese oxides 
through immersion in KMnO₄ solutions was not a viable method for this application. 
Hence, electrochemical deposition was therefore investigated.
6.3 Electrochemical Deposition of Manganese Oxides on Orgacon Fibres

Electrochemical deposition of manganese oxides was investigated, as it was believed to offer a less detrimental method of oxide formation, without damaging the PEDOT:PSS fibres. Initial experiments were carried out on D5 fibres (Orgacon, treated with DMSO). Manganese(II) acetate, and the voltage range employed (0.7 – 1.2 V) were chosen based on successes reported previously (191-193). Performance of deposition products was analysed via CV and charge discharge cycling. Other analysis was conducted using Raman spectroscopy and SEM imaging to analyse the composition of the products formed.

In the CV shown in Figure 90, it can be clearly seen that an increase in current compared with pre-deposition fibres is obtained for a deposition voltage of 0.7 V, with further increases observed from electrodeposition at 1.0 V. When the voltage is increased however to 1.2 V, a large decrease in current response is observed. This is attributed to a thick and non-porous oxide layer on the outside of the fibre, preventing capacitive mechanisms from occurring. From these results, it was decided that 1.0 V presents the optimal deposition voltage for this system.

![Figure 90 – CV for electrodepositions from 0.02 mol dm$^{-3}$ manganese(II) acetate using 10 min deposition times at 0.7, 1.0, and 1.2 V deposited on PEDOT:PSS (Orgacon) fibres treated for 5 min with DMSO (D5) before electrodeposition. Measured at 100 mV s$^{-1}$ vs. Ag/AgCl electrode in 1 mol dm$^{-3}$ sodium sulfate.](image-url)
To further investigate the effects of deposition voltage on the oxide layer produced, charge discharge measurements were performed on fibres (Figure 91). As seen in the CV in Figure 90, an increase in capacitance is seen with increasing voltage, until 1.0 V, therefore MnO$_2$ electrodeposition voltages of 0.7, 0.8 and 1.0 V were employed. All deposition times showed standard voltage shapes during charge and discharge, although a small level of voltage drop at the beginning of the discharge cycles was observed in each deposition time. Increases in capacity from the initial ~30 F g$^{-1}$ for D5 fibres to 76, 100, and 115 F g$^{-1}$ for deposition voltages of 0.7, 0.8 and 1.0 V respectively are seen (Figure 92). Depositions performed at 1.2 V, however, were found to render the fibre completely non-functional for charge discharge measurements: upon charging, a voltage above the cut-off of 0.8 V was recorded, and a voltage below 0.0 V was recorded immediately after beginning the discharge cycle. This is attributed to the formation of a non-conductive layer which is acting to block electron transfer between the PEDOT:PSS fibre core and the electrolyte. This causes a rapid charge build up within the fibre, and destroys the fibre’s capability to act as a capacitor.

*Figure 91 – Example charge discharge measurements for electrodeposition from 0.02 mol dm$^{-3}$ manganese(II) acetate using 30 min deposition times at 0.7, 0.8, and 1.0 V, deposited on PEDOT:PSS (Orgacon) fibres treated with 5 min DMSO before electrodeposition. Measured at a current density of 0.5 A g$^{-1}$, vs. Ag/AgCl electrode in 1 mol dm$^{-3}$ sodium sulfate.*
6.3.1 Electrodeposition Time Determination

As reported above, 1.0 V was found to be the best voltage to use for electrodepositions from manganese(II) acetate and this voltage was employed for all further depositions. To analyse the best deposition time to be used, a range of depositions were performed, with times of up to 2 h.

Figure 93 shows the results of charge discharge experiments on fibres subjected to these deposition times. A clear increase in the capacity of charge stored can be seen with increasing deposition time. The largest increase was found when moving from 10 to 20 min depositions, with continual increases in capacitance up to 120 min deposition. Deposition times above 30 min however produced fibres which suffered from total fibre failure, where many fibres would fail to charge, signified by black bars in Figure 93.

The same charge discharge results were observed for all ‘failing’ fibres, where charging cycles would immediately build up charge, producing voltages greater than 0.8 V, and discharge cycles would immediately drop to voltages less than 0.0 V, as was seen for deposition voltages above 1.0 V. Measurement of multiple fibres enabled the recording of the results presented in Figure 93, however most of the fibres produced at deposition times of 30 min or longer suffered from this issue. Although higher capacitances can be achieved
with longer deposition times, 20 min deposition times were found to be the best compromise between capacity and fibre reproducibility.

![Graph showing capacity vs. deposition time](image)

*Figure 93 – Charge discharge measurements for electrodepositions from 0.02 mol dm$^{-3}$ manganese(II) acetate using 1.0 V deposition voltages for times between 10 and 120 min, deposited on PEDOT:PSS (Orgacon) fibres treated with 5 min DMSO before electrodeposition. Measured at a current density of 0.5 A g$^{-1}$, vs. Ag/AgCl electrode in 1 mol dm$^{-3}$ sodium sulfate.*

### 6.3.2 Identification of Manganese Oxide Form Via Electrodeposition

#### 6.3.2.1 Raman Spectral Analysis

Analysis of the oxides produced was undertaken using Raman spectroscopy, to identify the form of manganese oxide(s) produced from electrodeposition. Raman spectra were taken of fibres after electrodeposition for 20 min at 0.7, 1.0 and 1.2 V using a 532 nm laser. Figure 94 shows the Raman spectra of these three fibres; wavenumbers above 1,500 cm$^{-1}$ are not shown as no further peaks are observed outside of the region shown. It can clearly be seen that all peaks attributed to PEDOT:PSS have been removed, due to the thickness of the manganese oxide coating being sufficient to block any laser photons from interacting with the PEDOT:PSS material. Four key peaks are observed, a weak peak at 390 cm$^{-1}$, with intense sharp peaks present at 506, 558, and a broader intense peak in the region of 628 cm$^{-1}$. The peak at 506 cm$^{-1}$ is attributed to deformation modes of the Mn-O bonds within Mn-O-Mn within the MnO$_2$ octahedral lattice, while the peaks at 558 and 628 cm$^{-1}$ are
attributed to stretching modes of Mn-O bonds within MnO₆ octahedra (120). The peaks observed correspond well with literature values for those of γ-MnO₂ materials (198) and (199). From these results, it is believed that γ-MnO₂ has successfully been produced on the fibres.

Figure 94 – Raman spectra using 532 nm laser for fibre D5, and manganese oxides formed from electrodepositions at 0.7, 1.0 and 1.2 V from manganese(II) acetate to D5 fibres.

6.3.2.2 Electron Microscope Images

Electron microscope images obtained for fibres after electrodeposition for 20 min at 0.7, 1.0 and 1.2 V are shown in Figure 95. It can be seen that a layer of manganese dioxide is formed on the surface of the fibre, acting as an outer shell coating. Breaks, chips and fractures are observed in the MnO₂ coating, suggesting that it is brittle, and not as flexible as the PEDOT:PSS fibre core. This suggests that a protective polymer coating may be required on the outside of the fibre.
EDX elemental mapping was carried out to analyse the distribution of manganese throughout the fibre and the coating, and is shown in Figure 96. The images clearly show the distribution of manganese through the coatings, shown in yellow, with original SEM images shown in greyscale. Much greater manganese coverage can be seen on the fibre surface compared to the PEDOT:PSS core suggesting little manganese growth/transport into the polymer, but high amounts being grown on the surface. The third set of images show the threshold where the fibre entered the electrolyte during electrodeposition, shown with a black line. The area above shows no deposition, while the area below shows manganese electrodeposition.
Figure 96 – EDX element maps of D5 fibres spun from PEDOT:PSS (Orgacon) after 20 min 1.0 V electrodeposition from 0.02 mol dm$^{-3}$ manganese(II) acetate. Greyscale images (left) show original SEM images, with yellow element maps (right) showing manganese distribution.

6.3.3 Capacity Retention Analysis

6.3.3.1 Manganese Charge Discharge

It has been found that deposition times of 20 min or below and voltages of 1.0 V or below produce fibres with the best compromise of initial capacitance and fibre reliability. The capacity retention of the fibres produced at each voltage was also measured (Figure 97).
It is apparent that all fibres analysed suffer from poor capacity retention when subjected to repeated charge discharge cycling at 0.5 A g\(^{-1}\). After 250 cycles, the fibres have lost the majority of their original capacitance. Capacity losses are summarised in Table 30.

<table>
<thead>
<tr>
<th>Fibre Deposition Parameters</th>
<th>Initial Capacity (F g(^{-1}))</th>
<th>Capacity After 250 Cycles (F g(^{-1}))</th>
<th>Capacity Retained After 250 Cycles (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7 V – 20 min</td>
<td>89.7</td>
<td>35.6</td>
<td>40.7</td>
</tr>
<tr>
<td>0.8 V – 20 min</td>
<td>120.5</td>
<td>35.6</td>
<td>29.5</td>
</tr>
<tr>
<td>1.0 V – 20 min</td>
<td>138.9</td>
<td>30.2</td>
<td>21.7</td>
</tr>
</tbody>
</table>

Table 30 – Initial and final capacitance values after 250 cycles for D5 fibres with 20 min manganese(II) acetate electrodepositions at 0.7, 0.8, and 1.0 V. Measured at 0.5 A g\(^{-1}\) between 0.0 and 0.8 V vs. Ag/AgCl electrode in 1 mol dm\(^{-3}\) sodium sulfate.

6.3.3.2 Conducting Polymer Coatings

To improve this capacity retention, with the aim of retaining as much of the initial capacity as possible after as many cycles as possible, layers of conducting polymer were deposited on the outside of the PEDOT:PSS-MnO\(_2\) fibres. Both sources of PEDOT:PSS (Orgacon
and Clevios PH1000) were tested using dip coating and employing varied coating times, polymer concentrations, and coating cycles. Electrochemical deposition of polypyrrole was also tested. In addition to protecting the MnO$_2$, these polymers may have a secondary benefit of potentially increasing the total capacity of the fibres. The addition of the polymers can provide extra conductivity to the manganese matrix, as well as storing charge themselves through pseudocapacitance.

The results shown (Figure 98) show a D5 fibre treated with a 20 min 1.0 V electrodeposition of MnO$_2$, as well as fibres with additional conducting polymer coatings. Chemical coatings of 1 wt.% Orgacon and PH1000, with an immersion time of 2 min each are shown, as well as a 3 min 0.8 V electrodeposition of polypyrrole (PPy). It was found that all coatings improved the capacity retention of the fibres. The best retention came from using only a PPy deposition directly on to the MnO$_2$ layer. Combinations of PEDOT:PSS dip followed by a polypyrrole deposition coating were also investigated (not shown), but were found to offer no notable benefit over a polypyrrole coating alone.

