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Electrochemical Energy Storage Properties of Nanomaterial Networks

Thomas M. Higgins



A thesis submitted for the degree of Doctor of Philosophy

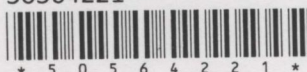
Supervised by Prof. Jonathan Coleman

Chemical Physics of Low Dimensional Nanostructures Group

School of Physics
Trinity College Dublin
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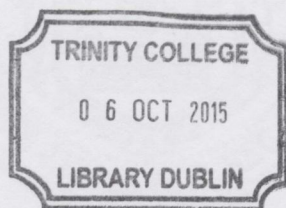


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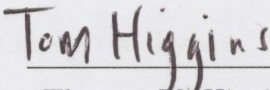
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Thomas M. Higgins

Publications

The work presented in this thesis also appears in the following publications:

1. King, P. J., Higgins, T. M., De, S., Nicoloso, N. & Coleman, J. N. Percolation Effects in Supercapacitors with Thin, Transparent Carbon Nanotube Electrodes. ACS Nano 6, 1732–1741 (2012).
2. Higgins, T. M. et al. Effect of percolation on the capacitance of supercapacitor electrodes prepared from composites of manganese dioxide nanoplatelets and carbon nanotubes. ACS Nano 8, 9567–9579 (2014).
3. Higgins, T. M.; Coleman, J. N., Avoiding Resistance Limitations in High-Performance Transparent Supercapacitor Electrodes Based on Large-Area, High-Conductivity PEDOT:PSS Films. ACS Applied Materials & Interfaces, 7 16495-16506 (2015)

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Summary

Recently, exciting progress has been made towards the creation of electronic devices *via* unconventional fabrication routes. For example, liquid processing techniques such as printing and spraying are enabling the production of nanomaterial-based electronic devices that are assembled directly on everyday substrates, such as plastic films. This approach is interesting as it presents an opportunity to develop electronic devices that are mechanically flexible and even transparent. Clearly, these possibilities will lead to a host of applications that are impossible using traditional manufacturing techniques.

However, realisation of this goal will also require the development of solution processed energy storage and management systems. This work explores the effects of percolation on the properties of transparent electrochemical capacitors using solution processed carbon nanotube networks as electrodes. It was found that the equivalent series resistance, R_{ESR} , and volumetric capacitance, C_V , were thickness independent for relatively thick electrodes. However, once the electrode thickness decreased below a threshold ($t \sim 100$ nm for R_{ESR} & $t \sim 20$ nm for C_A), the properties of the electrode became thickness dependent. This behaviour was found to be consistent with percolation theory and provides insights into the limitations on the achievable capacitance for transparent electrochemical capacitors. It was found that electrochemical capacitor making use of electrodes with thickness independent σ_{DC} and C_V occupy a well-defined region of the Ragone plot. However, electrodes limited by percolation occupy a long tail towards low values of energy and power density. For example, replacing electrodes with transparency of $T=80\%$ with thinner networks displaying $T=97\%$ results in a 20-fold reduction of both power and energy density.

To try and minimise the presence of percolation effects on the properties of transparent electrochemical capacitor electrodes, thin films of a conducting polymer, poly(3,4-ethylenedioxythiophene):poly(styrene-4-sulfonate) were prepared. This was achieved by spraying aqueous dispersions of the polymer onto plastic substrates, enabling the preparation of large area transparent films (up to 324 cm^2). The use of a formic acid post-treatment resulted in a DC conductivity of 936 S/cm . However, the biggest advantage of this material was the low optical conductivity of 24 S/cm (at 550 nm). Combined, these properties indicate excellent performance as a transparent conductor, with a figure of merit of $\sigma_{DC}/\sigma_{op} = 39$. Electrochemical mea-

measurements showed ideal double layer behaviour, with a volumetric capacitance of 41 F/cm³ that was stable with repeated cycling. In contrast to the nanotube networks, the properties of these films remained thickness independent even for the thinnest film prepared (T=99%), indicating a complete absence of percolation effects.

The dependence of charge storage properties on electrode lateral dimensions were also investigated. While absolute capacitance could be effectively improved by increasing the film dimension parallel to the electrode contact, extending the dimension perpendicular to the electrode contact caused a reduction in areal capacitance, C_A . These geometric effects were understood using a simple RC circuits, including a single-arm transmission line for the AC impedance behaviour. Two electrode measurements were obtained for large area transparent films (T=95%, A=108 cm²), providing a capacitance of 12.5 mF at 50 mV/s.

Lastly, significant improvements in the performance of electrochemical capacitor electrodes based on 2D MnO₂ nanoplatelets were achieved by the addition of carbon nanotubes. Electrodes based on MnO₂ do not display high areal capacitance because the electrical properties of such films are poor, therefore limiting the transport of charge between redox sites and the external circuit. In addition, the mechanical strength of these electrodes were low, limiting the achievable electrode thickness even in the presence of a polymer binder. By adding carbon nanotubes to the MnO₂-based electrodes, the electrical conductivity increased by up to eight orders of magnitude (for 40 wt% nanotubes) in line with percolation theory. The nanotube network facilitates charge transport, resulting in large increases in capacitance, especially at discharge and recharge rates at around 1 V/s. The increase in MnO₂ specific capacitance scaled with nanotube content in a manner consistent with percolation theory. It was found that maximum enhancement of the utilisation of MnO₂ can be achieved with the addition of only 10 wt% carbon nanotubes. Importantly, the mechanical robustness was also enhanced, allowing the fabrication of electrodes that were 10× thicker than could be achieved in MnO₂-only films. This resulted in composite films with areal capacitances up to 40× higher than could be achieved with MnO₂-only electrodes.

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Chapter 1

Electrochemical Capacitors

1.1 Introduction

Modern society is characterised by a continuous demand for new kinds of portable electronic devices for use in all the domains of our lives. This is made evident by the explosion in popularity of smart phones over the past decade; more recently, tablet computers have become pervasive; whilst today, wearable electronics such as smart watches and eye-wear are coming into vogue. Although it is impossible to foresee the form that future portable devices will take, we can be certain that their capabilities will continue to expand with time.

Crucial to the performance of portable electronic devices are the energy storage systems that power them. This essential role is played by three classes of electrical energy storage systems; batteries, dielectric capacitors and electrochemical capacitors (ECs). As indicated in Figure 1.1, these differ vastly in the energy and power combinations they are able to provide. Batteries use electrochemically driven bulk-phase transformations to deliver high gravimetric energy that may only be accessed slowly (<1 kW/kg). On the other hand, dielectric capacitors use electrostatic processes to provide small bursts of energy (<0.05 Wh/kg). Between these extremes lie a whole spectrum of energy and power combinations that may only be accessed using ECs. Also known as supercapacitors, these make use of both electrostatic processes and rapid chemical reactions occurring at electrochemical interfaces. The blue diagonal lines in Figure 1.1 provide an alternative comparison between the three energy storage classes, indicating the duration required to dispense or replenish their energy capacity; dielectric capacitors operate in the micro to millisecond range, batteries take a number of hours to completely discharge or recharge, while ECs typically operate over the seconds to hundreds of seconds range.¹

A further distinction can be made regarding the number of discharge/recharge cycles performed over the lifetime of the device. When operated correctly dielectric capacitors have an essentially unlimited cycle lifetime as device operation is entirely electrostatic. In contrast, batteries may sustain only a few hundred cycles before the onset of diminished performance.³ ECs lie between these extremes, with commercial devices often capable of millions of cycles; substantially more than batteries.

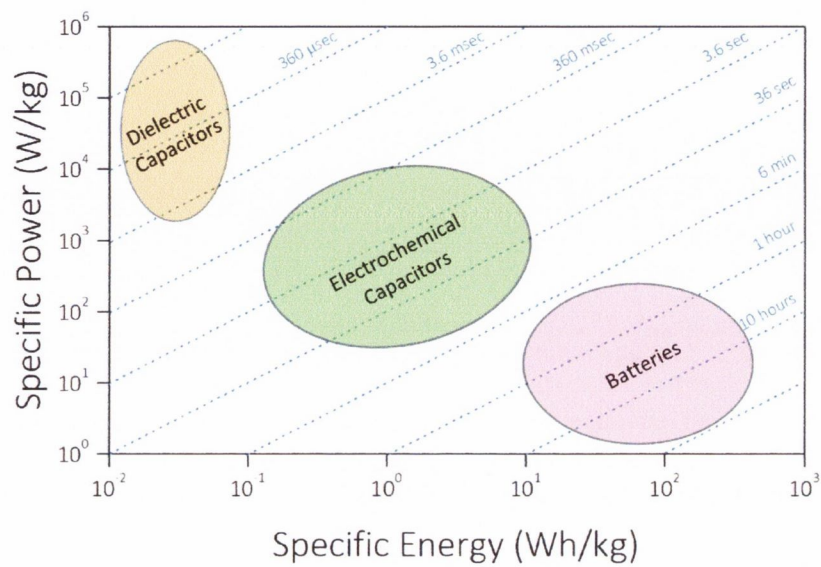


Figure 1.1: Energy-power diagram, also known as a Ragone plot, indicating the general specific energy and specific power combinations available to dielectric capacitors, ECs and batteries. Note that 1 Wh=3.6 kJ, which is the energy transferred in 1 hour at 1 Watt. Image adapted from source.²

Due to their unique position on the energy-power diagram, ECs are a compelling option for use in many emerging portable electronic devices. This is particularly true for applications requiring high current pulses where batteries are not suitable. In addition, there is a growing requirement for prudent energy management as we increasingly turn to renewable energy sources in preference over fossil fuels.⁴ In general terms, making ECs more attractive for applications requires demonstrating improved energy and power, improved cycle lifetime, increased safety and reduced cost. In addition, there are a range of more specific requirements which may be important for particular applications, such as unique self-discharge characteristics or the ability to operate at extreme temperatures. Although EC technologies are a long way from reaching maturity, their general characteristics are well understood.

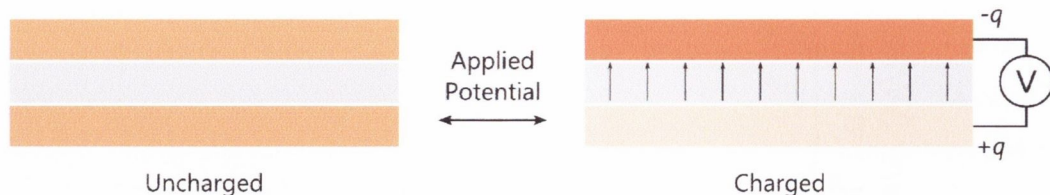


Figure 1.2: The simplest capacitor configuration consists of a pair of parallel plates with an insulator between them. An applied potential across the plates causes charge separation, and an electric field is established in the region between them. This field is a store of energy, able to perform electrical work.

1.2 General Characteristics

A capacitor is an electrical device that stores energy within an electric field. This is achieved most simply using a pair of parallel metallic plates that are separated by an insulating region (Figure 1.2). When a potential difference is applied across the plates a current flows as the capacitor charges, causing negative charges to accumulate on one plate with an equal quantity of positive charges left on the other. An electric field is created throughout the intervening space, and the device is now a source of electromotive force (*i.e.* able to perform work on an electrical circuit). Ideal capacitive behaviour is characterised by a linear relation between the quantity of charge, q , that is accumulated on each plate and the potential difference, ΔV , that is established between them; $q = C\Delta V$.⁵ The proportionality constant, C , is called the capacitance, whose unit is 'coulombs per volt'. This unit is more commonly termed the 'farad' (F).

An EC behaves in a similar manner to the parallel plate device, although it is constructed like a battery. The schematic presented in Figure 1.3 indicates that a typical EC device stack consists of a pair of electrodes that are immersed in an electrolyte solution. These are interposed with a porous inert membrane to ensure the electrodes remain electrically isolated, whilst also enabling the passage of electrolyte ions. The electrodes are the most

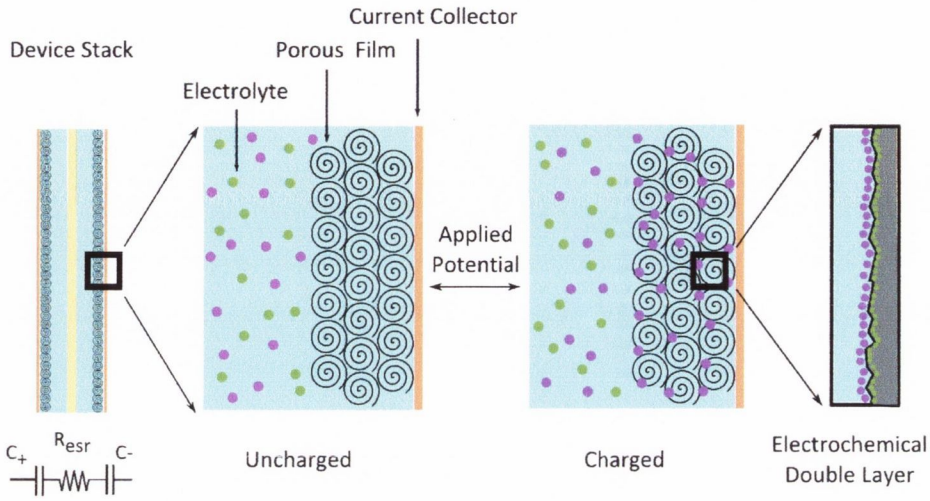


Figure 1.3: An EC device stack indicating in more detail the nature of the electrode/electrolyte interface. The application of a potential difference across the device causes the formation of an electrochemical double layer across each electrode/electrolyte interface.

important aspect of this device. They are normally composed of a metallic foil current collector, on top of which is a porous film of the electrode material. Porosity enables the creation of a large internal surface area into which the electrolyte solution is able to infiltrate, forming a pair of highly spatially extended electrode/electrolyte interfaces.

As for the parallel plate design, when a potential difference is applied across the device terminals, delocalised electrons migrate externally from one electrode to the other. This gives rise to an electric field between them. In this case, charged species from the electrolyte solution quickly migrate towards either electrode; anions to the positive side and cations to the negative one (see Figure 1.3). This action nullifies the electric field throughout the majority of the electrolyte solution, confining it to a very thin region at each electrode/electrolyte interface. As a result, a thin sheet of electrons (or their deficiency) are present on the electrode side of the interface, and a sheet of complementary charge-balancing ions build up in the adjacent electrolyte. These two charged layers are

separated by a sheet of solvent molecules acting as a molecular dielectric. The overall structure is called the 'electrochemical double layer', which behaves much like a parallel plate capacitor (*i.e.* $q = (C\Delta V)$), although in reality the structure is far more complex and consists of compact and diffuse charged layers.

An EC device therefore consists of two of these nanoscopic capacitor-like interfaces arranged in series. In the charged state, the cell voltage is partitioned between the two interfaces, while during device operation (*i.e.* when current, i , flows) the cell experiences an additional potential drop associated with an equivalent series resistance, R_{ESR} , that is: $\Delta V_{cell} = \Delta V_{+interface} + \Delta V_{-interface} + iR_{ESR}$. The R_{ESR} is the sum of various resistances occurring throughout the cell. This includes contributions such as the contact resistance between the current collector and the electrode film, the electronic resistance of the film itself and the ionic resistance associated with ionic motion through the electrode materials and the separator material. This overall quantity must be minimised as it influences the maximum theoretical power, P , with which device may be charged and discharged.⁶ This relationship is indicated in Equation 1.1:

$$P = \frac{1}{4} \frac{\Delta V_{cell}^2}{R_{ESR}} \quad (1.1)$$

The other cardinal measure of EC performance is the energy capacity, E , which depends on ΔV_{cell} and the overall capacitance, C_{cell} , as indicated in Equation 1.2:

$$E = \frac{1}{2} C_{cell} \Delta V_{cell}^2 \quad (1.2)$$

A capacitor is therefore the electrical analogue of a spring, with the potential difference and capacitance equivalent to the spring displacement and spring constant. Just as there are limitations on the maximum displacement of a spring, so too is there a maximum voltage to which a capacitor may be charged before the onset of damaging effects. This is often due to electrochemical breakdown of the electrolyte solvent by a process called electrolysis. For example, when using aqueous electrolytes, the reduction of water becomes thermodynamically feasible if the interfacial potential excursion at the negative electrode reaches $E^0 = 0.0$ V *vs.* the Standard Hydrogen Electrode (SHE). At the other electrode, water may be oxidised for positive potential excursions reaching $E^0 = +1.23$ V *vs.* SHE.