![Graph showing capacity retention of coated PEDOT:PSS-MnO$_2$ (Orgacon) fibres](image)

*Figure 98 – Capacity retention of coated PEDOT:PSS-MnO$_2$ (Orgacon) fibres. Measured at 0.5 A g$^{-1}$ between 0.0 and 0.8 V vs. Ag/AgCl electrode in 1 mol dm$^{-3}$ sodium sulfate.*

To further improve upon these results, the same processes were applied to fibres spun from PH1000 PEDOT:PSS to determine if the superior properties of the polymer translate to increased overall retention properties.
6.4 Electrochemical Deposition of Manganese Oxides on Clevios PH1000 Fibres

Fibres spun from Clevios PH1000 and treated with 5 min DMSO (PHD5) were demonstrated to exhibit multiple improved properties over the respective Orgacon spun fibres. Electrodeposition of manganese oxides on to these fibres was expected to further boost their performance, potentially showing greater results than those obtained thus far for Orgacon fibres.

6.4.1 Electrodeposition Voltage Determination

A deposition time of 20 min at a voltage of 1.0 V produced the highest specific capacitance in Orgacon fibres (without encountering fibre failure); as such these conditions were tested first on PHD5 fibres. It was found that a 20 min deposition produced the same issue as was observed in Orgacon fibres treated for 30 min or longer. While some fibres successfully functioned with improved capacity, the majority failed during charge/discharge cycles in the same manner as previously described. Because of this the deposition time was reduced to 10 min, which was found to produce successful fibres.

6.4.2 Electrodeposition Time Determination

Electrodeposition of manganese oxide for 10 min on PHD5 produced fibres with an initial capacity of 102 F g⁻¹, which was lower than Orgacon fibres from 20 min deposition, (initial capacity of 139 F g⁻¹). This decrease in capacitance was unexpected, as fibres spun from PH1000 displayed far higher conductivity, and higher/similar capacitance than fibres spun from Orgacon PEDOT:PSS. However, the larger diameter of the PH1000 fibres is believed to reduce the specific capacitance because of the extra weight of this fibre. Fibres spun from PH1000 have average diameters of 90 µm while Orgacon spun fibres are closer to 40 µm. This twofold increase in diameter would cause a ~ 500 % increase in the weight per length of the fibre.

To combat this, electrodepositions were performed on PHTD5 fibres (average diameter 20 µm) using the same conditions as previously described (0.02 mol dm⁻³ manganese(II) acetate at 1.0 V). Analysis of varying deposition times was performed (Figure 99). 5 min depositions proved to be the optimal time; shorter times yielded lower capacitances, while depositions for longer than 5 min produced fibres which failed during charge/discharge cycling. 5 min depositions were therefore used for all further work in this section.
Figure 99 – Capacitance of PHTD5 fibres after electrodeposition of manganese dioxide from 0.02 mol dm$^{-3}$ Mn(II) acetate solutions at 1.0 V vs. Ag/AgCl for varying deposition times. Measured at 0.5 A g$^{-1}$ between 0.0 and 0.8 V vs. Ag/AgCl electrode in 1 mol dm$^{-3}$ sodium sulfate.

Figure 100 – CV results of a PHTD5 fibre compared with a PHTD5 fibre after 5 min 1.0 V deposition from 0.02 mol dm$^{-3}$ Mn(II) acetate vs. Ag/AgCl. Measured at 100 mV s$^{-1}$ vs. Ag/AgCl electrode in 1 mol dm$^{-3}$ sodium sulfate.

As shown in Figure 100, CV comparing PHTD5 fibres before and after the 5 min deposition show a large increase in the area of the voltammogram, corresponding to the
increased capacitance. The shape shows a larger deviation from that of an ideal rectangle, likely due to the poor electrical conductivity of the manganese dioxide, contributing to slower reaction kinetics at the fast scan rate of 100 mV s$^{-1}$.

### 6.4.3 Identification of Manganese Oxide Form

Raman spectra of electrodepositions on PHTD5 fibres were obtained, and compared with spectra obtained for 20 min 1.0 V depositions on Orgacon fibre D5 (Figure 101). The spectrum observed for this deposition system is very similar to that observed previously for electrodepositions performed on Orgacon fibres. Peaks are present at 628, 558, 506, and 306 cm$^{-1}$. As such, it is again believed that $\gamma$-MnO$_2$ manganese dioxide has been produced (198-199).

![Figure 101 – Raman spectra of manganese oxide electrodepositions on PH1000 fibre PHTD5, and Orgacon fibre D5. Spectra are normalised around the peak at 627 cm$^{-1}$.](image)

Electron microscope images of PHTD5 fibres with 5 min 1.0 V electrodepositions were obtained, clearly showing the manganese layer formed on the outside of the fibre, shown in Figure 102. Fibre surface images suggest that the layer formed is brittle, due to fracturing seen in image A. The surface showed a smoother profile than that formed on Orgacon fibres (shown previously in Figure 96). This is possibly a function of quicker growth due to the higher electrical conductivity of the PH1000-based fibres.
6.4.3.1 Thermogravimetric Analysis

Figure 103 shows TGA traces for a PHTD5 fibre, and a PHTD5 fibre after a 5 min electrodeposition at 1.0 V from 0.02 mol dm$^{-3}$ manganese(II) acetate. Comparing the two fibres, it can be seen that the fibre with MnO$_2$ deposited shows a larger initial drop, suggesting that there may be water remaining within the fibre after electrodeposition. As the fibre is completely coated in manganese dioxide, this coating traps water within the fibre, inhibiting complete evaporation and drying of the inner fibre. Further mass loss continues to be seen, until 660 °C, after which no further loss of mass is seen. This yields a remaining mass of 59 % of the initial. 4.5 % remaining mass is observed for untreated PHTD5 fibres, therefore 54.5 % of the mass is attributed to the manganese dioxide formed during the electrodeposition, as almost all PEDOT:PSS material has been shown to have been lost by this temperature.
Figure 103 – TGA plots comparing PHTD5 PEDOT:PSS (PH1000) fibres with and without a 5 min 1.0 V electrodeposition from 0.02 mol dm$^{-3}$ manganese(II) acetate. 10 °C min$^{-1}$ ramp rate in air.

A capacitance of 213 F g$^{-1}$ was found for fibres after this 5 min deposition, with 38 F g$^{-1}$ being contributed from the PHTD5 fibre. The remaining 175 F g$^{-1}$ was therefore contributed from the manganese dioxide layer coating the fibre. This compares well with previously reported manganese dioxide materials, although still well below the theoretical maximum (200-202).

### 6.4.4 Capacity Retention Enhancement

In order to improve the capacitance retention of PHTD5 fibres with electrodeposition coatings, a conducting polymer coating of PPy was electrodeposited on top of the MnO$_2$ layer at 0.8 V for 3 min. Figure 104 shows Raman spectra at each stage of the two stage electrodeposition on a PHTD5 fibre. The bottom spectrum shows the peaks associated with PEDOT:PSS from the PHTD5 fibre, the middle shows the spectrum of the same fibre following MnO$_2$ electrodeposition, and the top spectrum is following a polypyrrole electrodeposition.
Figure 104 – Raman spectra using 532 nm laser of a PHTD5 fibre after each stage of formation. Showing the PHTD5 fibre, after 5 min 1.0 V MnO$_2$ electrodeposition, and after a following 3 min 0.8 V polypyrrole electrodeposition.

Each successive coating completely covers the fibre, since no peaks from the material in the layer beneath can be seen. For example, when analysing the fibre after MnO$_2$ electrodeposition, none of the PEDOT:PSS peaks observed in the PHTD5 fibre spectrum are present. The spectrum confirms that the outer layer is polypyrrole (203-205). Peaks in the spectrum of polypyrrole shown in Figure 104 at 931 cm$^{-1}$ are attributed to C-H out of plane vibrations, and at 969 cm$^{-1}$ to ring in-plane bending, while 1,090 cm$^{-1}$ originated from C-H in-plane bending. The key N-H in-plane bending peak was observed at 1,250 cm$^{-1}$, while the most intense peaks observed at 1,570 and 1,590 cm$^{-1}$ are due to the C=C polymer structure stretching.

The capacity retention of the coated PHTD5 fibres was analysed, with the results displayed in Figure 105. It can be seen that MnO$_2$ electrodepositions performed on fibres spun from PH1000 PEDOT:PSS (fibre PHTD5) show far higher capacity retention (~ 80 % after 500 cycles) than the equivalent deposition on fibres spun from Orgacon PEDOT:PSS (~ 20 % after 500 cycles) (fibre D5). The PPy coating increases the capacity retention of Orgacon and PH1000 fibres, although it was found that even after polypyrrole coating, Orgacon fibres were not able to match the retention of uncoated PH1000 fibres. PHTD5 fibres with electrodeposited manganese dioxide had an initial capacity of 212 F g$^{-1}$, retaining 58 % of
this capacity after 500 cycles to give $124 \text{ F g}^{-1}$. A similar fibre with a further PPy layer displayed a higher initial capacity, due to the additional polypyrrole material and increased outer conductivity, of $237 \text{ F g}^{-1}$, and retained over 82% of this to give a capacity of $195 \text{ F g}^{-1}$ after 500 cycles. This presents a dramatic improvement in capacity retention.

Figure 105 – Capacity retention for PEDOT:PSS fibres with successive manganese dioxide and polypyrrole layers. Red lines show PH1000-based PHTD5 fibres, and black show Orgacon-based D5. Solid lines represent manganese deposition, with dashed lines representing manganese and PPy layers. Measured at 0.5 A g$^{-1}$ between 0.0 and 0.8 V vs. Ag/AgCl electrode in 1 mol dm$^{-3}$ sodium sulfate.

SEM EDX images, obtained to analyse the PPy layer’s coverage of the fibre are presented in Figure 106. From the map of nitrogen distribution on the fibre, it can be seen that PPy appears to have been produced evenly across the fibre’s surface.

Figure 106 – SEM EDX elemental maps showing grayscale image (left), with carbon (centre) and nitrogen (right) element maps of a three-layer fibre produced from PHTD5, with MnO$_2$ and polypyrrole layers.
6.5 Summary

Several methods for incorporating MnO$_2$-based materials into PEDOT:PSS fibres were investigated. Dipping of fibres into solutions of potassium permanganate was found to be an unsuitable method for this work due to degradation of the fibres. Fibres were destroyed, or their electrochemical properties greatly reduced by following this dip treatment.

Electrodeposition from solutions of manganese acetate was investigated, and found to present a viable method of capacitive fibre production. By varying the electrodeposition time and voltage, the conditions were optimised for electrodeposition on PEDOT:PSS fibres produced from Orgacon as well as PH1000 sources. It was found that these two PEDOT:PSS sources can both be used to produce fibres with high initial specific capacitance values exceeding 200 F g$^{-1}$. Comparison of electrodeposition times found that shorter times were required for thinner diameter fibres, to avoid excessive MnO$_2$ growth. Electrodeposition voltages were varied, and it was determined that 1.0 V (relative to Ag/AgCl reference) provided the optimal voltage for electrodeposition. Combining these measurements allowed for the optimal conditions to be developed. For Orgacon fibres (40 µm), a 20 min electrodeposition from 0.02 mol dm$^{-3}$ manganese(II) acetate at 1.0 V was optimal, while only 5 min was required for thin Clevios PH1000 fibres (20 µm).

Although high initial specific capacitance values were optimised and obtained, these fibres displayed poor capacity retention upon repeated cycling. A range of conducting polymer coatings were applied and tested, with a 3 min 0.8V electrodeposited coating of polypyrrole found to give the best capacity retention. The optimised 3-layer fibres produced has an initial capacity of 237 F g$^{-1}$, with capacity retention of over 80 % after 500 cycles, compared with 58 % for an uncoated equivalent fibre.

The initial capacitance values obtained in this chapter, of up to 160 F g$^{-1}$ are roughly 30% lower than the highest other manganese dioxide-containing conducting polymer and carbon materials, at equivalent current densities and conditions, however the capacity retention on repeated cycling is inferior. Initial values of up to 210 F g$^{-1}$ were obtained for MnO$_2$/PEDOT coaxial nanowires (191), while electrochemically deposited MnO$_2$ on carbon fibres produced values of up to 400 F g$^{-1}$, calculated using on the mass of the MnO$_2$ (102), whereas capacitance values in this work were determined from total fibre mass. Values of up to 160 F g$^{-1}$ were obtained from coaxial composites employing MWCNTs, PEDOT and MnO$_2$ (182). It can be seen that the fibres produced within this chapter are
comparable with similar PEDOT:PSS-MnO₂ fibres. However, far higher capacitance values have been reported for flexible textile capacitors using carbon fibre with nickel-cobalt layered double hydroxides containing zinc nanowires. These were found to exhibit a specific capacitance approaching 2,000 F g⁻¹ (206). Specific capacitance values of 1,010 F g⁻¹ at 20 A g⁻¹ were also obtained using nickel-cobalt oxides grown on carbon fibre cloth (207), further demonstrating the potential of these materials to exceed the capacitance values typically seen for conducting polymer-MnO₂ composites. MnO₂ deposited on carbon fibre cloth were able to achieve a specific capacitance of 635 F g⁻¹, with capacity retention of 95% after 3,000 cycles (208) far higher than produced in this chapter for MnO₂-PEDOT:PSS fibres.
7 Addition of Nanomaterials into PEDOT:PSS Fibres

7.1 Introduction

It has been shown in a wide range of applications that the addition of extra materials can bestow improved properties upon fibres (209-210). For example, the addition of CNTs into polymeric fibres is an area of intense research (30) (112). Additional nanomaterials may improve the electrical or thermal conductivity (75) (30) (211), mechanical strength (30) (211), or the charge storage capacitance of the fibre (75) (211). Desired properties can often be obtained by tailoring the material and quantity(s) added, to provide the best benefit to the system.

As has been shown in Chapter 6 of this thesis, the addition of manganese dioxide to PEDOT:PSS fibres greatly enhances their charge storage capacitance, increasing from 50 F g\(^{-1}\) to over 200 F g\(^{-1}\). However, it was shown that electrochemical deposition of such oxides is limited by the poor capacity degradation upon repeated cycling (losing up to 40 % of initial capacity after 500 cycles), as well as the oxide coatings causing the fibres to become brittle, with the coating flaking and breaking away from the fibres. The incorporation of birnessite nanotubes, a form of nano-structured manganese oxides within PEDOT:PSS fibres presents another option for incorporating these materials. As these nanotubes were pre-formed, and would be contained within the fibres, they may enable higher capacitance retention than electrodeposited manganese dioxide layers.

Before nano carbons or birnessite can be added to a polymer, it is typical for them to be dispersed into solution to enable processing. As carbon nanomaterials do not disperse in water, an additional dispersant and/or stabiliser is added; this can be in the form of a surfactant (212) or, for example, a polymer matrix such as chitosan (213). The addition of a surfactant/polymer, however, can reduce the effectiveness of the nanomaterials within the bulk material.

An alternative method for dispersing carbon nanomaterials in water is to functionalise them. This has as similar effect to using a surfactant, except that the functional groups are bonded to the nanoparticles, rather than added as a separate component. This presents an opportunity for processing and incorporating carbon nanomaterials within polymeric fibres which may be advantageous when compared with the use of surfactants. To investigate this, several functionalised nanomaterials were obtained from Haydale Graphene Industries.
plc. Functionalised graphenes, as well as functionalised MWCNTs were obtained, with either carboxylic acid or amine groups (detailed in Table 31, Figure 107).

<table>
<thead>
<tr>
<th>Functionalisation Type</th>
<th>MWCNT Name</th>
<th>FLG Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic acid</td>
<td>MWCNT-COOH</td>
<td>FLG-COOH</td>
</tr>
<tr>
<td>Amine</td>
<td>MWCNT-NH₂</td>
<td>FLG-NH₂</td>
</tr>
</tbody>
</table>

Table 31 – Designations for carboxylic acid or amine functionalised MWCNTs and FLGs provided by Haydale.

A system was developed to first disperse these materials within aqueous Clevios PH1000 PEDOT:PSS solutions, before wet spinning the solutions into fibres.

7.2 Addition of Birnessite Nanotubes

7.2.1 Initial Dispersability Determination

Initial experiments were performed to determine the possibility and potential for dispersing birnessite nanotubes into PEDOT:PSS solutions, as no current literature on this topic was found. Small quantities of birnessite powder were added to varying concentrations of PEDOT:PSS solutions, and sonicated for different times to determine optimum conditions. Table 32 summarises the composition of the first dispersions produced.
These dispersions were manually mixed prior to being sonicated using a bath sonicator for 1 h. All solutions containing 1 wt.% PH1000 (1-A through 1-E) produced dispersions that were liquid, whereas for 2 wt.% solutions only dispersions 2-A, and 2-B produced liquid dispersions; 2-C, 2-D, and 2-E produced gel-like pastes which were not suitable for fibre spinning. It was found that after 1 h of sonication, a large amount of undispersed solid material was still observed in all dispersions (example optical microscope images are shown in Figure 108). No such solid material was observed in neat PH1000 analysis, suggesting undispersed birnessite.

Attempts to determine the potential for spinning fibres from solutions containing birnessite were performed. It was found that dispersions produced from 2 wt.% PH1000 could be spun to produce fibres, whereas it was not possible to spin fibres from dispersions of 1 wt.% PH1000 at any birnessite level (dispersions 1-A through 2-E) due to the low concentrations of polymer present.
7.2.2 Dispersion Parameter Optimisation

To attempt to increase the homogeneity of the birnessite dispersion within the PEDOT:PSS, further dispersions were produced and sonicated for longer time periods, as shown in Table 33. Codes were assigned to the dispersions in the format B-W-T where ‘B’ stands for the second set of dispersions, ‘W’ represents the truncated wt.% of birnessite in the original dispersion, and ‘T’ the bath sonication time in h. Fibres are given the same name as the dispersion from which they were spun, although it is noted that variation in the actual amount of birnessite in the final fibre is likely, due to imperfect stability in the dispersion and during the spinning process. Fibres in this chapter are named based on the amounts of material added to the dispersions from which they were formed. It is noted that this may not represent the exact amounts of each material in the fibres produced, due to imperfect dispersion, inhomogeneity in the fibres produced, and any agglomeration or precipitation of the dispersed materials occurring during the fibre production process.

<table>
<thead>
<tr>
<th>Dispersion Name</th>
<th>Birnessite Concentration (wt.%)</th>
<th>Bath Sonication Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-5-1</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>B-5-5</td>
<td>0.05</td>
<td>5</td>
</tr>
<tr>
<td>B-5-20</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>B-10-1</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>B-10-5</td>
<td>0.10</td>
<td>5</td>
</tr>
<tr>
<td>B-10-20</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>B-15-1</td>
<td>0.15</td>
<td>1</td>
</tr>
<tr>
<td>B-15-5</td>
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<td>5</td>
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<tr>
<td>B-15-20</td>
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<tr>
<td>B-20-1</td>
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</tr>
<tr>
<td>B-20-5</td>
<td>0.20</td>
<td>5</td>
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<tr>
<td>B-20-20</td>
<td></td>
<td>20</td>
</tr>
</tbody>
</table>

*Table 33 – Dispersion/fibre names for birnessite added to 2 wt.% PEDOT:PSS (PH1000) solutions with 2 h bath sonication.*
It was found that all dispersions containing more than 0.10 wt.% of birnessite produced a paste after all sonication times, making them unsuitable for further use. Dispersions with 0.10 wt.% of birnessite or less were still liquid, and were taken forward for fibre production. Microscopy analysis of the dispersions revealed that some amount of solid material, believed to be birnessite, was still present in the dispersions even after 20 h of bath sonication. Figure 109 shows two images of the remaining solid material, showing that the birnessite had not achieved complete dispersion into the PEDOT:PSS solution.

Figure 109 – Optical microscope images showing solid material in B-10-20 dispersions.

Fibres were spun using identical parameters to those employed for thin wet spun PH1000 fibres, described in chapter 5. It was possible to spin fibres from the dispersions in Table 33 containing 0.10 wt.% birnessite or lower.

Analysis of the fibres produced showed that the diameters of the fibres were lower than those obtained for pure wet spun PH1000 fibres (20 µm under the same spinning conditions). It can be seen that fibre diameters decrease with additional sonication time (Figure 110).
Raman spectra were obtained to confirm the presence of birnessite in these fibres. Figure 111 left shows Raman spectra for birnessite powder, a PH1000 fibre, and a PEDOT:PSS-birnessite fibre (fibre B-5-1 shown). All PEDOT:PSS-birnessite fibres analysed via Raman spectroscopy exhibited the same spectral characteristics. It can be seen that the Birnessite powder displays a prominent peak at 645 cm\(^{-1}\), which is not present in the pure PH1000 fibre. This peak corresponds to the symmetric stretching of the Mn-O groups present (198-199) (216). An increase in the peak intensity observed at 1,120 cm\(^{-1}\) is observed in the spectrum shown of B-5-1 fibre, however this is attributed to the parameters used to obtain the spectra. Higher laser powers (above 5 mW) were required to detect birnessite peaks in the fibre, whereas PEDOT:PSS fibre spectra were obtained at laser powers below 1 mW. This increase in laser power caused visible burning of the fibre, producing the difference in spectra observed. Comparison spectra of the same pure fibre obtained at 1 and above 5 mW laser power are shown in Figure 111 (right).
Electrical conductivity measurements shown in Figure 112 show the effect of increasing birnessite concentrations and sonication time on the fibres. It is apparent that increasing sonication time dramatically reduces the electrical conductivity of the fibres, down from 122 S cm$^{-1}$ for PHTU fibres (with no birnessite and no sonication), while increasing birnessite concentrations further reduces this conductivity. Sonication of polymers (including PEDOT:PSS at all but the lowest sonication powers (217-218) has been reported to damage the polymer chains, altering and deteriorating their properties (219-220) such as electrical conductivity.