These reactions produce gases at an exponential rate beyond their onset potentials, reducing charging efficiency and damaging the cell. It is therefore generally required that ΔV_{cell} doesn't exceed ~ 1.2 V for aqueous-based electrolytes.⁷ Measures can be taken to extend the electrolysis-free range, for instance, by selecting electrode materials where these reactions are kinetically hindered.^{8;9} However, a more common strategy is to use aprotic organic electrolytes or ionic liquids instead, which can allow more generous potential excursions before the onset of electrolysis (>2.5 volts). Although this can greatly enhance energy storage ($E \propto \Delta V_{cell}^2$), device power often suffers due to inferior ionic conductivity of these systems compared with aqueous electrolytes ($P_{max} \propto R_{ESR}^{-1}$). In addition, non-aqueous electrolytes are often expensive, and they complicate device manufacture due to the need to exclude moisture.

Regardless of which electrolyte system is used, efforts to improve the energy harnessed by ECs have often focused on improving capacitance ($E \propto C_{cell}$). This may be achieved by maximising the spatial extent of the electrode available to the electrolyte solution, through optimisation of its porous structure. Alternatively, there is growing interest in modifying the interface itself to store more charge than is possible using the electrochemical double layer alone. This approach draws upon rapid, reversible electrochemical reactions of a capacitive nature. Whilst an ideal electrode design would employ both of these strategies, whether or not these reactions are actively employed presents a convenient demarcation between EC electrode types, for which the terms 'faradaic' or 'non-faradaic' are used.

1.2.1 Non-faradaic Electrodes

Non-faradaic EC electrodes are designed to exhibit the property of being 'ideally polarisable', meaning that charge does not cross the electrochemical interface during device operation. In this case energy storage is entirely electrostatic, making use of the capacitive behaviour of the electrochemical double layer. The capacitance that arises at such an electrode is given by Equation 1.3:

$$C = \varepsilon\varepsilon_0 \frac{A}{d} \quad (1.3)$$

where A is the area of the electrode accessible to the electrolyte, d is the distance separating the oppositely charged layers at the interface, ε is the dielectric constant of the intervening region where the electric field operates and ε_0 is the vacuum permittivity ($8.65 \times 10^{-12} \text{ F.m}^{-1}$). Experimental values for the areal capacitance arising at non-faradaic electrodes typically fall between 20 and 50 $\mu\text{F}/\text{cm}^2$ depending on the dielectric thickness; over an order of magnitude greater than is obtained using dielectric capacitors.¹⁰ This difference is due to nanoscopic separation between the charged layers at the electrochemical interface, which is ~ 0.5 nm when using aqueous electrolytes compared with a few microns for many dielectric capacitors.¹¹ With this being the case, Equation 1.3 indicates that the dielectric constant of water is much reduced in this environment ($\varepsilon \sim 8$) compared with the bulk ($\varepsilon \sim 80$). This results from orientational confinement of its molecules in the very high electric fields present across the interface ($\sim 10^7$ V/cm).¹¹ We note that the breakdown voltage is usually much higher for dielectric capacitor due to the onset of Faradaic charge transfer reactions between the solvent and electrode interface at relatively low voltages (~ 1.2 V for aqueous based electrolytes).

The most attractive aspect of using the electrochemical double layer to store energy is the immense surface areas able to be created using many carbon-based electrode materials (*i.e.* $>1000 \text{ m}^2/\text{g}$).¹² These values are achieved by a combination of pyrolysis and activation processes¹³ applied to carbon precursors from an assortment of petroleum¹⁴ and biomass based sources.^{15;16} When coupled with an interfacial capacitance of 20 $\mu\text{F}/\text{cm}^2$ or more, specific capacitance values exceeding 200 F/g are possible.¹⁷ Becker from General Electric

was the first to realise the utility of this situation for energy storage, patenting a method to produce non-faradaic ECs based on activated carbon electrodes in 1957.¹⁸ The first commercial devices were made available by a company called SOHIO in 1971, and today there are numerous companies who specialise in EC technologies based on a wide range of non-faradaic type electrodes.^{2,19} Presently, these electrodes are able to provide around 120 F/g using organic electrolytes and around 200 F/g at a single electrode when using aqueous systems. Note that this value is decreased by a factor of ~ 4 for two electrode devices. Specific energy and power for devices based on these electrodes are presently around 3-6 Wh/kg at 5 kW/kg.²⁰

In addition to having very porous morphologies, many activated carbon materials also possess moderate electrical conductivity, ideal polarisability and thermal stability over a wide range and in many cases are cheap to manufacture. This combination of attributes provides carbon with unparalleled suitability as a non-faradaic EC electrode material. The specific structural and morphological characteristics of the carbon precursors are dramatically altered by the pyrolysis and activation processes, with commensurate changes to their physical and chemical properties.

One important consideration is the presence of functional groups on the activated carbon surface. Although these are useful to provide wettability, their presence also has repercussions for the cyclability and self-discharge characteristics of the electrode interface.¹⁰ Another important consideration is the electronic properties of the material produced, which vary greatly among carbon sources and the treatments imposed. These factors influence the proportion of sp^2 and sp^3 hybridised carbon atoms, the presence of lattice defects or heteroatom inclusions as well as crystallite size and orientation.²¹

Following synthesis of the carbon material itself, the next important optimisation process is the assembly of porous electrodes. The most common approach is to mix the activated carbon powder with a polymeric binder, adding a small quantity of solvent to enable the formation of a slurry. The resulting paste-like mixture may then be coated onto the surface of a metallic current collector such as aluminium with film thickness typically in the 10s to 100s of micron range. This method presents an opportunity to combine carbon

types with contrasting properties into the same film. A common example is to mix a high surface area activated carbon with a smaller quantity of another carbon type with superior electrical properties, such as carbon black. Here it is necessary to carefully select the ratio of the various components to confer the best overall properties to the composite. The need for a binder is a disadvantage of this approach as it provides little performance benefits (other than mechanical adherence), while taking up a significant proportion of the overall electrode mass (typically 5 – 10 wt%). As a result, alternative approaches have been explored such as pyrolysis of organic aerogels^{22;23} or woven fibrous structures.^{24;25} These enable the production of electrode materials that are mechanically robust as well as having improved electronic properties.

Common to all these materials is the need to control the distribution of pore sizes that constitute the internal space within the electrode structure. If the majority of pores are too small to accommodate the electrolyte species being employed, the available capacitance will be lower than expected. In certain cases it has been found that when the electrolyte and micropore diameter are well matched, desolvation of electrolyte ions is possible. This allows them to occupy very small micropores (<1 nm), giving rise to enhanced capacitance.^{26;27} One consequence of using porous electrode materials (compared with a planar surface) is the requirement for ions and electrons to translocate throughout the porous network during charge and discharge. This means that a variety of transport resistances are encountered depending on the distance charged species must travel to reach the electrode surface. This has ramifications for energy and power capabilities as the accessible capacitance will then vary with charge/discharge rate. The nature of this behaviour depends on the pore size distribution of the electrode material, whereby it is generally found that a combination of micro (diameter < 2 nm) and mesopores (diameter 2-50 nm) produce the best performance.¹⁹ A range of transmission line equivalent circuit models have been developed to account for this behaviour of porous electrodes.²⁸

Over the past few decades, two new carbon allotropes have come to prominence. These are the pseudo-one and pseudo-two dimensional nanostructures called carbon nanotubes^{29;30} and graphene.³¹ Their general structures are presented in Figure 1.4. Both of these materials have many characteristics that are attractive for use within EC electrodes.³²⁻³⁶

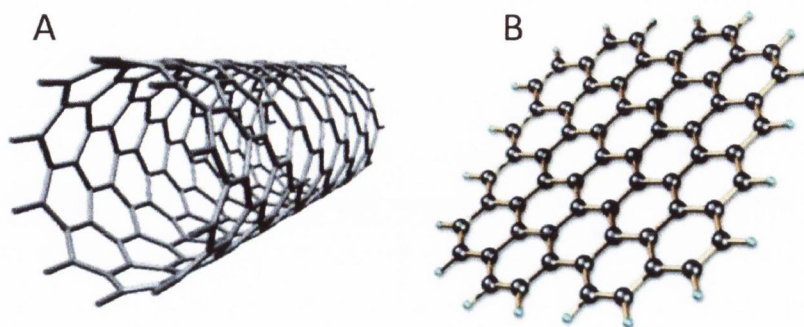


Figure 1.4: Two nanocarbon allotropes; (A) carbon nanotubes and (B) graphene. Image from source.⁴³

Like activated carbon, they possess excellent electrical and electrochemical properties. As every atom is present at the surface they can develop very high specific surface areas. However, one of the most distinguishing feature of these materials is that they are discrete objects with well defined structures, and therefore they can be considered fundamental building blocks from which new materials may be assembled from the nanoscale up.^{37;38} This offers many opportunities for materials with improved performance. Another advantage of carbon nanotubes and graphene is that they may be processed from the liquid phase,^{39;40} enabling electrode fabrication by established printing and spraying techniques. Although these materials have been difficult to produce cheaply and in large quantities in the past, this is gradually changing.^{41;42} It is likely that both these materials will soon play a role in many commercial technologies, including EC electrodes.

1.2.2 Faradaic Electrodes

In addition to the electrochemical double layer, there are a range of other electrode processes that produce a capacitive-like response. These involve the interconversion of species at the electrode *via* charge that is passed faradaically (*i.e.* crosses the electrochemical interface). Three main types of electrode processes exhibit this behaviour; (1) the adsorption and desorption of cations at noble metal surfaces, called 'underpotential deposition', (2) the reaction of redoxable species at the electrochemical interface with cations from the electrolyte and (3) the intercalation of cations within certain intercalation host materials. Common examples of these three reactions are provided in Figure 1.5.

For all three cases we can consider a quantity y (where $0 < y < 1$), which represents the progression of the electrode process, such as the fractional coverage of the electrode surface with an adsorbed species, the fractional conversion of redox species at the electrode surface, or the fractional occupancy of ions at the interlayer sites of an intercalation host material. For these types of systems y is a continuous function of the interfacial potential, V , *via* a Nernstian type relation shown in Equation 1.4.⁴⁴

$$\frac{y}{1-y} = K \exp(VF/RT) \quad (1.4)$$

Here K is an electrochemical equilibrium constant, F is Faraday's constant, R is the gas constant and T is the temperature. As the quantity of charge passed is proportional to the extent of the surface interconversion or intercalation process (*i.e.* $q \propto y$), when differentiated this expression has the form of a capacitance, as shown in Equation 1.5.

$$C_\phi = q_0 \frac{dy}{dV} = \frac{q_0 F}{RT} \frac{K \exp(VR/RT)}{[1 + K \exp(VF/RT)]^2} \quad (1.5)$$

Here q_0 is the charge passed when the conversion process is maximum (when $y = 1$). To distinguish energy storage stored in this manner from capacitance due to the electrochemical double layer, the term 'pseudocapacitance', C_ϕ , is commonly used.

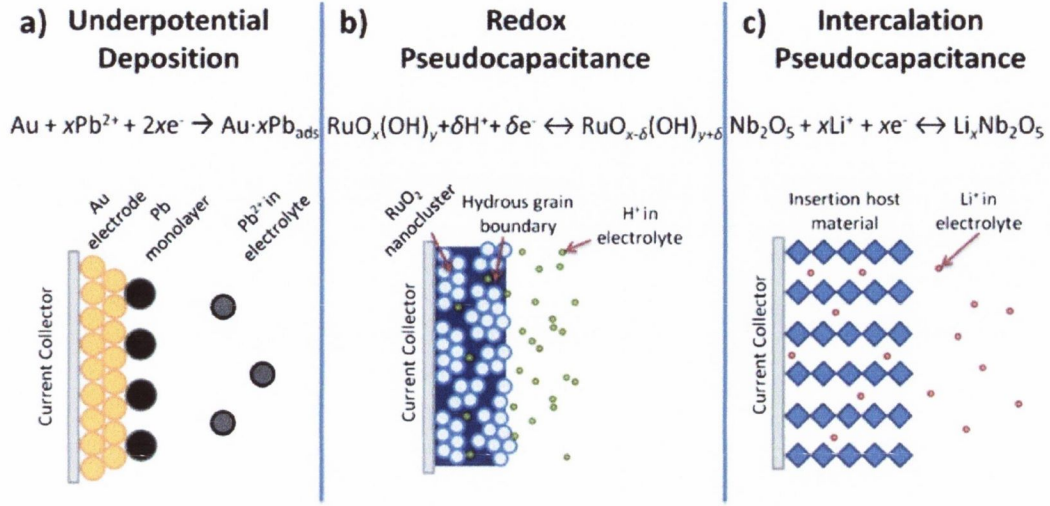


Figure 1.5: Faradaic electrochemical processes resulting in pseudocapacitive behaviour. (A) Cation adsorption/desorption at metal surfaces, also known as 'underpotential deposition', (B) redox pseudocapacitance and (C) intercalation of cations into insertion host materials. Image from source.⁴⁵

Conceptually, faradaic EC electrodes are a bridge between electrodes that exclusively use the double layer to store energy and those of battery systems which use redox induced phase transformations. The resulting interfacial pseudocapacitance can be significantly larger than may be achieved using the electrochemical double layer, and therefore provides a means of enhancing the energy capacity of ECs. For example, some underpotential deposition processes⁴⁴ can produce interfacial capacitance values $>2000 \mu\text{F}/\text{cm}^2$. These reactions can be expressed generally as:



Here M is a noble metal such as Au or Pt and C^+ is an electrolyte species that becomes adsorbed in its surface. In this situation, one or more electrons may be accommodated for every reactive atom at the electrode surface (depending on n), which is appreciably more than the ~ 0.2 electrons/atom accommodated at the electrochemical double layer.¹⁰ However, underpotential deposition reactions aren't particularly useful for energy storage applications as the potential window over which they operate is usually narrow (~ 100

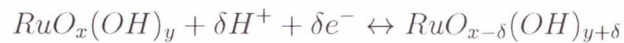
mV). Aside from being costly, these metals are also difficult to fashion into high surface area electrodes that would make them competitive with carbon-based EC electrodes. As a result, there is far more interest in developing faradaic EC electrodes making use of pseudocapacitive surface redox reactions and more recently, rapid intercalation processes.

A general electrode reaction for surface based redox processes can be expressed as:



Here a surface species in its oxidised form, $Ox_{surface}$, becomes reduced by electron injection. Electroneutrality is maintained by concurrent covalent interaction with a cation from the electrolyte, C^{+} . To be attractive for energy storage applications candidate electrode materials must undergo this process without large structural re-organisation, allowing it occur quickly and reversibly.

Ruthenium dioxide is prototypical for this type of electrode behaviour. First characterised for this purpose in 1971, RuO_2 demonstrates pseudocapacitance that is independent of voltage over the entire water window (1.23 V).⁴⁶ This characteristic has been attributed to its ability to undergo multiple redox processes which overlap across this voltage range:⁴⁷



When $\delta=2$, a theoretical capacitance of 1450 F/g results. Specific capacitance values of over 700 F/g have been realised experimentally when using protic electrolytes such as $H_2SO_4(aq)$.⁴⁸ An important advantage of this material is its propensity for both electronic and ionic transport, with high metallic conductivity (10^5 S/cm)⁴⁸ and the ability to rapidly conduct protons within the bulk when synthesised in a hydrated form.⁴⁹ Despite these excellent properties, RuO_2 is too expensive to allow its widespread use.