Figure 111 – Raman spectra of birnessite powder (1 mW), PH1000 fibre (1 mW), and B-5-1 fibre (5 mW) (left). Comparison of PEDOT:PSS (PH1000) fibre at above 5 mW and 1 mW laser power (right). Obtained using 532 nm laser.

Figure 112 – Electrical conductivity measurements for PEDOT:PSS-birnessite (PH1000) fibres. Error bars represent one standard deviation from repeat measurements with $n \geq 5$ fibre replicates.
Analysis of the fibres’ capacitance through charge discharge cycling shows results with high levels of error (up to 70 % RSD). At longer sonication times, this error is reduced to 26 %. It was not possible to obtain results for 20 h as fibres were too small to be tested. The capacitances observed are greatly increased compared with standard PEDOT:PSS fibres, however do not quite match the level obtained for electrodeposited manganese dioxide layers. Due to the poor dispersion of birnessite within the fibre it is possible that large clusters of birnessite are present. This poor homogeneity gives rise to the levels of error, and lower than optimal capacitance values through poor use of the full mass of birnessite.

This method of producing fibres was repeated with the addition of Triton X-100 surfactant, to aid the dispersion of birnessite. This was found to have little effect on improving the quality of the dispersions or the properties of the fibres, so was not studied further.

7.2.3 PEDOT:PSS-Birnessite Fibres from Aqueous Birnessite Dispersions

Previous experiments were with birnessite directly added to the PEDOT:PSS solutions. Aqueous birnessite solutions of 0.5 wt.% were prepared (optical microscopy shown in
Figure 114). These were found to be homogenous and stable over periods of days. This dispersion was then mixed with 2 wt.% PH1000 PEDOT:PSS solution in a range of loadings, shown in Table 34. As with previous multi-component mixture dispersion fibres, these fibres are named after the dispersion they were produced from, and as such may not represent the exact loading levels of each material. Some level of variation and deviation from the labelled proportions is unavoidable using these preparation and production methods (e.g. aggregation or precipitation of dispersions before and/or during fibre spinning).

![Image](107x450 to 502x593) 100 µm

**Figure 114 – Optical microscope image of 0.5 wt.% aqueous birnessite dispersions after horn sonication.**

<table>
<thead>
<tr>
<th>Variant Name Code</th>
<th>Dispersion Birnessite Content (wt.% ) (Relative to PEDOT:PSS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTU</td>
<td>0.0</td>
</tr>
<tr>
<td>5 wt.%</td>
<td>4.8</td>
</tr>
<tr>
<td>9 wt.%</td>
<td>9.1</td>
</tr>
<tr>
<td>13 wt.%</td>
<td>13.0</td>
</tr>
<tr>
<td>20 wt.%</td>
<td>20.0</td>
</tr>
</tbody>
</table>

*Table 34 – Name codes for PEDOT:PSS-Birnessite (PH1000) dispersions/fibres produced through mixing of PEDOT:PSS solutions (2 wt.%) and aqueous birnessite dispersions (0.5 wt.%).*

### 7.2.3.1 PEDOT:PSS-Birnessite Physical Properties

The aqueous PEDOT:PSS-birnessite dispersions were wet spun into fibres using the same parameters as used previously. These fibres had diameters similar to those of standard thin PH1000 PEDOT:PSS fibres, as shown in Figure 115.
Figure 115 – Averaged fibre diameters for fibres wet spun from mixtures of aqueous birnessite dispersions and 2 wt.% PEDOT:PSS (PH1000) solutions. Fibres contain between 0 and 20 wt.% birnessite relative to the total mass of the fibre. Error bars represent one standard deviation from repeat measurements with $n \geq 10$ fibre replicates.

SEM images of the fibres showing the core and surface of each PEDOT:PSS-birnessite fibre variant, as well as raw birnessite nanotube powder, were obtained (Figure 116). No birnessite can be seen, which is attributed to the low levels of birnessite used, as well as good dispersion of the birnessite throughout the polymer matrix of the fibre. Qualitative comparison of these fibres with previous Clevios PH1000 PEDOT:PSS fibres show no notable difference in the core structure, or the break pattern of the fibre. This information suggests that the addition of the varying levels of birnessite has no dramatic effect on the physical properties of the fibre (which was further investigated by DMA testing).
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Figure 116 – SEM images of fibres wet spun from mixtures of aqueous birnessite dispersions and 2 wt.% PEDOT:PSS (PH1000) solutions. Fibres contain between 5 wt.% birnessite (A), 9 wt.% (B), 13 wt.% (C) and 20 wt.% (D). Raw birnessite powder (41) (E).

To confirm the presence of birnessite, EDX images were obtained of a 20 wt.% birnessite fibre, shown in Figure 117. The original grayscale image is shown, as well as elemental maps for carbon, oxygen and manganese. The presence of manganese can clearly be seen, at expectedly low levels, dispersed well throughout the entirety of the fibre’s diameter. This result helps to confirm that birnessite has been successfully dispersed within the PEDOT:PSS, and was contained within the fibres.
7.2.3.2 PEDOT:PSS-Birnessite Raman Spectroscopy

Raman spectroscopy was employed to further investigate the presence of birnessite in these fibres. The resulting spectra are given in Figure 118. The left spectra show raw birnessite and a fibre of PH1000 PEDOT:PSS with no birnessite content, and the right shows fibres with 5, 9, 13 and 20 wt.% birnessite content respectively. A large peak is observed at 642 cm\(^{-1}\) in the birnessite spectrum, attributed to the stretching of the MnO\(_6\) octahedra (216), while no peak is observed at this wavenumber in the spectrum of PEDOT:PSS. Comparing this with the spectra of PEDOT:PSS-birnessite containing fibres in the right image, the peak at 642 cm\(^{-1}\) confirms the incorporation of birnessite into these fibres. Due to the necessity to use a higher laser power (greater than 5 mW) when detecting birnessite than is optimal for use with PEDOT:PSS (1 mW or lower), the spectrum of the PEDOT:PSS component of the birnessite containing fibres is altered at these high laser powers,
attributed to the visible burning of the polymer. This change is not observed at lower laser powers, as demonstrated in the left-hand image of Figure 118.

![Figure 118 – Raman spectra for raw birnessite powder and B-5-1 at 1 and >5 mW laser power (left), PEDOT:PSS-Birnessite (PH1000) fibres containing between 0 and 20 wt.% birnessite at >5 mW laser power (right). Obtained using 532 nm laser.](image)

7.2.3.3 PEDOT:PSS-Birnessite Electrochemical Properties

Charge discharge measurements were performed on the birnessite-containing fibres at 0.5 A g⁻¹, with discharge times extracted from the upper 50% of the discharge curve, and suggest that birnessite had been incorporated into the fibres, in a more homogenous manner than achieved previously in this work. Figure 119 shows example charge discharge curves for each fibre. It can be seen that all birnessite-containing fibres display greatly increased charge and discharge times than PHTU, with no birnessite content. All of the birnessite-containing fibres show very similar charge and discharge times, showing no notable difference in specific capacity between each birnessite loading. On addition, no apparent voltage jump is noticed on charging of the fibres, with only a negligible voltage drop occurring at the start of discharging. This result suggests that the decrease in electrical conductivity incurred due to the addition of birnessite is not enough to impact on the charging and discharging of the fibre system.
Capacitance values were found to be higher than fibres produced through bath sonication (shown previously), in the region of 180 F g\(^{-1}\) (Figure 120 left). RSD values between 10 and 20 % were found for these fibres, compared with up to 69 % for the bath sonicated fibres. This increase in capacitance is attributed predominantly to the birnessite material, but also to synergistic effects arising from the interactions between the conducting polymer and the birnessite. No increase in capacitance is fibres produced from dispersions with higher than 5 wt.% birnessite; this is believed to be caused by the low electrical conductivity of birnessite. If small, nano or micro-sized clusters of birnessite are present in the material; these may restrict efficient access to the birnessite mass in the core of the clusters. Although the aqueous suspensions produced were well dispersed, it is possible that during the mixing with PEDOT:PSS and coagulation stages that the dispersion underwent agglomeration, producing fibres with less than ideal birnessite distribution or content throughout the polymer.

Figure 120 right shows capacity retention measurements performed by repeated cycling. It can be seen that the fibre displays excellent capacity retention, with 89 % retention after 500 cycles. A decrease within the initial 50 cycles is observed, as is typical with birnessite-based systems (41) (221), with no further retention loss after this.
Figure 120 – Averaged charge discharge capacitance for fibres containing between 0 and 20 wt.% birnessite relative to the total mass of the fibre. Measured at 0.5 A g\(^{-1}\) vs. Ag/AgCl electrode in 1 mol dm\(^{-3}\) sodium sulfate (left). Error bars represent one standard deviation from repeat measurements with \(n \geq 5\) fibre replicates.

Capacity retention measurements performed on a 5 wt.% birnessite fibre using the same parameters (right).

As with fibres PHTU and PHTD5, a 5 wt.% birnessite fibre was also analysed via impedance spectroscopy. Nyquist plots for fibres PHTU, PHTD5, and 5 wt.% birnessite are shown in Figure 121.

Figure 121 – Nyquist plots for fibres PHTU, PHTD5, and 5 wt.% Birnessite. Performed between 10 µHz - 100 KHz with a perturbation voltage of 10 mV vs. Ag/AgCl electrode.

Values were again taken above the knee frequency for each fibre, and used to calculate the specific capacitance of each fibre. Values of 42, 54, and 222 F g\(^{-1}\) were obtained for fibres
PHTU, PHTD5, and 5 wt.% birnessite content respectively. These are shown compared against the same fibres analysed via charge discharge measurements (performed at 0.5 A g\(^{-1}\)) in Figure 122. As with fibres PHTU and PHTD5 presented previously, good agreement between both techniques is observed.

![Comparison of specific capacitance values for fibres PHTU, PHTD5, and 5 wt.% birnessite using charge discharge (CCD) and impedance techniques. Measured at 0.5 A g\(^{-1}\) vs. Ag/AgCl electrode in 1 mol dm\(^{-3}\) sodium sulfate. Error bars represent one standard deviation from repeat measurements with n ≥ 5 replicates.](image)

CV was also performed on the fibres, to further examine their electrochemical performance. As observed in Figure 123, all fibres containing birnessite show an increase in the currents observed relative to fibres with no birnessite content. No notable difference in current is observed between fibres, corresponding to the capacitance values observed from charge discharge measurements. A trend away from the ideal rectangular capacitor shape was observed with increasing birnessite load, corresponding to the lower electrical conductivity found in these fibres.
Figure 123 – CV on fibres containing between 0 and 20 wt.% birnessite relative to the total mass of the fibre. Measured at 100 mV s\(^{-1}\) vs. Ag/AgCl electrode in 1 mol dm\(^{-3}\) sodium sulfate.