As a result, numerous cheaper alternatives are being explored. Two important classes of these are the transition metal oxides (such as MnO_2 ,⁵⁰ Fe_3O_4 ,⁵¹ Nb_2O_5 ,⁵² and MoO_3 ⁵³). These materials can be prepared with a wide variety of crystalline forms with differing suitability to provide rapid and reversible pseudocapacitance. As a result many studies have been conducted which explore different synthetic approaches and the features which determine their performance within faradaic EC electrodes.

In recent years, a significant research focus has been dedicated to the control over the morphology of inorganic redox active materials. Nanostructured materials maximise the proportion of atoms exposed to the electrolyte, and hence are able to participate in charge storage.⁵⁴ When applied to intercalation materials, nanostructuring greatly reduces solid state diffusion within the host that would otherwise prevent these charge storage processes from operating at high rates. For this reason, the discharge and recharge behaviour of many typical intercalation materials can take on a pseudocapacitive character when present in a highly divided nanostructured form.^{52;55;56}

An impediment of many otherwise promising redox active electrode materials is poor electrical conductivity. This means that gravimetric pseudocapacitance approaching theoretical values is seldom achieved except when these materials are present as nanoscopic thin films deposited on metallic substrates. Although MnO_2 has a theoretical capacitance of 1370 F/g,⁵⁷ when it is present as thicker films necessary for large absolute capacitance, this value is greatly reduced. For example, Lee *et al.*, reported a specific capacitance of only 0.13 F/g for a 20 μm thick MnO_2 film (2 mV/s).⁵⁸ One common solution to this problem is to combine the pseudocapacitive material with a nanoconductor such as carbon-black, acetylene black, carbon nanotubes or graphene to form a composite electrode.⁵⁸⁻⁶⁴ In this situation it is also favourable to employ nanostructured materials to minimise the transport path length of electrons through the pseudocapacitive component and maximise its interfacial contact area with the conductive component. Numerous synthetic approaches have been explored to produce composite electrodes,⁶⁴ such as carefully decorating a high surface area and highly conducting carbon material with some pseudocapacitive material,⁶⁵ or simply mixing the two components together with the assistance of a polymeric binder.⁶⁶

There are a number of alternative material classes being investigated which display excellent pseudocapacitive behaviour while also possessing good intrinsic electrical conductivity. These include carbon materials that have been modified to possess redoxable functional groups⁶⁷ (a common example being graphene oxide^{68;69}), a range of conjugated polymers^{70;71} and an emerging class of conducting layered materials called the MXenes.^{72;73}

Pseudocapacitive processes always occur in parallel with charge and discharge of the electrochemical double layer. As a result, the total current that arises at faradaic EC electrodes can be expressed as the sum of these two contributions: $I_{total} = I_{non-faradaic} + I_{faradaic}$. This means that regardless of which pseudocapacitive material is employed, the additional charge storage provided by the faradaic pathway can only be accessed through an attendant resistance of some kind.⁴⁴ As all the resistances encountered throughout the cell contribute to the R_{ESR} , there will always be a penalty to the power capability of the electrode. Therefore, although the motivation behind using pseudocapacitive materials is to increase the energy density of ECs towards that of batteries, these improvements are only warranted if there is an acceptable compromise to resulting power density and cycle lifetime of the electrode. Of course, this compromise will depend on the end application of the energy storage device.

1.3 Emerging Transparent & Flexible Applications

With recent progress in the synthesis and processing of nanomaterials, it is becoming clear that future portable electronic devices will possess capabilities that are vastly different from those available today.⁷⁴ For example, there is growing interest the creation of electronic devices with unusual properties such as being flexible,^{75;76} stretchable,^{77;78} foldable⁷⁹ and even transparent.^{80;81} These will make available many applications that are impossible using traditional manufacturing techniques, for instance, electronic apparel,^{82;83} rollable displays,⁸⁴ discrete 'epidermal electronics'^{85–88} and a range of embedded environmental monitoring technologies that will constitute the 'Internet of Things'.^{89–91}

One of the most promising approaches to achieve devices such as these is *via* liquid phase processing. Here, nanomaterials are dispersed in suitable liquids, making them available to a host of methods to transform the suspended nanomaterials into macroscopic structures. For example, printing and spraying techniques allow controlled deposition of nanomaterials, converting them into films with well defined thickness and spatial features.^{87;92;93} If dispersions of different nanomaterials are mixed and processed in the same way, hybrid structures can be obtained whose properties may differ considerably from their components. Finally, layering different printed structures on top of one another can form the basis for all-printed electronic and electrochemical devices.

The realisation of all-printed devices will require combinations of many materials with differing electronic, optoelectronic and electrochemical properties. This necessitates the availability of a wide range of different nanomaterials in a liquid processable form. Probably the best way to achieve this is by liquid phase exfoliation.^{40;94;95} Here, energy is supplied to overcome the van der Waals forces that operate between nanomaterials, followed by stabilisation in liquids designed to prevent their aggregation. This can be accomplished using a variety of approaches and will be discussed in more detail in Chapter 2. Liquid phase exfoliation was pioneered for carbon nanotubes,⁴⁰ it was later applied to graphite to produce graphene³⁹ and more recently has proven an effective means of producing many other two-dimensional nanomaterials from layered crystals.⁹⁴ These are likely to play a

variety of roles in printed electronic devices due to their inherent processability and diverse properties.⁹⁵ Crucially, liquid phase exfoliation is simple and enables the production of high quality nanomaterials in large quantities.⁴¹

Using this approach in combination with other manufacturing techniques, a range of transparent and flexible device components have already been demonstrated. These include the elements of circuitry, such as conductors,^{96–99} dielectric capacitors,^{100–102} memory,¹⁰³ diodes¹⁰⁴ and transistors.^{92;105–113} These will be useful to process the information created by a range of sensing components for mechanical stimuli such as pressure^{114;115} and strain¹¹⁶ or the detection of chemical and biological species.^{91;117–119} This information may then be communicated to the user by various display technologies^{120–122} or audio speakers.¹²³ Transparent/flexible energy harvesting capabilities are also being explored using photovoltaic^{124–128} and piezoelectric^{114;115;129;130} technologies. These could enable device functions to be performed autonomously.¹³¹

The realisation of transparent/flexible devices will also require energy storage and management systems with equivalent atypical properties. Present day approaches to the design of energy storage devices, such as coin-cells and other rigid modules, are not appropriate for mechanically deformable applications. As a result, a number of alternative strategies are being explored to produce flexible ECs^{132–136} and batteries.^{137–140} These have been achieved by sandwiching flexible components together to form a complete device,^{137;141} or alternatively, constructing planar interdigitated electrode structures.^{142–144} Figure 1.6 presents an elegant example of this approach. Here a film of insulating graphene oxide has been reduced to a conducting form using an infrared laser. The resulting pairs of interdigitated electrodes form the basis for planar flexible ECs.^{142;145}

By either scaling down the electrode thickness or forming grid-like electrodes, similar devices can be produced that are also optically transparent. Whilst examples of transparent batteries are presently scarce,¹⁴⁶ a significant number of research groups are exploring the properties of transparent ECs.^{135;147–157} A wide range of electrode materials have been explored for this application, such as carbon nanotubes,^{135;155} graphene,¹⁵⁷ In_2O_3 ,¹⁴⁹ MnO_2 ,^{150;152} RuO_2 ¹⁵⁸ and polyaniline.¹⁵⁹ Therefore, as for traditional ECs, both faradaic

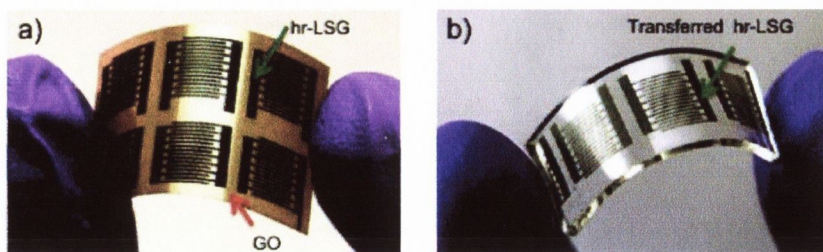


Figure 1.6: (A) Planar Interdigitated EC device created using a film of graphene oxide and then using Lightscribe infrared laser patterning to selectively reduce the material forming pairs of electrodes. An overlying electrolyte layer enables charge to be stored electrochemically. (B) These devices can be transferred onto flexible plastic substrates such as polydimethylsiloxane. Image from source.¹⁴⁵

and non-faradaic charge storage mechanisms are being explored. The majority of this work has focused on the properties of very thin films of nanomaterials supported on transparent/flexible plastic substrates.^{101;149;151;155;159;160} Using this approach, a complete device can be assembled by stacking two of these layers with an intervening electrolyte layer. The overall transmittance of the device stack is the product of transmittance of each constituent layer.

Conformal thin film electrodes have minimal processing requirements making this approach amenable to commercial manufacture, for example, by reel-to-reel processing. As this field is in its infancy, this simple approach provides the most convenient platform to investigate the fundamental charge storage properties of transparent electrodes. Although at present the principles dictating the performance of transparent ECs are poorly understood, transparent networks of nanomaterials have been extensively studied over the last decade for use as flexible/transparent conductors.^{98;161} Many of the insights provided by this work will be applicable to the creation of high performance transparent/flexible ECs.

Chapter 2

Experimental Methods and Characterisation

2.1 Nanomaterial Processing

2.1.1 Liquid Phase Exfoliation

2.1.1.1 Sonication

In their natural form, nanomaterials tend to exist as aggregated clumps due to the attractive van der Waals forces operating between them.¹⁶² This tendency is particularly problematic for nanomaterials with high aspect ratios, rendering many of their desirable properties inaccessible.⁴⁰ Thus, whether produced by synthetic methods or dug straight from the ground, nanomaterials often need to be individualised as much as possible before applications can ensue.

As discussed in Chapter 1, the process of liquid phase exfoliation provides an effective route to produce stably dispersed nanomaterials in a highly divided state, which may then be converted to nanostructured materials and devices. For the work presented in this thesis, nanomaterial dispersions have been prepared by this approach from nanomaterial powders.

This involves taking a quantity of powder and mixing it with a specifically chosen solvent or aqueous surfactant solution. The mixture is then subjected to probe or bath sonication. These impart energy to the system *via* ultrasonic pressure waves created by a piezoelectric crystal, causing a variety of effects such as local heating, cavitation and shear forces.¹⁶³ As a result, the crystalline powder is broken apart or 'exfoliated' into a variety of nanostructured constituents. Probe sonication provides more power, enabling the production of larger volumes (~ 100 mL) of dispersed material (Figure 2.1), while bath sonication is better suited to re-exfoliation of smaller quantities of previously probe sonicated dispersions. This is useful to reverse minor re-aggregation immediately prior to further processing into films.

This approach is applicable to carbon nanotubes, which tend to exist as ropes or bundles, and layered materials such as graphene or boron nitride, which tend to stack on

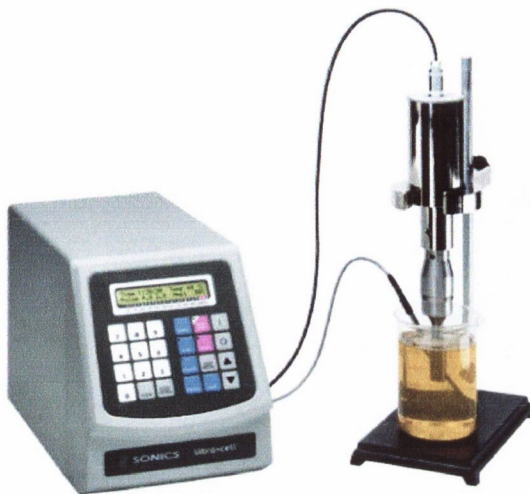


Figure 2.1: Sonic tip used for the preparation of exfoliated nanomaterials in liquids. Vibracell, GEX750, 750 W, 20 kHz from Sonics Materials Inc.

top of one another to form bulk crystals. Although complete individualisation of the nanoconstituents is generally not possible, this method enables the production of reasonable quantities of nanomaterials in a highly divided state.^{94;95} Although covalent bonds are less likely to be overcome than van der Waals interactions during sonication, this does occur and is termed 'sonication induced scission'. This process causes a reduction in mean flake length of material produced, which scales with sonication time as $t^{-1/2}$.^{59;164} Other than the creation of additional edge sites due to this process, sonication does not appreciably alter the properties of nanomaterials, such as the creation of defects or other structural changes.³⁹ Therefore, although sonication time must be minimised if large aspect ratio materials are required, it is a very useful processing method if the native properties of the nanomaterial need to be retained.

While this approach is an effective way to produce nanomaterial dispersions in the laboratory, it doesn't allow the throughput required for commercial applications. This being the case, shear mixing has recently been demonstrated for the production of similar quality dispersed material, though at the production rates necessary for industry-scale manufac-

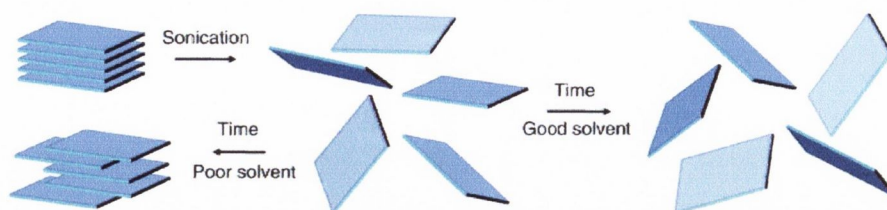


Figure 2.2: General liquid phase exfoliation process. Sonication imparts the energy required to separate the layers. However, solvent selection is important to prevent their re-aggregation. Image from source.⁹⁵

ture.⁴¹

2.1.1.2 Stabilisation

Once exfoliated, it is necessary to stabilise the dispersed material to inhibit re-aggregation. A large body of research has been created exploring this problem and has resulted in a number of effective strategies.⁴⁰ The first of these involves carrying out the exfoliation process using particular solvents that are known to interact favourably with the dispersed materials, stabilising it in solution (see Figure 2.2). Arguments founded using classical thermodynamics suggest that more effective solvents are those whose surface properties match the surface properties of the dispersed nanomaterial.^{165;166} A number of amine based solvents are effective for the production of high quality and stable dispersions of carbon nanotubes, graphene and other materials; champion solvents include N,N-dimethylformamide^{167;168} and N-methyl-2-pyrrolidone¹⁶⁹. Unfortunately, these are expensive, toxic and make further processing difficult due to high boiling points ($T_{\text{boiling}} \sim 150^{\circ}\text{C}$ and 200°C , respectively). As a compromise between these factors, isopropanol (IPA) has been demonstrated as a reasonably effective dispersant for a number of nanomaterials,^{59;97;170} while also being inexpensive, relatively non-toxic and more easily removed when converting the nanomaterial dispersion to films and other structures ($T_{\text{boiling}} \sim 80^{\circ}\text{C}$).

Alternatively, there are many benefits to dispersing nanomaterials in water. It is abundant and therefore inexpensive, non-toxic, and has a relatively low boiling point ($T_{\text{boiling}} \sim 100^\circ\text{C}$). Although water is an inherently poor dispersant, steps can be taken to modify the interfacial properties between the nanomaterials and solvent molecules to provide electrostatic or steric repulsion between the dispersed entities.⁴⁰ This strategy can be achieved by carrying out non-covalent or covalent functionalisation. A common non-covalent approach involves the addition of amphiphilic molecules to the dispersion when sonicating.¹⁷¹ Common surfactants include Triton X-100, sodium dodecyl sulfate and sodium dodecylbenzene sulfonate.⁴⁰ These adhere to the nanomaterial surface, exposing charged or polar functional groups to the solvent environment to provide stabilisation.¹⁷² These materials often remain adsorbed to the nanomaterial surface, which could be a disadvantage in certain applications. Covalent functionalisation means altering the surface chemistry of the nanomaterial, often to impart polar functional groups that may interact with the water, resulting in stabilisation.¹⁷³ Although this approach is very effective, it necessarily modifies the resulting properties of the nanomaterial,⁴⁰ hence must be used judiciously.