### 7.2.3.4 PEDOT:PSS-Birnessite Electrical Conductivity

The conductivity of the fibres was measured, and comparisons are shown in Figure 124 and summarised in Table 35. It can be seen that higher loadings of birnessite dramatically reduce the electrical conductivity of the fibres, which is to be expected when adding increasing loadings of an insulting material. The birnessite may disrupt the PEDOT nanocrystal matrix (58), thus lowering the conductivity between individual regions of the bulk material. Similar capacitance values were observed for all birnessite loadings, but lower loadings show less of a conductivity loss. Assumed loadings such as 5 wt.% birnessite therefore appear to be the most promising to obtain a balance of properties. The lower electrical conductivity of the fibres may also contribute to the lack of increase in capacitance observed for birnessite loadings above 5 wt.%. 


Figure 124 – Electrical conductivity of fibres wet spun from mixtures of aqueous birnessite dispersions and 2 wt.% PEDOT:PSS (PH1000) solutions. Fibres contain between 0 and 20 wt.% birnessite relative to the total mass of the fibre. Error bars represent one standard deviation from repeat measurements with \( n \geq 5 \) fibre replicates.

<table>
<thead>
<tr>
<th>Fibre Birnessite Content (wt. %)</th>
<th>0 (PHTU)</th>
<th>5</th>
<th>9</th>
<th>13</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (S cm(^{-1}))</td>
<td>112 ± 18</td>
<td>117 ± 28</td>
<td>69 ± 21</td>
<td>24 ± 4</td>
<td>24 ± 4</td>
</tr>
</tbody>
</table>

Table 35 - Electrical conductivity of fibres wet spun from mixtures of aqueous birnessite dispersions and 2 wt.% PEDOT:PSS (PH1000) solutions. Fibres contain between 0 and 20 wt.% birnessite relative to the total mass of the fibre. Error represents one standard deviation from repeat measurements with \( n \geq 5 \) fibre replicates.

7.2.3.5 PEDOT:PSS-Birnessite Mechanical Properties

Dynamical mechanical analysis of the fibres was performed to determine their physical strength. Figure 125 shows that a large decrease in mechanical strength occurs when birnessite is added to the fibre (details presented in Table 36). A sudden decrease is seen for mechanical strengths, compared to the gradual decrease seen for electrical conductivity, with 5 wt.% birnessite approximately halving the ultimate tensile strength of the fibre. However, the decrease plateaus at loadings higher than 5 wt.%, with no further decrease found, whereas electrical conductivity continues to decrease with higher loadings. The
addition of birnessite disrupts the polymer resulting in a lower tensile strength, independent of the mass loading used.

Figure 125 – Averaged ultimate tensile strength for fibres wet spun from mixtures of aqueous birnessite dispersions and 2 wt.% PEDOT:PSS (PH1000) solutions. Fibres contain between 0 and 20 wt.% birnessite relative to the total mass of the fibre. Error bars represent one standard deviation from repeat measurements with n ≥ 5 fibre replicates.

Averaged Young’s modulus values are presented in Table 36. Although a decrease was observed for tensile strength values, no measured decrease is observed in the Young’s modulus. All values are within the error of each other, although on average slightly lower than for PHTU fibres without birnessite. As such, no notable increase or decrease in stiffness is produced with the addition of birnessite.

<table>
<thead>
<tr>
<th>Fibre Birnessite Content (wt.%)</th>
<th>0 (PHTU)</th>
<th>5</th>
<th>9</th>
<th>13</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate Tensile Strength (MPa)</td>
<td>115 ± 21</td>
<td>61 ± 24</td>
<td>55 ± 24</td>
<td>49 ± 23</td>
<td>49 ± 29</td>
</tr>
<tr>
<td>Young’s Modulus (MPa)</td>
<td>2,900 ± 800</td>
<td>2,700 ± 1,200</td>
<td>2,100 ± 500</td>
<td>2,500 ± 1,400</td>
<td>2,600 ± 900</td>
</tr>
</tbody>
</table>

Table 36 - Averaged ultimate tensile strength for fibres wet spun from mixtures of aqueous birnessite dispersions and 2 wt.% PEDOT:PSS (PH1000) solutions. Fibres contain between 0 and 20 wt.% birnessite relative to the total mass of the fibre. Error represents one standard deviation from repeat measurements with n ≥ 5 fibre replicates.
7.2.3.6 PEDOT:PSS-Birnessite Thermogravimetric Analysis

While the amounts of birnessite added to the dispersions were known, how well this was transferred to the fibres is not exactly known. Factors such as dispersion quality and stability could affect the amounts of birnessite that was incorporated into the fibres. To analyse this, TGA was carried out in the same manner as previous fibres, and results are shown in Figure 126.

While some difference is observed, no trend is apparent. Fibres containing 5 wt.% birnessite had the highest mass remaining, with almost 30% remaining after all PEDOT:PSS material was lost. Other birnessite containing fibres were also found to have masses remaining well above 10%. 7.9% mass was found to remain for PHTU fibres, with 27.6%, 15.2%, 14.7%, and 21.0% mass remaining for 5 wt.%, 9 wt.%, 13 wt.% and 20 wt.% birnessite fibres respectively. This result is suggestive of poor homogeneity within the fibres produced, causing variation in the amount of birnessite in each fibre.

![Figure 126 – TGA plots for PEDOT:PSS (PH1000) fibres containing between 0 and 20 wt.% birnessite nanotubes. Performed with 10°C min⁻¹ ramp rate in air atmosphere.](image)
7.3 Addition of Haydale Functionalised Carbon Nanomaterials

From the earlier work described in this chapter, it was found that the most reliable method for incorporating hydrophilic nanomaterials into PEDOT:PSS fibres was to mix their aqueous dispersions with solutions of PEDOT:PSS. These solutions were then wet spun to produce fibres.

7.3.1 Determination of Haydale Functionalised Carbon Nanomaterial Dispersion Limits

Before spinning solutions could be prepared, it was necessary to determine the concentrations at which each of the four Haydale carbon nanomaterials could be successfully dispersed within water. Horn sonication was used to disperse varying concentrations of each nanomaterial, and the dispersions produced analysed via optical microscopy.

0.5 wt.% dispersions of each nanomaterial were produced: at this concentration it was found that none of the four materials produced a suitable dispersion. Both FLG types produced dispersions which initially appeared of good quality, but quickly dropped out of dispersion, while both MWCNT types produced an undesirable thick paste. Examples of these are shown in Figure 127.

![Figure 127 – Aqueous dispersions after 1 h sonication, left to settle for 1 h. 0.5 wt.% FLG-COOH (left) and 0.5 wt.% MWCNT-COOH (right).](image)
Reducing the concentration of nanomaterial to 0.1 wt.% for each FLG material yielded stable dispersions suitable for use. No difference was observed between FLG-COOH and FLG-NH₂ materials.

Figure 128 - Digital photograph (left) and optical microscope image (right) of 0.1 wt.% aqueous FLG-COOH dispersion after 1 h bath sonication and 24 h settling time. shows an example of a 0.1 wt.% dispersion of FLG-COOH, and optical microscopy of the dispersion.

It was found that no concentration between 0.01 and 0.5 wt.% of either MWCNT material produced dispersions. Sonication powers from 30 % up to 80 % and sonication times of up to 3 h showed no improvement on dispersing the materials. This is attributed to the higher degree of entanglement present in nanotubes, compared with graphene materials. It was decided not to use any surfactant or dispersing agent, as the use of these would negate any reason for originally using functionalised nanotubes.

To produce fibres, varying amounts of each FLG dispersion (0.1 wt.%) were mixed with 2 wt.% Clevios PH1000 PEDOT:PSS solution, in the same manner as was employed for Birnessite dispersions (section 7.2). Details of these FLG dispersions are given in Table 37, where PEDOT:PSS-C and PEDOT:PSS-N fibres refer to fibres containing FLG-COOH and FLG-NH₂ dispersions respectively. As with previous fibres, the fibres in this section are named from the dispersion used to produce them. As such, the names may not directly represent the final loading levels of each material.
Table 37 – Spinning solutions produced from PEDOT:PSS (PH1000) and Haydale FLG-COOH or FLG-NH₂ dispersions at varying concentrations.

7.3.2 PEDOT:PSS-FLG Physical Properties

The diameters of the wet spun fibres were measured, and found to be $20 \pm 3 \, \mu m$, which is a similar value to the wet spun PEDOT:PSS fibres discussed in chapter 5, which were spun using the same parameters. Figure 129 shows the averages of these values. However, higher levels of variation within the diameters of these FLG-containing fibres were found.
Figure 129 - Averaged fibre diameters for fibres wet spun from PEDOT:PSS (PH1000) mixed with varying amounts of FLG-COOH or FLG-NH₂. Error represents one standard deviation from repeat measurements with \( n \geq 10 \) fibre replicates.

### 7.3.3 PEDOT:PSS-FLG Raman Spectroscopy

Raman spectra were obtained for FLG-COOH and FLG-NH₂ raw powders, as well as for all variants of each fibre type produced. In the spectra of the raw powders (Figure 130), clear peaks can be seen at 1,340, 1,570, and 2,680 \( \text{cm}^{-1} \). These peaks correspond to the D, G and G’ bands respectively, of FLGs. The D and G band peaks are seen to overlap with peaks observed in the spectrum of PEDOT:PSS fibres (Figure 131 and Figure 132), thus not presenting a possibility for confirmation of incorporation of the nanomaterials in to the fibres by the presence of those peaks alone. The G’ band at 2,680 \( \text{cm}^{-1} \) does not overlap with any peaks in the spectrum of PEDOT:PSS, so can be used to confirm the presence of the FLGs in the fibres produced.

Figure 131 and Figure 132 show Raman spectra for each fibre variant containing FLG-COOH and FLG-NH₂ respectively. Both sets of spectra were normalised around the PEDOT:PSS peak at 1,430 \( \text{cm}^{-1} \) for visual comparison. Comparing the intensity of the peaks at 1,340 and 1,570 \( \text{cm}^{-1} \) in both figures, shows an increase in intensity when the amount of nanomaterial in the fibre is increased. Peaks are also observed at 2,680 \( \text{cm}^{-1} \) in
both figures, arising from the G’ band of the FLG sheets in the fibres. These sets of peaks confirm the presence of the functionalised FLGs within the fibres.

**Figure 130** – Raman spectra of raw FLG-COOH and FLG-NH₂ powders. 532 nm laser used.

**Figure 131** – Raman spectra of PEDOT:PSS (PH1000) fibres containing FLG-COOH at varying amounts. 532 nm laser used.
Figure 132 - Raman spectra of PEDOT:PSS (PH1000) fibres containing FLG-NH$_2$ at varying amounts. 532 nm laser used.

SEM images of each fibre type were obtained, and are shown in Figure 133 and Figure 134. It can be seen that all fibre types have similar shapes, showing no physical differences, as well as not showing visible graphene sheets. It is not expected that the FLG sheets would be visible at these concentrations within the fibre, due to the low amounts present, coupled with their nano-scale size, and dispersion throughout the fibre.
Figure 133 – SEM images of PEDOT:PSS-FLG-COOH (PH1000) fibres containing 1 (A), 2 (B), 3 (C), and 5 (D) wt.% FLG-COOH. PHTU also shown (E).
EDX images of select fibres were obtained, to confirm the presence of nitrogen within the fibres. As nitrogen is not present in the PEDOT or PSS components, any nitrogen found within the fibre must originate from the NH$_2$ functionalised FLG sheets. Figure 135 shows the results of these EDX scans, the grayscale image as well as elemental maps for carbon, nitrogen and oxygen are shown. It can be seen that there is a low level of nitrogen detected throughout the fibre, not present in PEDOT:PSS-FLG-COOH fibres, confirming the presence of FLG-NH$_2$ sheets dispersed through the fibre.
Figure 135 – EDX maps showing grayscale, carbon, oxygen and nitrogen content within a 5% N (PH1000) fibre.

7.3.4 PEDOT:PSS-FLG Electrochemical Properties

Analysis of these fibres’ electrochemical properties via CV is shown in Figure 136. It can be seen that the addition of the functionalised FLG materials has an effect on the overall voltammogram shape of each fibre, although currents remain unchanged. Fibres containing FLG-COOH and FLG-NH₂ both show a change towards that of an ideal rectangle, with a larger effect found in the FLG-COOH containing fibres. This is suggestive of the nanomaterials enhancing the electrical conductivity of the fibres, or enabling more efficient mass transport within the system. Functionalisation of carbon nanomaterials has been shown to deteriorate their electrical and electrochemical properties, as such, reducing their contribution to fibre property enhancement (86) (222). Further investigation through electrical conductivity measurements and charge discharge analysis will further probe if the addition of these nanomaterials can convey useful properties to the fibres.
Figure 136 – CV of PEDOT:PSS (PH1000) fibres containing between 0 and 5 wt.% FLG-COOH (top) and FLG-NH$_2$ (bottom). Measured at 100 mV s$^{-1}$ vs. Ag/AgCl electrode in 1 mol dm$^{-3}$ sodium sulfate.

Averaged charge discharge capacitance values are shown in Figure 137 (and summarised in Table 38) for both fibre variants, calculated from discharge times extracted from the gradient of the upper 50% of the discharge curve. It can be seen that both fibre groups possess similar capacitance values, although neither are significantly higher than for fibres with no added nanomaterials (PHTU). Some increase is seen for specific fibres, however,
due to the level of variation of carbon nanomaterial incorporation within the fibres. The level of variation between fibres of the same type may be indicative of a non-perfect dispersion of the nanomaterials in the spinning solution. Although the FLGs were both found to disperse well at the concentrations used (0.1 wt.%) in water, during the mixing with PEDOT:PSS and spinning process it is possible that the nanomaterials may have aggregated, producing a lower quality dispersion. This would thus give rise to the higher levels of variation observed in results for these fibres. While the addition of nanomaterials such as graphenes can often increase the capacitance of a composite material (223-224), no evidence of increased capacity was found in CV, attributed to the functionalisation present on the nanomaterials.

Figure 137 – Averaged charge discharge capacities of PEDOT:PSS (PH1000) fibres containing between 0 and 5 wt.% FLG-COOH and FLG-NH2 (Measured at 0.5 A g⁻¹ vs. Ag/AgCl electrode in 1 mol dm⁻³ sodium sulfate). Error bars represent one standard deviation from repeat measurements with n ≥ 5 fibre replicates.
### Table 38 - Averaged charge discharge capacities of PEDOT:PSS (P1000) fibres extracted from the data in Figure 137.

<table>
<thead>
<tr>
<th>Fibre Treatment</th>
<th>FLG-COOH</th>
<th>FLG-NH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTU</td>
<td>35 ± 1</td>
<td></td>
</tr>
<tr>
<td>1 wt.%</td>
<td>44 ± 4</td>
<td>38 ± 10</td>
</tr>
<tr>
<td>2 wt.%</td>
<td>41 ± 6</td>
<td>30 ± 11</td>
</tr>
<tr>
<td>3 wt.%</td>
<td>37 ± 14</td>
<td>30 ± 8</td>
</tr>
<tr>
<td>5 wt.%</td>
<td>41 ± 12</td>
<td>36 ± 5</td>
</tr>
</tbody>
</table>

#### 7.3.5 PEDOT:PSS-FLG Electrical Conductivity

Analysis of the fibres’ electrical conductivity shows that the addition of the functionalised nanomaterials has a detrimental effect on the conductivity (shown in Figure 138 and Table 39). This effect is less severe than that observed for birnessite addition, likely due to the higher electrical conductivity of the carbon nanomaterials, as well as the lower concentrations used (up to 5 wt.% for CNTs, and up to 20 wt.% for birnessite). While the addition of nanocarbons is often used to increase the conductivity of a material, this is typically done through incorporation of pristine nanocarbons. The functionalised graphenes used in this chapter have been shown not to improve electrochemical properties of the materials (section 7.3.4). Increasing levels of nanomaterials continue to lower the electrical conductivity of the fibres, showing no benefit to either conductivity or electrochemical properties.
Figure 138 – Averaged four-point electrical conductivities of PEDOT:PSS (PH1000) fibres containing between 0 and 5 wt.% FLG-COOH and FLG-NH$_2$. Error bars represent one standard deviation from repeat measurements with $n \geq 5$ fibre replicates.

<table>
<thead>
<tr>
<th>Fibre Treatment</th>
<th>FLG-COOH</th>
<th>FLG-NH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTU</td>
<td>125 ± 11</td>
<td></td>
</tr>
<tr>
<td>1 wt.%</td>
<td>90 ± 25</td>
<td>61 ± 13</td>
</tr>
<tr>
<td>2 wt.%</td>
<td>77 ± 26</td>
<td>55 ± 26</td>
</tr>
<tr>
<td>3 wt.%</td>
<td>74 ± 8</td>
<td>74 ± 8</td>
</tr>
<tr>
<td>5 wt.%</td>
<td>42 ± 5</td>
<td>37 ± 12</td>
</tr>
</tbody>
</table>

Table 39 – Averaged four-point electrical conductivities of PEDOT:PSS (PH1000) fibres containing between 0 and 5 wt.% FLG-COOH and FLG-NH$_2$. Error represents one standard deviation from repeat measurements with $n \geq 5$ replicates.

7.3.6 PEDOT:PSS-FLG Mechanical Properties

Dynamic mechanical analysis was used to analyse the ultimate tensile strength values of these fibres with added FLGs. From the results in Figure 139 and Table 40, it can be seen that the addition of FLG with both amine and carboxylic acid functionality causes a
decrease in ultimate strength at all loadings. The individual values for all fibres within each functionalisation type are within the error of that group, therefore not allowing for any clear differentiation between different loadings. However, it can be concluded that the addition of these functionalised FLG nanomaterials does not present a means to improve the mechanical properties of the PEDOT:PSS fibres.

![Graph showing ultimate tensile strength values for PEDOT:PSS (PH1000) fibres containing between 0 and 5 wt.% FLG-COOH and FLG-NH₂. Error bars represent one standard deviation from repeat measurements with n ≥ 3 replicates.](image)

Young’s modulus values for both sets of fibres are shown in Table 40. All values obtained are within the margin of error for each other, showing no clear difference or trend between functionalisation type or level of nanomaterial inclusion. As per the ultimate tensile strength results, it can be seen that this method of incorporating functionalised nanomaterials does not present a means to positively affect the tensile strength, or Young’s modulus of these fibres.
### Table 40 – Averaged ultimate tensile strength values of PEDOT:PSS (PH1000) fibres containing between 0 and 5 wt.% FLG-COOH and FLG-NH₂. Error represents one standard deviation from repeat measurements with n ≥ 3 fibre replicates.

<table>
<thead>
<tr>
<th>Fibre Treatment</th>
<th>FLG-COOH (MPa)</th>
<th>FLG-NH₂ (MPa)</th>
<th>FLG-COOH (MPa)</th>
<th>FLG-NH₂ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHTU</td>
<td>115 ± 21</td>
<td>2,900 ± 800</td>
<td>2,400 ± 700</td>
<td>2,500 ± 800</td>
</tr>
<tr>
<td>1 wt.%</td>
<td>57 ± 11</td>
<td>100 ± 17</td>
<td>2,400 ± 700</td>
<td>2,500 ± 800</td>
</tr>
<tr>
<td>2 wt.%</td>
<td>73 ± 22</td>
<td>93 ± 25</td>
<td>2,800 ± 700</td>
<td>3,300 ± 1,000</td>
</tr>
<tr>
<td>3 wt.%</td>
<td>81 ± 17</td>
<td>77 ± 22</td>
<td>2,500 ± 1,000</td>
<td>3,100 ± 1,000</td>
</tr>
<tr>
<td>5 wt.%</td>
<td>65 ± 20</td>
<td>90 ± 18</td>
<td>2,100 ± 500</td>
<td>2,500 ± 500</td>
</tr>
</tbody>
</table>

7.3.7 PEDOT:PSS-FLG Thermogravimetric Analysis

In the same manner as for Birnessite-containing fibres, Haydale nanomaterial fibres were analysed via TGA. Fibres from both types were individually analysed and compared (shown in Figure 140). It was found that no clear differentiation could be determined between each fibre loading, with no logical trend appearing. This is attributed to the very small proportion differences between the mass loadings of each fibre. Agglomeration occurring upon mixing nanomaterial dispersions with PEDOT:PSS prior to spinning would then inhomogeneity within the fibres, yielding differences in the amount of nanomaterial mass present.

![Figure 140 – TGA plots for PEDOT:PSS (PH1000) fibres containing between 1 and 5 wt.% carboxylic functionalised FLGs.](image-url)
7.4 Summary

The work in this chapter has incorporated three different nanomaterials into PEDOT:PSS fibres and characterised their properties. It was found that all three nanomaterials could be incorporated into the fibres using a simple method involving aqueous nanomaterials dispersions, without the use of any additional surfactant or dispersing agent.