2.1.1.3 Centrifugation

Regardless of whether sonication or shear mixing is used to achieve exfoliation, the dispersed material is polydisperse, meaning it contains a range of nano-sized objects with differing exfoliation states and lateral dimensions. Exfoliation state is often characterised by the distribution of bundle diameter (for 1D objects) or layer thickness (for 2D objects) of the material present in dispersion. Control over this aspect of the produced dispersion is crucial from two standpoints; larger material is less stable in solution, falling out with time due to gravity and control over the dispersion composition is important for its optimal use in many applications. The electronic properties of nanostructured materials can vary greatly with exfoliation state.^{174;175} Also, the lateral dimensions determine the ratio of edge to basal plane sites^{176;177} as well as intercalation characteristics.⁵⁵ These aspects are both important for electrochemical applications. Accurate information about the exfoliation state of the produced dispersion has, until recently, only been possible using

time consuming analysis by techniques such transmission electron microscopy (TEM) and atomic force microscopy (AFM). However, spectroscopic metrics have started to become available which greatly simplifies this process.¹⁷⁵

Presently, the most effective way to alter the polydispersity of exfoliated nanomaterial is by centrifugation. Centrifugation facilitates the sedimentation process by applying a centripetal acceleration that is far greater than gravity. This is achieved by using a motor to rotate the dispersion at high speeds, causing a force perpendicular to the rotation axis. Larger particles reach the bottom of the sample vial faster than smaller ones and therefore presents a means of selecting different components of the dispersed material. Parameters influencing the selection process are the rotation speed and spinning time.¹⁷⁸ Either the supernatant can be retained if small material is required, or it can be discarded and the sediment re-dispersed in fresh solvent if large material is required. While reasonably effective, with the availability of spectroscopic metrics for exfoliation state,¹⁷⁵ it is likely that superior size selection techniques will soon be developed.

2.1.1.4 UV-visible Spectroscopy

In this work, dispersion production was achieved using protocols developed previously in our laboratory. As such, characterisation of nanomaterial dispersions was simply to determine the concentration of the dispersed material prior to the production of films. For this purpose, UV-visible spectroscopy has been employed.

In the near ultra-violet and visible spectral range (200-800 nm), absorption of light by matter results in excitation of outer electrons to higher energy states. The lowest energy transition is from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), whereby the difference in energy between the two states determines the absorbed photon wavelength. Due to transitions between various vibrational and rotational states, absorption spectra typically appear as bands.¹⁷⁹

In a typical experiment, monochromatic light with irradiance (energy per unit area per second), I_0 , is directed at a sample and the irradiance of the light which emerges, I , is

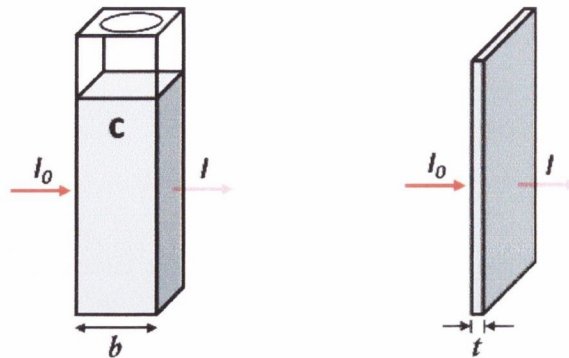


Figure 2.3: In a typical absorbance spectroscopy measurement, a liquid sample is placed in a transparent container with known pathlength, b , called a cuvette and irradiated with monochromatic light with intensity I_0 . The intensity of the light that penetrates the sample, I , is measured. Alternatively, for solid state measurements a film material with some thickness is placed in the beam path, and the same quantities are measured.

measured by a photodetector. These quantities are related to the absorbance, A , using Equation 2.1, known as the Beer-Lambert law.

$$I = I_0 e^{-A} = I_0 e^{-\alpha t} \quad (2.1)$$

A is related to the concentration of the absorbing species, C , as $A = \epsilon b C$, where ϵ is known as the extinction coefficient, and b is the pathlength. A similar measurement can also be made using film materials which are partially transparent to visible light. Here t is the thickness of absorbing medium, and α is known as the absorption coefficient. Both of these configurations are demonstrated in Figure 2.3. There are a number of opportunities for attenuation of the incident light that aren't due to the sample, such as reflection at the air/cuvette and solution/cuvette interfaces, or absorbance due to the solvent. To account for these, I_0 can be measured for using a blank sample (*i.e.* with everything present except the analyte). The transmittance, T , of the absorbing medium is the ratio of incident and measured irradiance, $T = I/I_0$, which is often calculated for the transparent films prepared in this work. These measurements can be repeated at a variety of incident wavelengths and used to create an absorbance or transmittance spectrum, which provides a range of useful information about the analyte.

To determine the concentration of a nanomaterial dispersion, a range of volumes, V , are pipetted onto pre-weighed glass cover slides. After gentle heating ($T=80^{\circ}\text{C}$), the mass of material, M , can be determined for each sample by reweighing and subtracting the cover slide mass. A calibration curve can then be created whereby the concentration is determined using $M = CV$. Taking the dispersion, a dilution series can then be prepared and the optical absorbance of each be measured. A plot of A vs. C can be used to determine ε at some wavelength. Once known, extinction coefficient can be used to determine the concentration of subsequent dispersions of the same material.

2.1.1.5 Film Formation

Thin film materials form the basis of countless technologies we rely upon every day. The most basic property of any film is its thickness. Depending on the application, this can vary from only a few atoms thick to hundreds of micrometers. Although present commercial EC electrode materials are usually at the upper end of this range, for emerging applications such as transparent and flexible ECs, film thickness can be substantially lower ($< 100\text{ nm}$). The properties of these ultra-thin films are often very different from a thick film of the same composition. This is to the need for greater diffusion times for charged species for thicker films which in turn alters the rate performance of a given electrode material.¹⁸⁰ As such, comparison between the performance of EC electrodes can only be made if they have similar thickness. From an economic standpoint, a given film should be as thin as possible while maintaining its intended purpose.

Many film formation techniques have been developed. These differ in the thickness range over which they are best suited, as well as the control they provide over the film composition, porosity, lateral dimensions and throughput. As has been mentioned in Chapter 1, electrode formation for EC applications is usually achieved by mixing the components with a small amount of solvent to form a slurry.¹⁸¹ Following this, doctor blading can be used to transform the slurry into a film onto the substrate and passing a blade over the surface at a set height to spread out the material. This is often followed by the use

of pressure to cause compaction of the film, which decrease porosity and increases both mechanical adherence and electrical conductivity.

For the work presented here, liquid phase processing has been used to convert the nanomaterial dispersions into films. Numerous techniques being employed to do so include evaporative casting, spin coating, dip coating, mayar rod coating, Langmuir-Blodgett coating, vacuum filtration, freeze drying, airbrush spraying, inkjet printing, rotogravure printing, screen printing and electrophoretic deposition¹⁸². These each have their own particular advantages and disadvantages depending on the intended application of the films. For the work presented here, vacuum filtration and airbrush spraying have been used.

Vacuum filtration involves application of negative pressure using a pump to draw a liquid dispersion through a filter membrane, retaining solids larger than the pore size of the membrane. When all the liquid is removed a mat-like film of the nanomaterial contents of the dispersion is created on surface of the filter membrane. This set-up and an example film are presented in Figure 2.4. This technique provides excellent control over the quantity of material deposited onto the membrane by filtering selected volumes of a dispersion for which the concentration is known. This determines the mass per unit area, M/A , of material on the membrane surface as well as the film thickness, t . Mass per unit area and film thickness are related *via* $M/A = \rho t$. Here, ρ is the film density. Although the nanomaterials are deposited with random lateral orientation, they tend to fall along the plane of the film. As the flow rate through the membrane can vary locally, this promotes the production of films that are spatially uniform. As once some material has been deposited in a certain location the deposition rate at that point is reduced, favouring deposition elsewhere on the membrane. This self-regulating quality is difficult to achieve using many other methods, and it is important when producing ultra-thin films where the resulting properties are sensitive to spatial uniformity of the nanoscale constituents on the surface.¹⁸³ This an important theme of the research presented in Chapters 4 and 5. Once a film has been formed on the filter membrane surface, a simple transfer process is used which involves sandwiching the film face down on the substrate of choice (such as plastic film) and exposing the filter membrane to acetone vapour followed by a series



Figure 2.4: Vacuum filtration apparatus for the production of nanostructured films.

of acetone baths. This leads to dissolution of the nitrocellulose leaving the nanomaterial network on the new substrate.

One of the most important advantages of liquid phase processing of nanomaterials is the ease by which composite films can be prepared. To do so, two or more dispersions are mixed together and processed as described. Through judicious partnering of select materials, composites with new combinations of properties can be easily obtained.^{184;185} Crucially, the ratio of the component materials is readily controlled by the individual volumes of the dispersions that are combined, giving an additional dimension of control over the resulting composite. This opportunity is an important theme of the research presented in Chapter 5.

Although vacuum filtration is an effective means for producing films for laboratory use, it isn't an ideal approach for commercial manufacture of nanomaterials. This is because the maximum film dimensions are defined by the size of the filtration apparatus, the filtration membranes aren't able to be reused, and further processing steps are required to transfer

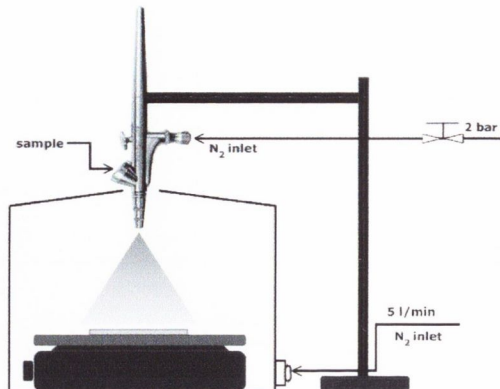


Figure 2.5: An airbrush spraying set-up used in this work to produce uniform transparent flexible films. Image from source.¹⁸⁶

the film onto other substrates. As a result, a wide range of liquid handling techniques have been developed to provide more sophisticated control over the deposition of nanomaterial dispersions, in a manner more amenable to mass production.

Airbrush spraying is probably the best way to produce large area films of materials in a continuous manner. In Chapter 5 of this work, this technique has been employed for the production of transparent films of a conducting polymer directly onto flexible plastic substrates. The airbrush set-up delivers liquid onto a substrate by the process of nebulisation. Here, air is passed through a small nozzle which creates negative pressure, at which point a controlled volume of the liquid phase is injected into the path of the gas *via* a external reservoir. The liquid is converted into droplets due to its interaction with the high velocity stream of air and is directed towards a nearby substrate. By heating the substrate the carrier solvent will evaporate rapidly on contact, avoiding 'coffee staining' effects associated with slow drying of droplets. A robot arm has been used to control the spraying process, which greatly improves uniformity and reproducibility of the films that are produced. This set-up is demonstrated in Figure 2.5.

2.1.2 Characterisation of Nanomaterial EC Electrodes

2.1.2.1 Thickness Measurements

Contact profilometry was used to measure the thickness of the transferred nanomaterial films produced in this work. Here, the sample is transferred onto a rigid substrate such as glass or silicon and placed onto profilometry stage. A profile of the sample is then able to be created by passing a sensitive stylus laterally over the substrate and onto the a region of the film. This creates data based on the stylus height as a function of its lateral position. The obtained film profile can then be used to provide measurement of the film thickness. In this work, all thickness measurements are the average of four profiles obtained at different regions of the film.

2.1.2.2 Scanning Electron Microscopy

This technique was used to gain information about the surface morphology of samples with much higher spatial resolution than may be achieved with optical microscopy (typically < 10 nm). A fine electron beam is created by an electron source (thermionic emission from a tungsten element). The beam is passed through a two stage magnetic lens system separated by an aperture, which together control its diameter and current as it is rastered along the specimen.

The electrons may interact with the sample in a variety of ways, as indicated in Figure 2.6. Electrons entering the sample undergo scattering, the penetration of which is determined by the electron energy and atomic mass of elements present. Secondary electrons are produced by emission of valence electrons, which are detected and used to create an image of the sample. Secondary electrons have low energy (< 50 eV), and therefore only those close to the surface are able to reach the detector. The angle of incidence between the beam and the sample strongly influences the intensity of secondary electron emission and therefore they are very sensitive to surface topology. Back scattered electrons possess much higher energy than secondary electrons and are sensitive to a specimen's

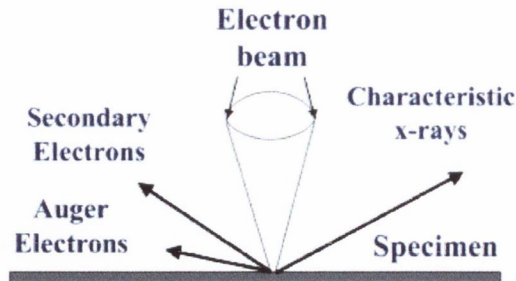


Figure 2.6: Schematic of the SEM technique depicting different types of interactions of electrons with the specimen. Image adapted from source.¹⁸⁷

atomic composition and crystalline orientation at the surface. The intensity of these electrons also varies with incident angle of the sample with the beam, providing topological information. Characteristic X-rays and Auger electrons may also be detected, which provide information about the atomic composition of the specimen.

2.1.2.3 Current-Voltage Measurements

The electrical properties of films prepared in this work were examined by the four point probe technique. Here four parallel contacts are made to the surface of the film sample as demonstrated by Figure 2.7. A current is passed through outer contacts which passes through the test sample. The voltage drop across the inner contacts is measured and the ratio of this voltage with the current is calculated. This quantity defines the resistance across the two internal connections, R (*i.e.* $R=V/I$). Using this configuration, resistive contributions due to the contact electrodes and external leads do not contribute to the calculated resistance. As such, this quantity is determined only by the properties of the test sample; its resistivity, ρ and the geometry (width, W , thickness, t and separation, L) *via* equation 2.3.

$$R = \rho \frac{L}{tW} = \frac{1}{\sigma_{DC}} \frac{L}{tW} \quad (2.2)$$

Here t is the sample thickness and σ_{DC} , is the direct current conductivity, the reciprocal of resistivity. When measuring the electrical properties of thin films it is useful to normalise

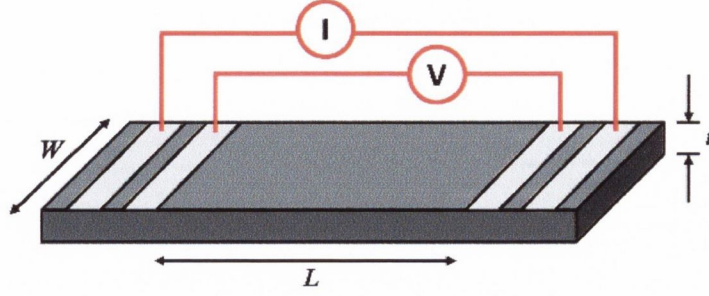


Figure 2.7: Experimental set-up for four point probe electrical measurements of a film sample.

resistivity to the film thickness, t , to produce a quantity called the sheet resistance, R_s , shown in Equation 2.3.

$$R = R_s \frac{L}{W} \quad (2.3)$$

Thus R_s is related to the DC conductivity *via* Equation 2.4.

$$R_s = \frac{1}{\sigma_{DC} t} \quad (2.4)$$

The sheet resistance therefore has the units Ohms. To distinguish this quantity from a regular resistance, this quantity is referred to as Ohm/square. This is the resistance that would be measured for a film material with square dimensions (*i.e.* $L=W$).