The addition of birnessite nanotubes was found to greatly boost the specific capacitance of the fibre with values approaching 200 F g\(^{-1}\) achieved (increased from 35 F g\(^{-1}\) with no birnessite). A minor loss in electrical conductivity was observed in the 5 wt.% fibre, which was found to be the optimal mass loading for energy-related applications. Birnessite loadings above 5 wt.% were found to dramatically reduce the electrical conductivity of the fibres. It was determined that 5 wt.% loadings of birnessite presented the optimal addition to the fibres to enhance the specific capacitance, while having minimal detrimental effect on conductivity. Mechanical analysis found birnessite addition halved the mechanical strength values. The higher initial capacitance values obtained in this chapter, compared with those (of up to 160 F g\(^{-1}\)) obtained for electrochemical MnO\(_2\) deposition in chapter 6 bring them in line with similar published work discussed already (102) (182) (191). A further advantage over the work discussed in chapter 6, again brining these results in line with published work, is the improved capacity retention.

Functionalised FLG sheets were also incorporated into the fibres, through the same aqueous dispersion method. Although no extra surfactant was used, the functionalisation of the sheets produced results more typical of surfactant-assisted addition of nanomaterials than those of pristine nanomaterials. A small negative effect was observed in the fibre’s CV, with larger decreases noticed for electrical conductivity and charge storage capacity. No increase in mechanical strengths was observed.

Overall, it was determined that addition of birnessite could produce fibres with high specific capacitance values, and high levels of capacity retention, while having minimal detrimental effect on other properties. The addition of functionalised FLGs did not improve the properties of the fibres. As such, functionalised FLGs do not present a viable means for improving the properties of this PEDOT:PSS fibre system.
8 Flexible Fibre-Based Supercapacitor Device Production

The preceding chapters of this thesis have described the development of fibres made from a range of materials with the aim of employing them in supercapacitor devices. It was decided that fibres produced from PEDOT:PSS (PH1000) containing 5 wt.% birnessite would be used to produce solid state supercapacitors. This fibre was chosen due to its high capacitance (200 F g\(^{-1}\)). While this is not as high as was obtained for electrochemically deposited manganese dioxide layers (over 250 F g\(^{-1}\)), PEDOT:PSS-birnessite fibres have higher capacity retention, retaining 90% of their initial capacity after 500 cycles, while coated manganese electrodeposited fibres retained only 82%. Birnessite-containing PEDOT:PSS fibres also have the benefit of being flexible, whereas coated fibres were found to be brittle. A comparison device using a fibre containing 1 wt.% of amine functionalised CNTs in place of birnessite was also produced.

8.1 Device Fabrication

Symmetric supercapacitor devices were produced by aligning two 5 wt.% PH1000 PEDOT:PSS-birnessite or 1 wt.% PEDOT:PSS-FLG-NH\(_2\) fibres parallel to each other, and coating with an electrolyte gel containing 1 wt.% phosphoric acid with 1 wt.% PVA. This electrolyte is commonly used in several fibre-based devices previously reported (80) (109) (225), and as such served as a suitable electrolyte for comparison. The fibres were aligned on a hydrophobic paper backing, coated in electrolyte, before being dried at 50 \(^\circ\)C for 1 h to dry the electrolyte. This resulted in a solid-state flexible fibre supercapacitor.

<table>
<thead>
<tr>
<th>Device Name</th>
<th>Fibre 1</th>
<th>Fibre 2</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS-Birn</td>
<td>PEDOT:PSS with 5 wt.% birnessite</td>
<td>PEDOT:PSS with 5 wt.% birnessite</td>
<td>50:50 PVA:H(_3)PO(_4)</td>
</tr>
<tr>
<td>PEDOT:PSS-FLG</td>
<td>PEDOT:PSS with 1 wt.% FLG-NH(_2)</td>
<td>PEDOT:PSS with 1 wt.% FLG-NH(_2)</td>
<td>50:50 PVA:H(_3)PO(_4)</td>
</tr>
</tbody>
</table>

*Table 41 – Names and details of produced supercapacitor devices.*

These supercapacitor devices were labelled as described in Table 41. Figure 141 shows a schematic of such a device (top), and a picture of an example supercapacitor device (bottom). The two aligned fibres can be seen, connected to tweezers which were in turn connected to the potentiostats. A small piece of copper tape was used in such devices to ensure a good electrical connection was made. The devices were produced in varying...
lengths and shape, and were typically produced in 5 cm or shorter lengths for testing purposes.

![Schematic Example supercapacitor device. Two fibres are aligned parallel and coated in electrolyte on a flexible backing. Tweezers and copper plates allow connection of the fibres to the potentiostat.](image)

8.2 Cyclic Voltammetry

CV was used to analyse the electrochemical properties of these devices, as well as to explore the voltage window in which the devices can be cycled. In this setup, one fibre was connected to the working electrode, with the other as counter and sense. As shown in the voltammograms in Figure 142, PEDOT:PSS-FLG and PEDOT:PSS-Birn devices show similar responses; square profiles approaching that of the ideal rectangle are seen at rates up to 25 mV s⁻¹, with more angular shapes observed at faster rates. As expected, the birnessite-containing device shows higher currents than were observed for the FLG device, due to the extra capacitance arising from the inclusion of birnessite in the system.
Figure 142 – CV of PEDOT:PSS-FLG (left), and PEDOT:PSS-Birn (right). Measured as a two electrode system at scan rates between 1 and 200 mV s⁻¹.

Figure 143 shows voltammograms performed at different voltage ranges for both supercapacitor devices. PEDOT:PSS-FLG was found to exhibit a stable response at voltage windows of up to 1.8 V; with deviation observed at higher voltages. PEDOT:PSS-Birn shows a stable response up to 1.5 V, with deviation observed any higher (226), attributed to the instability of birnessite at higher voltages. These results suggest that the devices can be employed at voltages higher than the typical ~1 V frequently used (80). This is attributed to the solid-state nature of the polymer gel electrolyte, and absence/limited amount of water in the dried gel electrolyte (80).

Figure 143 – CV of PEDOT:PSS-FLG (left), and PEDOT:PSS-Birn (right). Measured as a two electrode system at 100 mV s⁻¹ at maximum voltages between 0.8 and 2.0 V.

8.3 Charge Discharge Cycling

Cyclic charge discharge experiments were performed, to determine the charge storage capability of the supercapacitor devices. As with earlier voltammetry experiments in this chapter, the electrode was connected as a two electrode system. The specific capacitance was calculated using the combined mass of both electrodes, due to the two electrode setup employed.
Charge discharge profiles for each supercapacitor are shown in Figure 144, performed at a range of maximum voltages (0.8 – 1.8 V). Based on the results of the CV experiments, the PEDOT:PSS-FLG device was cycled up to 1.8 V, whereas the PEDOT:PSS-Birn cycled to 1.5 V. Both supercapacitors show typical capacitive CV profiles up to a charge voltage maximum of 1.5 V, however PEDOT:PSS-FLG shows a change in profile at 1.8 V suggesting hydrogen evolution in the gel electrolyte (226).

Longer charge and discharge times are observed for the PEDOT:PSS-Birn supercapacitor, as expected due to the inherently higher specific capacitance of fibres containing birnessite than those containing FLG-FLG. Initial voltage jumps are observed upon charging, and discharging, for both devices. This is a product of the internal resistance of the devices (177), which had not been observed to this extent in analysis of the individual fibres due to the use of aqueous electrolytes in the three-electrode system. Voltage jumps in both systems are observed, and are similar to those observed in equivalent devices previously reported (227-228).

### 8.3.1 Capacity and Retention

Capacitance measurements were performed on both devices at 0.5 A g$^{-1}$ between 0 and 0.8 V. Values of 28 and 72 F g$^{-1}$ were obtained for PEDOT:PSS-FLG and PEDOT:PSS-Birn devices respectively. For the PEDOT:PSS-Birn device this corresponds to a volumetric capacitance of 56 F cm$^{-3}$, calculated using the total volume of both fibre electrodes. This compares well with several similar fibres previously published (80), for example a MnO$_2$ nanowire with graphene fibre supercapacitor exhibited a volumetric capacitance of 66 F cm$^{-3}$ (228), while a supercapacitor produced from wet spun PEDOT:PSS fibres had a
capacitance of 20 F cm\(^{-3}\) (229), however, this result is several times lower than some of the highest values reported (80), with maximum capacitance values of 179 F cm\(^{-3}\) reported for composites of CNTs infused with conducting polymer (230), and over 200 F cm\(^{-3}\) reported for devices produced from graphene/PVA composite fibres (231).

The device energy was calculated using the following equation, considering only the mass of the active fibre material. Where \( C_s \) represents the specific capacitance of the device, calculated as a two-electrode system, and \( V \) is the voltage range over which the device was cycled. Through this method a device energy of 1.6 Wh kg\(^{-1}\) was determined, at 0.8 V, and 5.6 Wh kg\(^{-1}\) at 1.5 V (the maximum usable voltage determined for the PEDOT:PSS-Birn device). This value is limited by the relatively low maximum voltage obtainable due to the electrolyte chosen, different electrolytes may allow higher voltages to be employed. The device power density was determined from the energy density and discharge time. Values of 41 and 144 W kg\(^{-1}\) were obtained at maximum charge voltages of 0.8 and 1.5 V respectively.

\[
\frac{1}{8} C_s V^2
\]

*Equation 10: Device energy calculation for fibre supercapacitor (13).*

These values compare well with several similar devices; such as 5 Wh kg\(^{-1}\) with a power density of 14 W kg\(^{-1}\) for a carbon nanoparticle with MnO\(_2\) fibre-based device (227) and 5 Wh kg\(^{-1}\) with a power density 24 W kg\(^{-1}\) for a PVA-graphene fibre device (231). However, this result is lower than any of the highest values achieved in literature; for example, a carbon nanotube-MnO\(_2\) fibre supercapacitor achieved energy density values of 42 Wh kg\(^{-1}\), at a power density of 480 W kg\(^{-1}\) (211).
Repeated cycling of these devices was performed, and is shown in Figure 145. High levels of capacity retention are observed for both devices. PEDOT:PSS-Birn shows an initial decrease in capacity from 82 to 66 F g\(^{-1}\), which is typical for birnessite materials (41). After this initial decrease the capacity is found to show no notable further decrease over the 1,000 cycle period, with a final capacity of 67 F g\(^{-1}\). The PEDOT:PSS-FLG supercapacitor also shows a stable capacitance during 1,000 cycles, similar to other carbon nanomaterial-PEDOT:PSS composite capacitor devices (232).

The performance of the PEDOT:PSS-Birn supercapacitor was also measured at a range of current densities, between 0.3 and 10 A g\(^{-1}\). Figure 146 shows the results of this testing. The highest capacitance, 147 F g\(^{-1}\), was obtained at the lowest current density of 0.3 A g\(^{-1}\), decreasing to 5 F g\(^{-1}\) at 5 A g\(^{-1}\). Current densities above this could not be measured, as the device was unable to function at this level of current. A sharp decrease in capacitance was seen with increasing current densities. This decrease is similar to that of many devices previously reported (211) (227-228). This is believed to be a product of the internal resistance of the device, which will be increased due to the solid-state nature of the dried gel electrolyte employed. As such, mass transport within the electrolyte will be, compared with an aqueous solution, due to reduced ion mobility, as well as slower diffusion.
Capacitance of the PEDOT:PSS-Birn supercapacitor at current densities between 0.3 and 10 A g\(^{-1}\). Measured using cyclic charge discharge between 0.0 and 0.8 V as a two electrode system.