2.1.2.4 Electrical Percolation and Nanomaterial Networks

For nanomaterial films with transmittance in the relevant for transparent technologies ($T > 90\%$), electrical percolation also influences the performance of transparent networks.^{161;188}

Electrical percolation describes the onset of electrical conductivity across a previously insulating region, once conducting links have been added at a density exceeding some critical value. This is called the percolation threshold. For conducting elements randomly deposited in-plane and above the percolation threshold, the conductivity follows a percolation scaling given by Equation 2.5.¹⁸⁹

$$\sigma_{DC} \propto (N_A - N_{A,C})^{n_{DC}} \quad (2.5)$$

Here N_A is the number of elements per unit area, $N_{A,C}$ is the percolation threshold and n_{DC} is the percolation exponent. Equation 2.5 can also be expressed in terms of film thickness, t , rather than conductor density,¹⁹⁰ given by Equation 2.6.

$$\sigma_{DC} \propto (t - t_c)^{n_{DC}} \quad (2.6)$$

Here t_c is the threshold thickness below which there are no conducting pathways. This equation often describes the electrical properties of nanotube networks until another transition thickness, called t_{min} , where conductivity becomes thickness invariant.^{191;192} The critical exponent for 2D systems is 1.33. Although experimental values for this exponent can differ from the universal value¹⁸⁸, behaviour has been observed for a variety of nanomaterial network types.^{97;98;161;188} A recent review has examined the network transmittance at which the t_{min} transition occurs among a wide range of published networks.⁹⁸ This transmittance varies from around 45% to 92%. With regards to preparing thin films with technologically relevant transmittance ($T > 90\%$), this means that for the majority of networks, the electrical conductivity is within the percolative regime. Although transparent networks of carbon nanotubes are inferior to transparent networks of metallic nanowires,⁹⁷ they may find use in applications where metallic nanowires don't possess the requisite chemical stability.¹⁹³

Percolation theory can also be applied to electrical properties of conductor-insulator composites, such as when carbon nanotubes are embedded in an insulating polymer¹⁹⁴ or inorganic matrix.¹⁸⁴ Here the electrical conductivity with volume fraction, ϕ , as a power law, shown in Equation 2.7.

$$\sigma_{DC} \propto (\phi - \phi_c)^{n_{DC}} \quad (2.7)$$

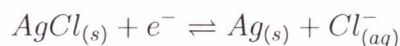
Similarly to the two-dimensional case, ϕ_c is the critical percolation threshold where the first conducting pathway is formed through the sample. For well exfoliated nanotubes with high aspect ratios, low percolation threshold can be found ($< \text{vol}\%$).¹⁸⁴ Theory predicts a higher universal exponent for 3D systems, $n_{DC} \approx 2.0$,¹⁸⁹ and as for 2D systems, experimentally determined values for the exponent vary.¹⁹⁵

2.1.2.5 Electrochemical Characterisation

Electrochemical measurements are concerned with the relationship between current and potential that arises in electrochemical systems under different conditions. In its simplest arrangement, an electrochemical cell consists of a pair of electrodes that are immersed in an electrolyte solution. If a wire is connect between the two electrodes, a current, I , may flow which reduces the free energy of the system due to a chemical change within the cell. This thermodynamic driving force can be measured by the open circuit of the cell, ΔV_{oc} , and it reflects the free energy at both electrode interfaces. Alternatively, an externally applied potential can be used to alter the cell composition.

An electrochemical cell necessarily contains two electrodes which work against one another. However, it is convenient to study the properties of a single electrode interface without having to be concerned about what is happening at the other electrode interface. This is made possible using a three-electrode electrochemical cell. The features of this experimental set-up are depicted in Figure 2.8. In addition to the electrode under study, called the 'working electrode', this set-up contains a 'counter electrode' and a 'reference electrode'. The former allows current to enter/exit the cell (as well as at the working electrode) and is often prepared from carbon or a noble metal such as gold or platinum. The latter is used to monitor the potential difference across the working electrode interface. Using this three-electrode configuration, the current flowing through the working electrode interface and the potential difference across it can be monitored and altered.

The reference electrode is designed to provide a fixed interfacial potential to which the potential across the working electrode can be monitored. Although many electrode systems have been devised which display this behaviour, in this work the silver/silver chloride reference electrode has been used. It consists of a Ag wire coated with a porous layer of AgCl and is immersed in a saturated NaCl solution. The redox couple for this system is



The Nernstian relation for this reaction, shown in Equation 2.8, indicates that if the solution remains saturated with $NaCl$, and hence fixing the chloride activity a_{Cl^-} , the

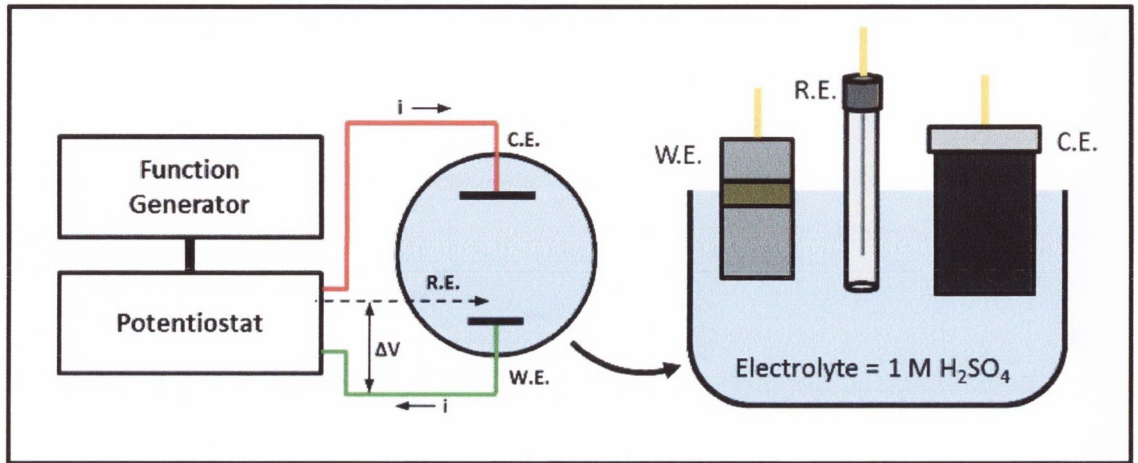


Figure 2.8: Experimental set-up for a three-electrode electrochemical cell.

potential across the electrode electrolyte interface, $\Delta V_{reference}$, remains constant.

$$\Delta V_{reference} = V^0 - \frac{RT}{F} \ln a_{Cl^-} \quad (2.8)$$

Here R is the gas constant, T is the absolute temperature and F is Faraday's constant. V^0 is the reduction potential of the cell under standard conditions when used in conjunction with the Standard Hydrogen Electrode. As $\Delta V_{reference}$ is constant, the potential between the working and reference electrode, ΔV_{cell} (a directly measurable quantity), is given by Equation 2.9.

$$\Delta V_{cell} = \Delta V_{working} + \Delta V_{reference} + iR_u \quad (2.9)$$

Here $\Delta V_{working}$ is the potential difference across working electrode. The third term, iR_u , is a potential drop due to so-called uncompensated solution resistance between the working and reference electrodes. By reducing the distance between the two electrodes, this resistance can be minimised such that when small currents pass, the iR_u can be ignored. This is also assisted by the use of a supporting electrolyte to provide ionic sufficient conductivity. Due to this experimental arrangement, any change in ΔV_{cell} can be attributed to changes in $\Delta V_{working}$.

An instrument called a potentiostat is used to measure the current flowing through the cell (between the working and counter electrode) and also alter the potential between the

working and counter electrodes such that $\Delta V_{\text{working}}$ takes on whatever value is required by the experiment. As indicated by Figure 2.8, the potentiostat is used in conjunction with a function generator, which enables the cell to be stimulated in a variety of ways.

The relationship between current through and potential across the working electrode is complicated by a variety of processes that occur within the cell. These include reaction kinetics at the interface, diffusive transport to/from the electrode surface and charge migration within the electrolyte solution. As these processes occur simultaneously, the slowest among them determines the current that is measured in a given experiment. Using the three-electrode cell, many experimental techniques have been devised to investigate these different processes¹⁹⁶. Physical theories are employed to quantitatively interpret measurable parameters (in particular, current and voltage) and relate them to the underlying properties of the system. In this work, cyclic voltammetry and electrochemical impedance spectroscopy (EIS) have been used to investigate the charge storage properties of nanomaterial network electrodes.

Cyclic Voltammetry

This technique is commonly employed to evaluate the capacitive behaviour of EC electrode materials. As is demonstrated in Figure 2.9, a potential is applied, starting at some initial potential, V_1 , which increases linearly at some scan rate, dV/dt , (with units mV/s) until a final potential, V_2 . At this point, the polarity of the potential ramp is reversed, returning the electrode potential to its original value. When repeated, the excitation signal is a triangular waveform, shown in Figure 2.9.

The scan rate may be varied over a wide range to examine the current response of the electrode when charged both slowly and quickly. For an ideal capacitor with capacitance C , the current that arises is given by $i = (dV/dt)C$. In this case, the current response is a perfect rectangle. However, invariably some resistance is encountered during charge and discharge process. This can be accounted for by the inclusion of a resistor, (*i.e.* R_{ESR} , introduced in Chapter 1) in series with the capacitor. The current response arising for this

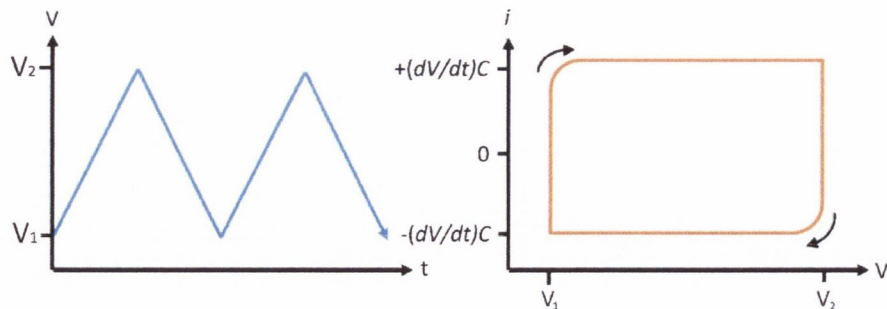


Figure 2.9: Schematic of cyclic voltammetry experiment for an ideally capacitive electrode material.

simple equivalent circuit due to an imposed linear potential sweep is given by Equation 2.10.

$$i = (dV/dt)C[1 - \exp(-t/\tau)] \quad (2.10)$$

Here t is the time passed during the voltage sweep and $\tau = R_{ESR}C$, the time constant associated with charging the capacitance through a resistance. Thus, upon initiation of a potential sweep, the measured current will increase from zero until it reaches a steady state value given by $i = (dV/dt)C$. By performing the experiment at a range of scan rates, a plot of this steady state current *vs.* scan rate can be used to determine the electrode capacitance. In Chapter 5, $\dot{V}$ is used in place of dV/dt to make the equations look tidier.

Although the capacitance associated with charge and discharge of the double layer behave reasonably ideally over wide range of potentials, the pseudocapacitance associated with many faradaic EC electrode systems varies significantly.¹⁰ If this is the case, when evaluating the properties of an electrode material for energy storage applications, it is common to calculate an average capacitance over the entire potential window (*i.e.* $C = \Delta q/(V_2 - V_1) = \Delta q/\Delta V$). The total charge accumulated can be found by integrating the current passed over this region using equation 2.11.

$$C = \frac{1}{\Delta V} \int_{V_1}^{V_2} i dV \quad (2.11)$$

Once obtained, the capacitance of an electrode is often normalised to the total mass, M ,

volume, V , or cross sectional area, A , of the electrode material to enable comparison with other electrodes. For the work presented in Chapters 4 and 5, emphasis is placed on the areal capacitance (C/A), whereas in Chapter 6 more attention is given to the specific capacitance (C/M).

Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is another useful technique for the investigation of electrochemical systems including EC electrodes. An impedance measurement is generally made by applying an alternating potential to the cell, which can be expressed as $V = V_0 \cos(\omega t)$. Here V_0 is the amplitude of the signal varying with time, t , at an angular frequency, $\omega = 2\pi f$ (f is the frequency expressed in hertz). V_0 is chosen to be sufficiently small (~ 10 mV) such that the system response is pseudolinear. This enables the resulting current to also be a sinusoidal wave of angular frequency ω , with some magnitude, I_0 , and phase shift, θ , able to be expressed as $I = I_0 \cos(\omega t - \theta)$.

The ratio of these functions is defined as the impedance, having the components of magnitude, Z_0 , and phase angle, θ . This notation is intuitive; a small Z_0 indicates that a large alternating current will result for a given voltage perturbation and a large θ indicates that the current will significantly lead or lag the input signal. Impedance data can be visualised on a polar plane, or alternatively, expressed as a complex number by determining the projection these points make on an rectangular plane (Figure 2.10). In this case, Z' and Z'' denote the real and imaginary components of impedance. Impedance data may be plotted in a variety of ways. The two most common approaches are to plot Z_0 and θ *vs.* ω , (called Bode and phase plot) or Z' *vs.* $-Z''$ (called complex plane plot, Nyquist plot or Cole-Cole plot).

By measuring the impedance of an electrode system over a wide range of frequencies, typically 1 mHz to 1 MHz, an impedance spectrum is obtained. Analysis is then carried out by constructing an appropriate equivalent circuit to model the processes occurring in the system. For electrochemical systems, these mainly consist of combinations of resistors

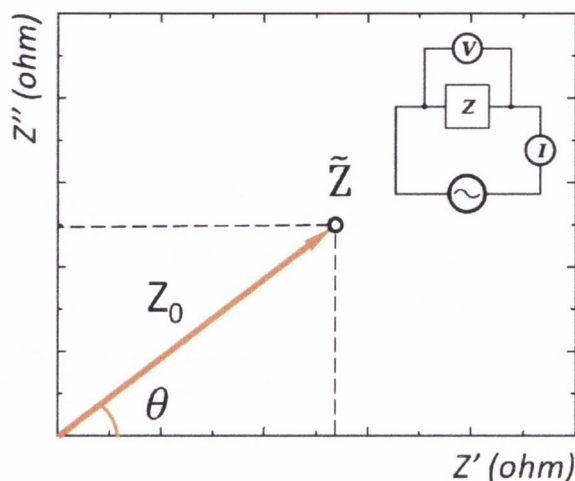


Figure 2.10: Complex plane representation of impedance.

and capacitors, as well as some other less familiar circuit elements. These include the 'constant phase element', to represent some distributed characteristics of electrochemical systems and the Warburg element, often used to represent ionic diffusion.¹⁹⁷

Resistive behaviour arises physically due to losses associated with the movement of species through a medium. It is characterised by the voltage and current being in phase ($\theta = 0^\circ$) regardless of the magnitude and frequency of the input function. Therefore a resistance appears as a point on the real axis of the complex plane at all frequencies.

As was described in Chapter 1, capacitive behaviour arises when opposite charges are separated in space when a potential difference is applied. Due to the definition of capacitance ($C = q/V$), current flow within a capacitor only occurs when the potential across it is changing with time (*i.e.* $I = C(dV/dt)$). As a result, the response of a capacitor to an oscillating voltage is determined by $Z_C = 1/j\omega C$ and as such the current response leads the voltage ($\theta = 90^\circ$). At high frequencies, Z_C approaches zero (acts like a short circuit), and at low frequencies it approaches ∞ (acts like an open circuit). This property of capacitors is the reason they have found widespread use for signal processing as they can be used to filter electronic signals with certain frequencies. As the impedance of a capacitor is purely imaginary, it appears on the complex plot as a vertical line along the

$-Z''$ axis when plotted as a function of frequency.

The parameters of the proposed circuit model may be found by fitting it to the data, which can then be related to various physiochemical processes that determine the behaviour of the electrode system. These quantify processes such as ionic and electronic transport, interfacial polarisation and charge transfer.^{10;28} When interpreting EIS spectra it is good practice to compare the electrode properties to other experimental techniques in order to provide evidence that the proposed model is an accurate representation of the behaviour of the electrode system under study.

Chapter 3

Materials

3.1 Introduction

This thesis presents research into the properties of nanomaterial network electrodes for use in emerging EC applications. In this chapter, the electrode materials featured in this work are introduced; carbon nanotubes, manganese dioxide and the conducting polymer, PEDOT:PSS. General information is provided about their structure, synthesis and properties pertaining to their use as EC electrodes.

3.2 Carbon Nanotubes

Carbon nanotubes came to wide recognition in 1991 when they were identified and described by the Japanese scientist Sumio Iijima.²⁹ When using an arc-discharge method to produce fullerenes, he discovered that a variety of tube structures were also produced, concentrically nested within one another. Regardless of the number of layers of carbon present for a given structure (ranging from around 2 to 50), each tube was separated from its internal and external neighbour by 0.34 nm, similar to the distance separating the sequential layers of graphite. The carbon atoms composing each tube formed a hexagonal lattice, with each atom bonded to three others in a sp^2 -hybridised orbital scheme, also reminiscent of graphite layers. In addition to multi-walled carbon nanotubes, Iijima later discovered a single-walled variety using a modified synthesis technique.³⁰ These also possess a honeycomb-like structure, depicted in Figure 3.1. Following these discoveries, many researchers began investigating the synthesis, properties and potential applications of this new carbon allotrope.³⁷

SWNTs can possess a range of diameters; typically they are 1-2 nm, although instances with tube diameter up to around 10 nm and as small as 0.4 nm also occur.¹⁹⁸ While possessing diameters on nanoscale, the length dimension of these materials can extend into macroscopic domain. As an example, carbon nanotubes have now been synthesised that are over 55 cm long.¹⁹⁹



Figure 3.1: Cartoon of a single-walled carbon nanotube. Image from source.²⁰⁰

As well as possessing a range of diameters, SWNTs also vary based on the orientation of the hexagonal carbon lattice relative the length axis. Figure 3.2 presents the two forms with highest symmetry. These are termed 'armchair' and 'zig zag' based on the appearance of the tube end when looking at it side on. A helical (or chiral) example is also shown, although there are many different kinds. Notation has been developed to identify all of the possible nanotube types using a vector that occupies different positions on a hexagonal lattice. This vector can uniquely define each nanotube type using a pair of integers, (n,m) , while also providing a useful way to classify different nanotube types.²⁰¹

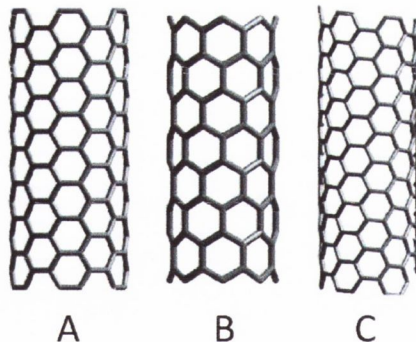


Figure 3.2: The orientation of the hexagonal lattice relative to the tube axis results in carbon nanotubes with differing helicity and properties. (A) Arm chair, (B) zig zag and (C) a helical nanotube.

Experimental measurements of the electrical properties of carbon nanotubes were carried out during the late 90's. The sp^2 -hybridised bonding scheme that operates between carbon atoms means that electrons occupying π orbitals are delocalised. A consequence of

the one dimensional geometry of nanotubes is that electrons are able to conduct ballistically,²⁰² imparting mobilities of around $10^5 \text{ cm}^2/\text{Vs}$.²⁰³ Studies also found that the electrical properties of SWNTs are sensitive to nanotube chirality.^{204–206} As a result, around one third of the possible SWNTs are metallic and the rest are semiconducting with bandgaps that decrease with tube diameter.²⁰⁴ For the metallic SWNTs, DC conductivities as high as $200\,000 \text{ S/cm}$ and large current carrying capacities of $6 \times 10^6 \text{ A/cm}^2$ have been measured.²⁰⁶ In addition to these excellent electrical properties, carbon nanotubes are both strong and stiff, with tensile strength of $\sim 60 \text{ GPa}$ and Young's modulus of $\sim 1 \text{ TPa}$.²⁰⁷ They are able to sustain large bending radii and even recover from kinking, features that are advantageous for their use in flexible electronics applications.²⁰⁸

There are three main approaches for the formation of carbon nanotubes. These include arc-discharge^{29;30}, laser ablation²⁰⁹ and chemical vapour deposition.^{210;211} The arc-discharge method involves the creation of an electric arc between two graphite electrodes in an inert gas atmosphere. Although fullerenes are produced as a soot under the conditions employed, multi-walled carbon nanotubes can also be found on the cathode. The inclusion of metal particles within the graphite anode results in the production of SWNTs, which can be found in the soot material.^{29;30}

Alternatively, pulsed lasers can be used to ablate a graphite/catalyst target.²¹² A carrier gas is used to transport the vaporised materials away from the hot target which condenses to form nanotubes and other impurities. Like the arc discharge method, laser ablation produces a nanotube-containing soot.

Chemical vapour deposition involves the decomposition of a gas phase carbon feedstock (such as C_2H_2 , or CH_4) at elevated temperatures in the presence of metal catalyst particles (such as Fe or Co). Interaction between the reactive gases and catalyst results in the growth of nanotubes.²¹³ The nature of the metal catalytic particles strongly influence the the nanotube product, such as its diameter. An advantage of this method over arc-discharge and laser ablation is that nanotube architectures can be produced directly on pre-patterned substrates in an ordered manner.²¹⁴

For all of these methods, absolute control over the diameter, helicity, length of nanotubes is not yet possible.²¹⁵ Although arc-discharge and laser ablation can produce nanotube powders in large quantities, their synthesis is also accompanied by the creation of amorphous carbon impurities and contaminants arising from the necessary metal catalysts. As a result, post-processing measures are often necessary to clean up the obtained material.²⁰¹ The most common means of doing so involves acid refluxing, for example, using mixtures of H_2SO_4 and HNO_3 .²¹⁶ This successfully removes large amounts of impurities, although it also has damaging effects such as reducing the mean nanotube length and introducing oxygen containing functional groups.²¹⁷

A key challenge associated with the use of carbon nanotubes is translating the excellent properties of individual nanotubes into assembled structures. As was described in Chapter 2, many nanomaterials tend to form aggregated clumps due to attractive van der Waals forces between them. SWNTs are highly susceptible to this effect due to their large aspect and they often exist as bundles and ropes.²⁰⁹ Liquid phase exfoliation is an effective way to overcome these interactions. SWNTs have been dispersed in a variety of liquid media; organic solvents,^{165;166;168} aqueous surfactant systems,^{172;218–220} and polymers.^{221;222} Conveniently, this method opens the door to a range of further processing methods.

Once a SWNT dispersion has been obtained, one of the simplest ways to produce macroscopic assemblies of carbon nanotubes is *via* vacuum filtration.²²³ This produces flexible and robust paper-like films of entangled nanotubes, often referred to as bucky-paper (Figure 3.3). This was one of the first ways to characterise nanomaterials as assembled structures and remains a common way to explore the properties of these materials today.

SWNT network materials are disordered in a number of respects and these influence properties that result. Although the nanotubes tend to lie in the plane of the film, they have no fixed lateral orientation. Morphological features such as film porosity and the mean bundle diameter are highly influential,²²⁴ as well as the distribution of nanotube lengths (dependent on synthesis and processing) and conductivity (dependent on chiral identity of the tubes, the presence of sidewall defects and doping effects).^{225;226} The ensemble of these factors determine the overall electrical properties of nanotube networks.²²³ For undoped films, DC conductivity of 6600 S/cm have been achieved,¹⁸³ while much higher values are possible by employing dopants. For example, 12 826 S/cm was reported when using camphorsulfonic acid.²²⁵ The theoretical maximum value for nanotube network conductivity is thought to be around 90 000 S/cm.²²⁷

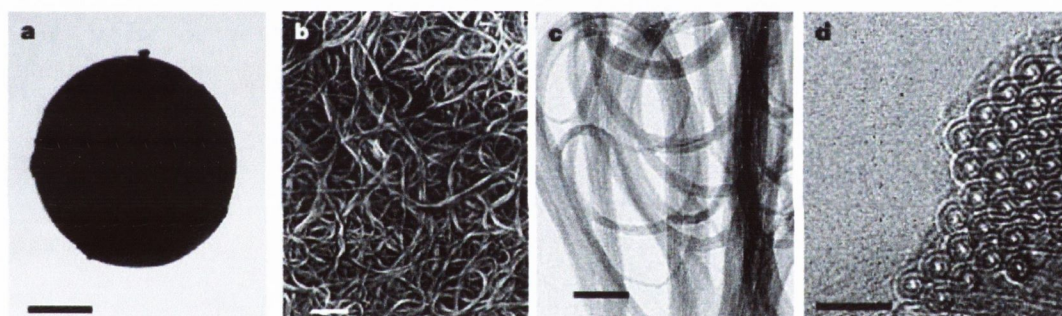


Figure 3.3: (A) Double-walled carbon nanotube 'buckypaper' formed by vacuum filtration. (B) SEM images of nanotube network morphology. (C) TEM images of constituent nanotube bundles and (D) HR-TEM images of a bundle to emphasise the triangular packing structure. Scale bars: (A) 1 cm, (B) 300 nm, (C) 50 nm, (D), 5 nm. Image adapted from source.²²³

Although they have been explored for a wide range of applications,^{37;228} one of the most vigorously studied use of this nanomaterial is as transparent/flexible electrodes.^{193;225} By scaling down the bucky paper thickness to the sub-100 nm range, disordered nanotube networks become highly transparent while retaining good electrical conductivity and flexibility (Figure 3.4).¹⁸³ Nanotube-based transparent conductors have been the subject of much research over the last decade, in addition to a range of other nanomaterials such as

graphene and metallic nanowires.¹⁹³ Much of this work has been motivated by the need to find a replacement for the presently relied upon indium-tin oxide based transparent conductors; this material is expensive, brittle and requires high-temperature processing, precluding its use in flexible/transparent electronics applications.¹⁹³ On the other hand, nanotube networks are robust and remain conducting with sustained flexing.¹⁹¹ To be competitive with ITO as a transparent conductor, industry stipulates the need for film transmittance greater than 90% with a sheet resistance less than 100 Ohm/sq. As such, research in this field has been driven towards this goal.^{161;193;229}

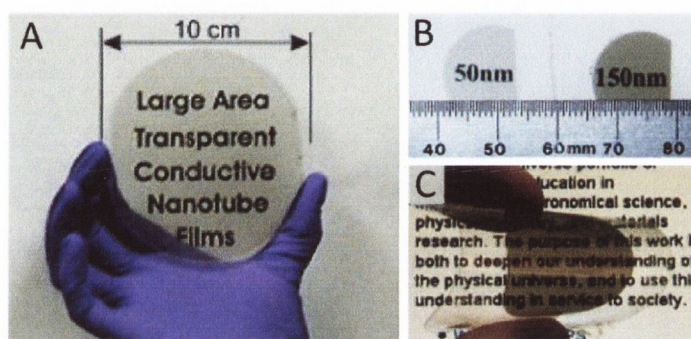


Figure 3.4: (A) Transparent carbon nanotube network electrode on sapphire substrate. (B) Films with differing thickness and hence transparency. (C) Flexed film on mylar sheet. Image adapted from source.¹⁸³

Although greater transmittance is achieved by using thinner films (Figure 3.4B) this compromises electrical transport (*i.e.* increased R_s) due to reduction in the number of conducting pathways across the network. As for thicker nanotube network films, numerous characteristics such as the mean nanotube length^{230;231}, bundle diameter²³², sidewall functionalisation and doping²²⁵ all influence the electrical performance of transparent nanotube networks. As electrons must pass from one nanotube to another in order to cross the network, transport is greatly encumbered by inter-nanotube junction resistance²³³. This is influenced by factors such as bundle diameter and the presence of residual surfactants or dopants.²³⁴ As was discussed in Chapter 2, percolation effect also play an important role in determining the properties of transparent nanomaterial networks.

Due to their excellent combination of properties, carbon nanotubes are a desirable replacement for activated carbon in commercial EC electrodes. If bundling could be eliminated, SWNTs could be used to create electrode architectures with very high specific surface areas; over $1000 \text{ m}^2/\text{g}$.²³⁵ Although in reality electrode surface areas less than half this value are achieved, carbon nanotubes remain an ideal material for the formation of highly extended electrochemical double layers necessary for large capacitance values requiring little electrode mass.

Specific capacitance values that are obtained vary greatly, falling in the range from tens to hundreds of farads/gram.^{33;67} As an example, randomly entangled SWNT electrodes have been shown to provide specific capacitance values of 180 F/g , which approaches the theoretical limit for a carbonaceous electrode with a measured specific surface area of $375 \text{ m}^2/\text{g}$.³³ However, a particular advantage of this material is the very low resistance of nanotube electrodes enabling operation with very high power. This entangled network electrode provides an energy density of 7 Wh/kg at power density of 20 kW/kg , much superior to electrodes prepared using activated carbon, which can deliver a similar energy density though at less than 50% of the power. In addition, entangled nanotubes tend to form open structures with porosity in the mesoporous range (2-50 nm), ideal for allowing unoccluded ion transport.²³⁶

The ability to process SWNTs in the liquid phase presents opportunities for the creation of electrodes with other characteristics not possible using traditional materials, such as being flexible,^{237;238} stretchable^{239;240} and transparent^{149;155}. The excellent mechanical and electrical attributes of nanotubes mean that they may be used without the need for a supporting current collector¹⁴¹ or polymeric binders,²⁴¹ allowing significant reduction in total device mass. This is particularly important for printed flexible and transparent devices which will probably use plastic films as the device substrate and rely entirely on the conducting properties of the nanotubes for current collection.

Functional groups introduced onto nanotubes during post-synthesis treatments can be advantageous for the use of this material as EC electrodes. These can greatly assist with stable dispersion formation,⁴⁰ improve electrode wetting with the electrolyte²⁴² and im-

part appreciable pseudocapacitance.^{243;244} This is typically achieved by oxygen containing functional groups,^{244;245} although nitrogen-doped nanotubes can also be used.²⁴⁶

Alternatively, many researchers are exploring the combination of carbon nanotubes with high pseudocapacitance materials such as conducting polymers^{247–250} and transition metal oxides^{34;60}. This can be achieved by simple mixing of the components in some ratio¹⁴⁹ or alternatively, by deposition of the faradaic component directly on the surface of the nanotubes by chemical^{251–254} or electrochemical^{238;255} means. In either case, the nanotubes are included to improve electrical performance of the electrode, providing rapid electronic access to the high capacitance electrochemical interface. A particular advantage of using nanotubes in this application compared with other carbon types is the very low percolation thresholds obtained when nanotubes are mixed into a matrix materials.^{60;184} This topic is discussed in more detail in the sections following and is a major theme of the work presented in Chapter 6.

3.3 PEDOT:PSS

During the 1980s, a range of polymeric materials were developed which possess substantial electrical conductivities. This was initiated by work on polyacetylene²⁵⁶ and led to other plastic conductors such as polypyrrole, polyaniline, polythiophene and derivatives of these.²⁵⁷ Although polyacetylene has been prepared with an impressive DC conductivity of 10^5 S/cm,²⁵⁸ it is unstable in air and therefore impractical for most applications. As a result, research into conducting polymers has been motivated by the need for plastics that are not only highly conductive but also easily processed and environmentally stable.