8.4 Device Properties

To test the physical characteristics of the device produced, the PEDOT:PSS-Birn supercapacitor was subjected to bending and straightening during charge discharge cycles. Figure 147 shows images of a device before and during being bent. The device was repeatedly bent through 180 degrees before being returned to straight. The device was successfully put through 100 repeat bending/straightening cycles with no apparent physical damage.
Charge discharge measurements were taken before, during, and after bending. No difference in storage capacity or profile was observed during any stage of this process, as demonstrated in Figure 148. No notable loss in physical capacitance was found after 100 cycles, comparing well with devices previously reported (233-234).

![Charge discharge plots for PEDOT:PSS-Birn supercapacitor showing before first bending, during 50th bending, and after 100 bending cycles were applied to the device. Measured as a two electrode system at 0.5 A g⁻¹.]

**Figure 148**

### 8.5 Summary

Fibre supercapacitor devices have been produced using fibres described in chapter 7 of this thesis. Two symmetric devices were presented in this chapter, one produced from fibres of Clevios PH1000 PEDOT:PSS combined with 5 wt.% birnessite nanotubes, and the second produced from fibres containing NH₂ functionalised FLG sheets, to serve as a comparison device. The electrochemical properties of the devices produced were measured via CV at a range of scan rates and voltage windows. Charge discharge measurements were performed at current densities between 2 and 10 A g⁻¹ and at varied voltage windows. The repeated charging cycle stability of each device was measured using charge discharge at a current of 0.5 A g⁻¹.

As with analysis of the individual fibres in chapter 7, it was found that the PEDOT:PSS-Birn supercapacitor presented higher capacitance values than the PEDOT:PSS-FLG...
device. Specific capacitance values of 27.6 and 71.9 F g⁻¹ were found for PEDOT:PSS-FLG and PEDOT:PSS-Birn devices respectively. The PEDOT:PSS-FLG device showed no capacity degradation after 1,000 cycles, while the PEDOT:PSS-Birn device had an initial capacity loss of 7 % within the first 50 cycles, with no further loss occurring during 1,000 cycles. Both devices were found to be compatible with voltage windows up to 1.5 V, with higher voltages beginning to deteriorate the devices. Physical bending of the devices showed no damage or change to the devices, with charge discharge capacitance values remaining unchanged during and after subjecting the devices to 100 bending/unbending cycles.
9 Conclusions and Future Work

9.1 Conclusion of Results

Fibre production by wet spinning and film scrolling methods were investigated. Fibres were developed from materials including insulating and conducting polymers, and incorporated nanomaterials including graphenes, carbon nanotubes (CNT), and manganese dioxide. The production of these fibres was optimised by determination of the optimal spinning solutions, coagulation conditions, post-treatment step(s), and combinations of materials. These fibres were characterised, leading to the production of functional, flexible, fibre-based supercapacitor devices.

The use of a room temperature ionic liquid (RTIL) as a dispersant for carbon nanomaterials to produce spinning solutions was investigated. However, these did not yield fibres which were suitable for device production due to insufficient mechanical strength and electrochemical performance. The fibres produced from wet spinning of RTIL dispersions had electrical conductivities up to 31 S cm\(^{-1}\), and displayed rectangular cyclic voltammetry. However, these fibres did not possess the physical strength properties required to make the fibres suitable for the wearable applications, with ultimate tensile strength values between 1 and 7 MPa. The fibres also had high levels of variation in all properties, with relative standard deviations (RSDs) over 100 %, arising from the poor dispersion quality achieved at the concentrations required to produce fibres.

The production of multi-component fibres produced via scrolling polymer films was also investigated. These fibres were treated with sulfuric acid, formic acid, or dimethyl sulfoxide (DMSO), for durations between 5 and 120 min, to enhance their properties and allow them to be used in aqueous environments. The fibres produced were found to be stronger than those produced from RTILs, with ultimate tensile strengths up to 103 MPa. These strengths decreased after treatment, to a minimum value of 29 MPa after treatment with sulfuric acid. The DMSO treated fibres displayed electrical conductivities of up to 130 S cm\(^{-1}\) and specific capacitance values between 1 and 2 F g\(^{-1}\) at 0.5 A g\(^{-1}\), although they showed angular cyclic voltammetry. Fibres treated with formic acid did not survive this treatment process, and fibres treated with DMSO could not be produced in lengths above 1 cm, due to fibre breakage during treatment. Treated fibres were found to be compatible with aqueous systems, without unscrolling during immersion.
Building on the use of conducting polymers in the scrolled film fibres, fibres were wet spun from the conducting polymer PEDOT:PSS, using Orgacon and Clevios PH1000 suppliers. These fibres were treated with sulfuric acid, formic acid, and DMSO, for treatment times between 5 and 120 min. It was found that 5 min treatments were sufficient for all fibres, and treatments had the greatest effect on fibres with thinner diameters. DMSO treated fibres displayed the highest electrical conductivities, with values of 802 S cm\(^{-1}\). Rectangular cyclic voltammetry was obtained, with treated fibres displaying more rectangular results than untreated fibres. The highest charge discharge values, of up to 50 F g\(^{-1}\), were obtained for 5 min DMSO treated fibres, along with the highest ultimate tensile strength values of 145 MPa. Sulfuric acid treated fibres were found to exhibit tensile strength values reduced by an average of 51 % relative to untreated fibres; this was attributed to residual sulfate ions in the fibres. 5 min DMSO treated thin fibres spun from PH1000 PEDOT:PSS (PHTD5) were found to be the overall best performing fibres.

To increase the specific capacitance of PHTD5 fibres, the incorporation of manganese oxides was investigated. Several methods of incorporating these oxides within or on PEDOT:PSS fibres were compared. It was found that chemical formation of the oxides within the fibre from potassium permanganate was not possible, due to degradation of the polymer. Electrodeposition from manganese(II) acetate was found to produce fibres with high initial capacities, up to 200 F g\(^{-1}\) at 0.5 A g\(^{-1}\). However, even with an additional protective coating layer of polypyrrole or PEDOT:PSS, these fibres were found to be brittle, as well as showing high capacity degradation on repeated cycling, with maximum capacity retention of 82 % after 500 cycles. This decrease was found to be continual throughout repeated cycling, with further decreases expected if more than 500 cycles were performed.

Fibres that incorporated birnessite manganese dioxide, or functionalised few layer graphenes (FLGs) (COOH or NH\(_2\) functionalisation) were also produced. The addition of functionalised FLGs to PEDOT:PSS fibres was found not to improve any measured properties of the fibres. The optimal birnessite loading was determined to be 5 wt.% relative to PEDOT:PSS mass. These birnessite-containing fibres were found to have initial capacitance values of 180 F g\(^{-1}\) at 0.5 A g\(^{-1}\), decreasing to 89 % of this value within 500 cycles, and showing no further loss up to a total of 500 cycles. Electrical conductivity and ultimate tensile strength values were measured at 117 S cm\(^{-1}\) and 61 MPa, decreased from
122 S cm\(^{-1}\) and 115 MPa for the equivalent fibres with no birnessite content (PHTU). Rectangular cyclic voltammetry was obtained for all loadings of birnessite, with higher loadings showing greater deviation from an ideal rectangle.

From these fibres it was determined that wet spun PEDOT:PSS fibres containing 5 wt.% birnessite nanotubes presented the best overall fibre to produce a supercapacitor device. A symmetrical supercapacitor was produced using two of these fibres, using a PVA-H\(_3\)PO\(_4\) gel electrolyte. This capacitor was found to have an initial capacity of 72 F g\(^{-1}\) at 0.5 A g\(^{-1}\). Repeated cycling showed a decrease in capacitance to 66 F g\(^{-1}\) within 50 cycles, with no further loss occurring thereafter, up to 1,000 cycles. The device showed no mechanical degradation upon repeated bending/unbending cycles, and could be charged to 1.5 V.

### 9.2 Avenues of Future Investigation

Several avenues for future work building upon this thesis are possible. As an extension of the research conducted, a wider range of chemicals used to treat PEDOT:PSS fibres could be analysed. While three such chemicals have been studied in this work, many more (such as other organic and mineral acids, organic solvents, and metals) may have an effect on the properties of the fibres, and as such a superior treatment may be identified. Combined or successive treatments by multiple chemicals may prove beneficial. Following on from this, more detailed investigation in to the effect of diameter on the increase in properties observed post-treatment could be conducted. By performing one chemical treatment on a range of differing diameter fibres, the effect could be analysed relative to decreasing diameter of the fibres.

Combining the effects of nanomaterial additions, such as that of birnessite, with DMSO treatments, as this was found to be the best treatment, should further boost the properties of the fibres developed. DMSO is an applicable treatment for this, as acids may degrade the manganese oxide (235). In this work fibres with nanomaterials were compared directly against those without nanomaterials, with no further post-treatment. The combination of these two procedures may yield a synergistic effect, allowing for a greater increase than that of each addition/treatment (236-237).

The enhanced use of electrochemical impedance spectroscopy may enable greater insight in to the fibres and more specifically the devices produced. This technique has been used previously to measure properties of fibre materials, such as their specific capacitance.
(238), potentially revealing more information than galvanostatic charge discharge measurements (239-241). Preliminary experiments were performed on several of the fibres produced in this work. Impedance spectra have been presented for PH1000 fibres PHTU (untreated) and PHTD5 (5 min DMSO treatment), as well as a PH1000 fibres containing 5 wt.% birnessite. It is observed that the values obtained through impedance and charge discharge methods are in excellent agreement with each other, showing highly similar values for all three fibre types. The further use of impedance spectroscopy may also allow for greater information to be obtained on supercapacitor devices produced, to further optimise their development. Due to the increased complexity of the devices relative to single fibres, impedance measurements are likely to yield more information over charge discharge measurements.
10 Appendix Items

10.1 List of conferences/events attended, prizes, awards, and grants

- 2014 Surrey Postgraduate Research Conference
  - Presented poster presentation

- 2014 Cheltenham Science Festival
  - Awarded full cost bursary award to attend - £500

- 2015 Royal Society of Chemistry energy materials division young member’s symposium – Derby UK
  - 3rd place poster presentation prize
  - Awarded Royal Society of Chemistry travel grant - £300

- 2015 Surrey PGR conference
  - 2nd place judge’s oral presentation award
  - 2nd place people’s choice oral presentation award

  - Presented oral presentation

- 2015 Fibre Society Fall Conference – North Carolina USA
  - Presented oral presentation
  - Awarded Royal Society of Chemistry travel grant - £600

- 2016 Surrey PGR Conference
  - Presented oral presentation
11 Bibliography


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