One material that perhaps meets these criteria better than any other is a copolymer called poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid). Commonly referred to as PEDOT:PSS, this material was created in the late 1980s by polymer scientists working in the research laboratory of Bayer AG in Germany.²⁵⁹ Today it is commercially available from H.C. Starck Clevious GmbH as a range of ready-made formulations under

the trade name Clevios™. These consist of the copolymer dispersed in water to form a gel.²⁶⁰

Like many conducting polymers, PEDOT may be produced by the oxidation of its monomer (3,4-ethylenedioxythiophene, also known as EDOT) by both chemical and electrochemical means. The latter route results in deposition of the polymer onto an anode at potentials greater than 1.25 V *vs.* Ag/AgCl.²⁶¹ Electrochemical synthesis enables the creation of films of this polymer on conducting substrates, and the identity of the supporting electrolyte plays an important role in the properties of the produced material. However, as it is insoluble and produced in small quantities by this method, it is not ideal for large scale-manufacture of PEDOT materials. Despite this, electropolymerisation has been important for the elucidation of the properties of PEDOT and conducting polymers generally.²⁶²

On the other hand, oxidation by chemical polymerisation is more amenable to large-scale production of this polymer. Although iron(III) based oxidants are commonly used for this reaction (such as FeCl_3 and $\text{Fe}(\text{OTs})_3$),²⁶³ the synthetic route devised at Bayer AG involves oxidation of EDOT using $\text{Na}_2\text{S}_2\text{O}_8$ in the presence of PSS. This reaction scheme is shown in Figure 3.5.

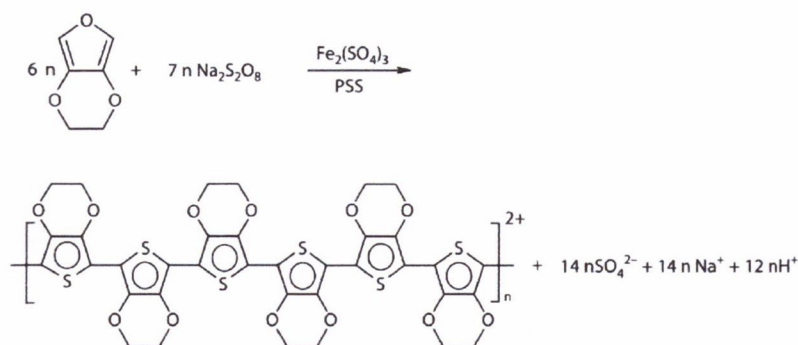


Figure 3.5: Reaction scheme for PEDOT synthesis when using sodium peroxodisphate oxidant, in the presence of aqueous PSS. Fe(III) is used as a catalyst. Image from source.²⁶⁰

Initially this reaction produces a neutral polymer which, despite possessing a conjugated backbone, has limited conductivity. This occurs due to a phenomenon called *Peierls distortion*, which results in the splitting of what would be a metallic π -band into a pair of bands separated by around 2.0 eV.²⁶¹ However, further oxidation of the polymer backbone can be carried out to produce mobile electronic states able to provide reasonable conductivity (~ 1 S/cm). Although the density of these states along the backbone varies from chain to chain, generally around two positive charges are associated with every six repeat units,²⁶³ as indicated by Figure 3.5. As an analogy to inorganic semiconductors, this oxidation process is referred to as 'p-doping' due to the generation of mobile positively charged states.

As the doping process converts PEDOT to a polycation, this necessitates the presence of charge balancing counter ions from the surrounding media. In the case of electrochemical polymerisation, this role is played by the supporting electrolyte anions, while for chemical polymerisation the counter ion to the oxidant generally becomes incorporated with the PEDOT. However, in the presence of deprotonated PSS, a polyelectrolyte complex is formed, enabling PEDOT to remain dispersed in solution.²⁶⁴ A schematic of the resulting copolymer is presented in Figure 3.6. The PEDOT chains are found to be oligomeric and associate with the longer chain PSS in sections consisting of fewer than 20 repeat units.²⁶⁵ The ratio of EDOT to PSS can be varied to tune the conductivity and other characteristics of the formulation. After synthesis, clean-up measures such as ion exchange and dialysis can be employed and the particle size distribution altered by application of shear forces or centrifugation. These steps can be important for subsequent processing if certain rheological properties are required. It is generally thought that the dispersion consists of random coils of PSS with the PEDOT oligomers ionically attached.²⁶⁶

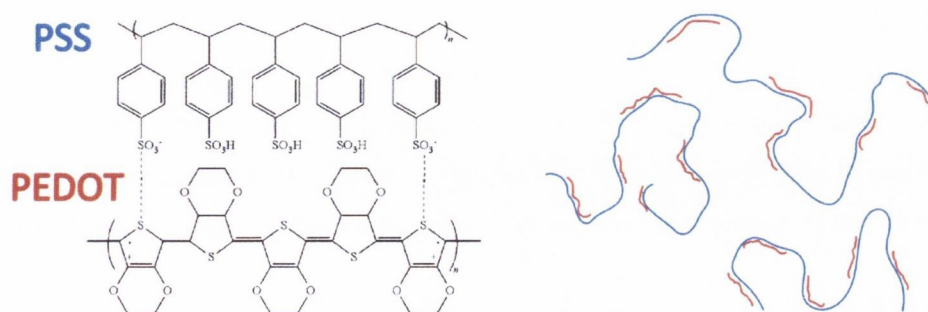


Figure 3.6: PEDOT:PSS chemical structure with a cartoon indicating the association of the PEDOT oligomers with the longer chain PSS. This polyelectrolyte complex forms a gel in solution.

Being soluble in water, PEDOT:PSS can be transformed into a range of materials by liquid phase processing. Examples include spin coating,²⁶⁶ spraying coating,²⁶⁷ screen printing²⁶⁸ and inkjet printing.²⁶⁹ Once dried, the resulting films are mechanically robust and insoluble in many solvents.²⁶³ Like traditional polymers, conducting polymers are disordered by nature, containing a range of chain lengths with a variety of defects and combinations of crystalline or amorphous regions. In addition, excess PSS can lead to the occurrence of insulating regions the film. All these characteristics influence the overall electrical properties the resulting material.

As-prepared, films of PEDOT:PSS possess conductivities $<10 \text{ S/cm}$.^{266;270;271} However, a range of simple treatments have been developed which improve this value by 2-3 orders of magnitude. These involve exposure of the films to a variety of substances and is termed 'secondary doping'. This behaviour was observed for polyaniline on exposure to *m*-cresol.²⁷² Here, improved conductivity was retained after removal of the secondary dopant by heating, indicating that the change in film properties was more likely due to the altered film morphology. Similar behaviour has been observed for PEDOT:PSS films using a range of polar solvents such as dimethyl sulfoxide,²⁷¹ sorbitol,^{273;274} ethylene glycol²⁷⁵ as well as a range of carboxylic acids²⁷⁶, formic acid²⁷⁷ and H_2SO_4 .²⁷⁰ It is generally thought

that the treatment with polar molecules causes screening effects that induce conformational changes to the polymer chains. Temperature dependent conductivity measurements indicate a reduction in the barrier to charge hopping for the treated films as well as a reduction in the presence of PSS within these films.²⁷⁶ It has been suggested that excess PSS not associated with PEDOT chains form a 'shell' around the copolymer grains which are potentially removed with secondary doping, improving inter-grain electrical contact.

Due to its excellent electrical properties, mechanical flexibility and optical transparency in the visible range, PEDOT:PSS shows promise for a range of thin film applications such as transparent/flexible/stretchable layers,²⁷⁸ counter electrodes within plastic solar cells,²⁷⁹ electrochromic windows, neural prosthetic electrodes^{280;281} and EC electrodes.^{282–284}

Probably the biggest issue associated with this material (and conducting polymers generally) is electrical stability. PEDOT has shown sensitivity to environmental factors such as high temperatures, humidity and sunlight.^{274;285;286} As a result, it is important that oxygen be eliminated from devices making use of PEDOT:PSS, especially when they are used in the presence of UV light. Protective measures may be required for outdoor applications such as hermetic sealing and the addition of stabilisers.²⁶⁰

There is much interest in the use of PEDOT materials within EC electrodes. Its polymeric nature means it can potentially take the place of inert polymeric additives that are often used to bind together other inorganic electrode material components, while also providing the composite with improved charge transport. It has been combined with a number of other nanostructured electrode materials such as carbon nanotubes,^{247;250} graphene oxide,²⁸⁷ MoO₃,²⁸⁸ MnO₂,²⁸⁴ and CoAl double layer hydroxides.²⁸⁹ Studies have demonstrated its compatibility with a range of electrolyte types including aqueous²⁹⁰, organic²⁸² and ionic liquid systems.²⁹¹

An important feature of PEDOT regarding its use in electrochemical applications is its reversible redox capability. As is indicated in Figure 3.7, reduction converts the polymer to its neutral (undoped form), no longer requiring the presence of charge compensating cations. The opposite process also occurs, re-oxidising the polymer backbone to its charged (p-doped) form. This change is accompanied by modulation of the appearance

of the film, from transparent pale blue (p-doped) to an opaque blue appearance (undoped). As a result, PEDOT can be used within electrochromic devices^{261;292} showing rapid switching²⁹³ and efficient colouration.²⁶⁷ However, this faradaic process may also be used to provide additional pseudocapacitance in faradaic EC electrodes. For example, PEDOT nanotubes have been synthesised electrochemically and fabricated into symmetric EC devices (*i.e.* both electrode the same composition) that provide a capacitance of 130 F/g and energy and power density of 5.6 Wh/kg at 25 kW/kg.²⁸³ Although reduction of PEDOT converts it to an insulating form, it is still able to be reoxidised back to the conducting form even in the absence of an underlying current collector or other conductive additives.²⁹⁴ This enables its use as a stand alone electrode material for pseudocapacitive energy storage (and electrochromism) within printed devices. The combination of excellent processability in the liquid phase, ability to produce high quality transparent, flexible and stretchable films and stable pseudocapacitive behaviour makes PEDOT:PSS a very attractive material for emerging EC applications.

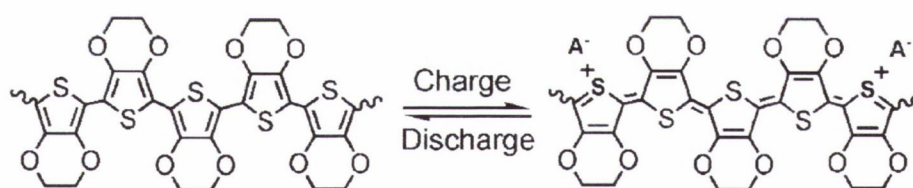


Figure 3.7: Reduction and oxidation of PEDOT can provide additional pseudocapacitance. The neutral (de-doped) form is dark blue while the charged (p-doped) form is transparent. Image from source.²⁸³

3.4 Manganese Dioxide

MnO₂ belongs to a family of inorganic compounds that also includes MnO, Mn₂O₃ and Mn₃O₄. These materials are all produced by the assembly of MnO₆ octahedral units through the sharing edge or corner sites.²⁹⁵ Depending on way the units are arranged in

space, a range of crystalline forms can be produced. As indicated in Figure 3.8 a number of these possess 3D structures containing tunnels with different shapes and sizes or even stacked layers of pseudo-infinite sheets. These structural features are responsible for many of the interesting properties of manganese oxides because they allow guest species to be freely accommodated within the available internal space.

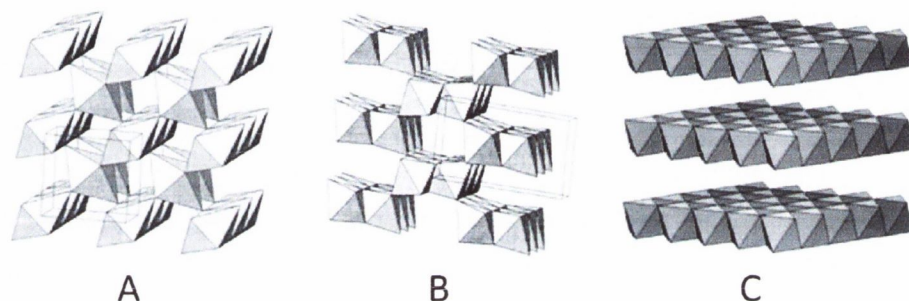


Figure 3.8: (A) Rutile, (B) Diaspore and (C) Birnessite type polymorphs of MnO_2

When certain guest species enter the crystal they can interact with it *via* redox processes, causing the manganese metal centers to interconvert between the 3+ and 4+ oxidation states. Useful chemical functionality can arise in this situation, and as a result manganese oxide crystals are being studied for use in fields such as catalysis²⁹⁶, ionic and molecular sieving²⁹⁵ and electrochemistry.^{62;297–300} In addition to these functional properties, manganese oxides are abundant and environmentally benign; factors which have also encouraged widespread interest in this family of materials.

Considering only the binary oxides, there are a wide range of crystalline structures available. Some examples include $\alpha\text{-MnO}_2$,³⁰¹ $\beta\text{-MnO}_2$,³⁰² $\gamma\text{-MnO}_2$,³⁰³ $\delta\text{-MnO}_2$,³⁰⁴ $\epsilon\text{-MnO}_2$,³⁰⁵ $\lambda\text{-MnO}_2$ ³⁰⁶ as well as mixed-phase,³⁰⁷ mixed-valence,^{296;308} mixed-metal³⁰⁹ and amorphous compositions.⁶² Due to the difficulty in synthesising pure forms of the ideal polymorphs, unambiguous classification of a given material is often difficult.³⁰³ This situation also hampers the formation of definitive conclusions regarding why one form of MnO_2 is better than another for a given application. On the other hand, numerous avenues for compo-

sitional variation can be seen as an advantage as it potentially enables the production of materials with specifically tailored properties.

The production of manganese dioxide is often achieved using redox chemistry; by the oxidation of Mn(II) precursors, the reduction of Mn(IV) precursors,^{310;311} or by reacting these species with one another (called co-precipitation):^{62;312}



For all of these cases, the nature of the colloidal particles that are produced depends on the specific reductant or oxidant employed, the counterions that are present, the solution pH and the reaction temperature.³¹⁰ In addition, surfactants can be included to influence the product formed.^{313;314} Annealing is frequently performed to improve the crystallinity of the product.³¹⁵

Alternatively, electrochemical deposition can also be employed to produce MnO₂ using similar redox chemistry. Here, the reduction of Mn(IV)-based precursors^{316;317} or oxidation of Mn(II) based precursors^{318;319} occurs due to electrons being supplied or removed by an electrode immersed in the reaction solution. This results in precipitation of the product directly onto the electrode surface. In addition to the electrochemical control parameters available using this method, temperature, pH and the other species present in solution (such as the supporting electrolyte) also influence the nature of the product that is formed.³¹⁹

Probably the most successful commercial use of manganese dioxide has been within primary alkaline battery electrodes (*i.e.* the Zn/MnO₂ system) developed in the mid 1800s.³⁰³ Currently a number of other electrochemical applications are being investigated, such as cathode materials for Li-intercalation batteries,^{298;299;320} electrocatalyst for oxygen gas evolution³²¹ and as an active component within electrochromic devices.³²²

The application that has gained the most interest in recent years has been its potential use as a faradaic electrode material for high energy density ECs.³¹⁵ This was initiated by the work of Lee *et al.* in 1999, which demonstrated near ideal pseudocapacitive behaviour

of amorphous MnO_2 when produced by a co-precipitation method.³²³ Having measured specific capacitance of ~ 200 F/g, MnO_2 was posited as an inexpensive alternative to RuO_2 . Studies have found the charge and discharge process to be quite stable; over 200 000 cycles have been demonstrated,³²⁴ which bodes well for the use of this material in commercial ECs.

Subsequent studies exploring the charge storage mechanism has resulted in a double injection reaction becoming widely accepted. This involves the interaction of a single electron and charge balancing cation with every electrochemically available Mn(II/III) ion:³²⁵



This suggests a very large theoretical specific capacitance of 1370 F/g.⁵⁷ However, values this high aren't often achieved except for when the material is present as an extremely thin film on a metallic current collector and when charged and discharged slowly.³¹⁸ Studies have shown that only the surface layers contribute to the capacitance.³¹² Although the measured capacitance varies substantially among different crystalline forms,^{50;318;326} the majority of studies find specific capacitance values in the range 100-300 F/g.³¹⁵ On the other hand, Song et al. reported mixed valence a manganese oxide material with very high capacitive value of ~ 2530 F/g³⁰⁸ while Cross et al. attained 2986 F/g for thin films of manganese dioxide produced by electrodeposition.³²⁷ While these authors emphasise the difficulty in accurately determining the mass of active material produced,³²⁸ these examples are very interesting as they suggest that with sufficient synthetic control, very high specific values are possible.

To best employ the high intrinsic pseudocapacitance of any material requires the maximum number of redox active sites be in contact with the electrolyte and therefore available for charge storage.³¹² This makes the layered form of manganese dioxide extremely attractive so long as they can be exfoliated into thin nanosheets (see Figure 3.8C). It is likely that electrodes fabricated from monolayers of MnO_2 would be expected to display very high capacitances as all redox sites would be adjacent to the electrolyte. Probably the best way to achieve this in practice is to employ liquid exfoliation of layered compounds to give large quantities of suspended nanosheets in a processable form.^{95;170} Even though the

nanosheets produced by such techniques may not be exclusively monolayers, rather containing nanosheets of up to 10 layers thick, the scalability⁴¹ of such exfoliation processes coupled with the intrinsic processability of liquid suspensions makes liquid exfoliation an attractive way to produce supercapacitor electrodes.

Regardless of which crystalline form of MnO_2 is used to provide pseudocapacitance, the Mn(III/IV) redox couple limits the available potential window to around 1.2 V when using neutral electrolytes.³²⁹ This is limited by reduction of Mn(III) to soluble Mn(II) at excessive negative potentials, while excessive anodic potentials result in oxidation of Mn(IV) to soluble Mn(V) . To extend this potential window, there has been a number of studies which make use of MnO_2 only within the positive electrode, while a carbon-based electrode is used as the negative electrode.^{9;330;331} As indicated in Figure 3.9, these two electrode materials provide stable capacitance over different ranges of potential. This occurrence can be used to create an 'asymmetric' device whereby these two electrodes are charged against one another, enabling considerable expansion of the potential window that is available (in this case $\Delta V_{\text{cell}} = 2 \text{ V}$ when using aqueous electrolytes). Considering Equation 1.2, this increases the energy able to be stored $\times 4$ compared with a pair of MnO_2 used as both the positive and negative electrodes. This strategy requires careful control over the mass of each electrode to maximise the overall capacitance and the available voltage window.

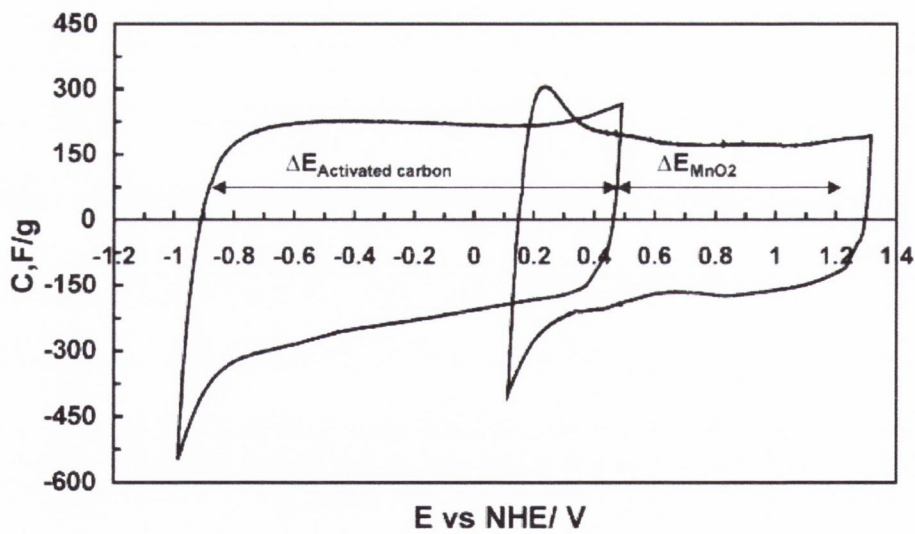


Figure 3.9: Asymmetric capacitors enable the potential window of aqueous systems to be greatly expanded, in this cases to a stable voltage window of 2 V. Image from source.⁹

Probably the biggest problem associated with the use of MnO_2 within EC materials is poor electrical conductivity ($\sigma_{DC} = 10^{-5}$ to 10^{-6} S/cm).^{332;333} This dominates the R_{ESR} , preventing high power operation (Equation 1.1). Another consequence of this that specific capacitance generally falls with increased electrode thickness due to the inability of electrons to access charge storage sites far from the current collector.²⁵² Such unfavourable thickness dependence is a general problem for low-conductivity electrode materials, including a number of other promising pseudocapacitive transition metal oxides.^{332;333}

As a result, many researchers are exploring the creation of composite electrode structures which combine nanostructured forms of manganese dioxide with carbon materials that offer improved electrical properties.⁵⁸⁻⁶⁴ This could enable large loadings of the pseudocapacitive component by using thick films, while also enabling electrical access to a maximum number of redox active sites.

There are a number of different strategies for the production of composite electrodes. The more traditional approach involves mixing the individual components, often with the assistance of a polymer binder to provide mechanical adherence. The mixture is then converted to a film using any of the film formation techniques discussed in Chapter 2. Here, the component materials can be optimised separately before mixing and then combined in any desired ratio. Due to its simplicity, some variation of this is to prepare most commercial ECs and battery electrodes.¹⁰

Alternatively, composite electrode formation can also be achieved by firstly preparing a high surface area conductive scaffold, generally using some form of nanostructured carbon, such as carbon nanotubes or activated carbon. Next, the active component is deposited in the surface of the scaffold as a very thin layer on the surface, thereby modifying the interface and greatly improving the capacitance of the overall structure. This can be achieved with MnO_2 by methods such as electrochemical^{318;334}, electrophoretic^{335;336} or electroless²⁵² deposition. Although an elegant approach, it is yet to be seen whether electrodes produced in this manner can be scaled-up to the large quantities required for commercial manufacture.

Regardless of which strategy is employed, probably the most important characteristic of

composite EC electrode is the ratio of the conducting component to the pseudocapacitive component. While enough of the former must be present to provide sufficient electrical conductivity to the overall structure, its addition in excess will cause reduced gravimetric or volumetric energy storage by taking up mass or volume otherwise available for the high pseudocapacitance component.

Despite the importance of this aspect of composite electrode design, it is given insufficient attention by many EC researchers. To demonstrate this point, Figure 3.10 presents a plot of the carbon content that was used within a variety MnO_2 -containing composite electrode structures published in the literature over the last 15 years. In many cases, the carbon loading is chosen without justification, ranging anywhere between 5 and 40 wt%. As a result, it is likely that the properties of the resulting composites are suboptimal. Exploring the effect of carbon content on the charge storage properties of MnO_2 is an important theme of the work presented in Chapter 6.

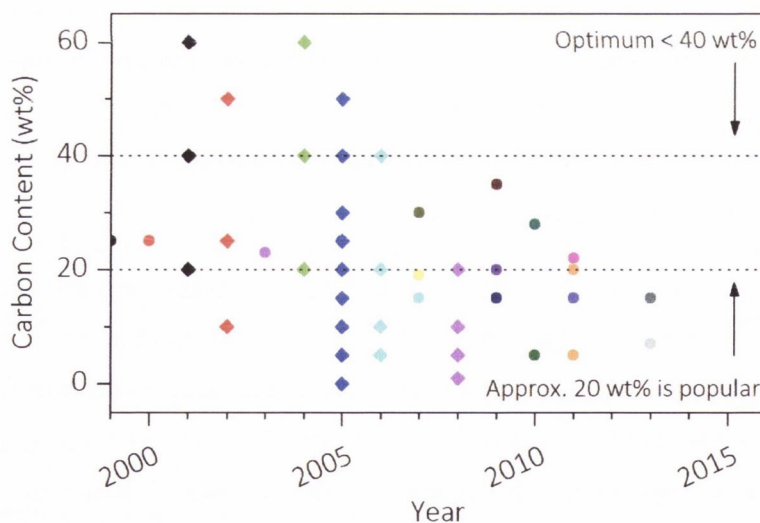


Figure 3.10: Literature survey of MnO_2 /carbon composite electrodes from 1999 to present, summarising the carbon filler content used to create electrochemical capacitor electrodes. A detailed legend is available in the Figure (3.10) indicating the authors of included studies and the carbon filler type employed.

Chapter 4

Single-Walled Carbon Nanotube Network Electrodes

4.1 Introduction

Over the last decade much research has been conducted exploring the electrical properties of disordered networks of nanomaterials such as carbon nanotubes, graphene and metallic nanowires. The primary motivation for this work has been to develop high performance, transparent and flexible electrodes for future optoelectronic applications.

Such studies have found that the macroscopic electrical properties of nanomaterial networks are very sensitive to the identity of the nanoscale entities making up the network. Further, research indicates that as these networks are made increasingly thinner and more transparent, their properties become highly dependent on the spatial arrangement of their nanoscale constituents on the surface. For example, the DC conductivity becomes thickness dependent in a manner that severely impairs their performance as transparent conductors.

In addition to optoelectronic devices, disordered nanomaterial networks will be useful within future transparent and flexible electrochemical devices. For example, electrochromic windows and displays, solar cells, sensors and energy storage devices such as batteries and supercapacitors. All these applications require the passage of charge through the plane of the network, and therefore insights gained *via* their characterisation as transparent conductors can be directly applied. However, electrochemical applications also entail interfacial processes (*i.e.* with the electrolyte) that occur perpendicular to the plane of the network. Like the aforementioned 'in-plane' electrical properties, interfacial electrochemical properties will depend on the network constituents and their spatial arrangement on the surface. Accordingly, these properties are also likely to vary with thickness when disordered nanomaterial networks are very thin.

Identifying and understanding these effects will be crucial for the development of transparent and flexible electrochemical devices. Therefore, in this chapter, the charge storage properties of transparent carbon nanotube networks are investigated.

4.2 Experimental Methods

P3-SWNTs were obtained from Carbon Solutions Inc. These nanotubes are produced by the electric arc-discharge method using a nickel/yttrium catalyst and consist of a 2:1 mixture of semiconducting and metallic tubes. A nitric acid purification treatment is carried out by the manufacturer which also imparts carboxylic acid functions groups at 1-3% atom/atom. These tubes are present as bundles with lengths in the range 0.5 to 1.5 μm .

4.2.1 SWNT Dispersion Preparation

The SWNTs were added to Millipore water (1 mg/mL) and sonicated using a high power sonic tip (VibraCell CVX, 750W) for 30 min at 20% amplitude and 60 kHz. The formed dispersions were left overnight to allow large aggregates to settle, and then centrifuged (Heraeus Multifuge X1) for 90 min at 5500 rpm to facilitate removal of undispersed material. The supernatant was retrieved and the resulting concentration of dispersed SWNTs was determined by UV-visible absorption spectroscopy at 660 nm using a Varian Cary 6000i. Using Equation 2.1 (Beer-Lambert relation), the dispersion concentration was found using the extinction coefficient for this system, 3389 mL/mg.m.²¹⁹

4.2.2 SWNT Electrode Preparation

Electrodes of varying thickness were prepared by vacuum filtering set volumes of dispersion (and therefore mass of nanotubes) through porous cellulose membranes (MF-Millipore membrane, mixed cellulose esters, hydrophilic, 0.025 μm pore size, 47 mm diameter), leaving film-like networks of nanotube bundles. The films were transferred to polyethylene terephthalate (PET) substrates by a transfer process involving dissolution of the nitrocellulose support membrane. This was achieved by sandwiching the SWNT film between the PET and nitrocellulose, while applying heat (75°C) and pressure (~ 1 kPa) to create

adhesion between the SWNT network and the plastic substrate. Next, the combination was exposed to acetone vapour, a series of acetone baths and finally a single methanol bath to remove the filter membrane.

4.2.3 Electrode Characterisation

Optical transmittance spectra of the SWNT films were obtained in the visible range (400-800 nm), subtracting the PET background absorbance. The four-point probe technique was used to characterise the DC electrical properties of the PET transferred nanotube films. To do so, electrodes were created on the film surface using an alcohol based conductive silver paint (Agar Scientific). The electrode separation and width were ~ 1 cm and ~ 0.5 cm, respectively. Current-voltage curves were obtained using a Keithley 2400 source meter. Scanning electron microscope (SEM) images were obtained by transferring the SWNT films onto Au-Pd sputtered glass substrates. This was carried out using an identical process as for the PET substrates.

For electrochemical measurements the PET transferred SWNT films were cut into strips with consistent dimensions, giving a geometric surface area of 2.8 cm^2 . The upper edge of the electrode was defined using adhesive tape, and silver paint was again used to form a low resistance electrical contact. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to characterise the SWNT network working electrodes. Here a three-electrode electrochemical cell with a Gamry 600 potentiostat was used. Potential was measured against a Ag/AgCl reference electrode (3M NaCl), and a large graphitic carbon counter electrode completed the cell. Measurements were performed in a 1 M H_2SO_4 electrolyte solution (Sigma-Aldrich). Electrode capacitance (C/A) was determined from the CVs obtained within a potential window from 0 to 0.8 V *vs.* Ag/AgCl at 50 mV/s. Electrode equivalent series resistance R_{ESR} was determined from the EIS spectra; specifically, from the real impedance at high frequency (0.1 MHz). Here a 10 mV perturbation was used at a DC bias of 0 V *vs.* Ag/AgCl.

4.3 Results & Discussion

4.3.1 Thickness Dependent Electrical Properties

Carbon nanotube networks were prepared with various loadings (mass per unit area, M/A) and were transferred onto Au-Pd sputtered glass substrates for SEM imaging. Figure 4.1 indicates that for very low loadings (5 and 12 nm average thickness), nanotubes are present in bundles with mean diameter and length of ~ 23 nm and ~ 1.3 μm respectively. The bundles are spatially non-uniform, whereby clustered regions of high density are interspersed with sparsely populated regions. This feature of thin nanotube networks has been observed previously by Raman mapping and spatially resolved transmittance measurements.^{190;191} Non-uniformity in the spatial distribution of the deposited material means that certain regions are either isolated or weakly connected to the network. For all subsequent characterisations the various M/A networks were transferred onto PET substrates (Figure 4.2).

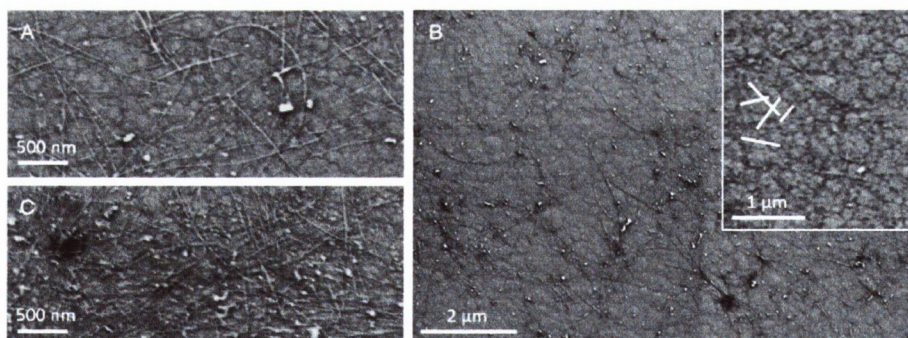


Figure 4.1: SEM images of P3-SWNT nanotube networks. (A) A 5 nm thick SWNT film. (B) Wide field image of the same film. Inset: Thin networks such as this contain nanotubes which are isolated or only weakly connected to the network. This is shown in the SEM, although the poor contrast achieved for these sparse networks makes it difficult to see isolated nanotubes. The motif in white is a schematic demonstrating the shape of the array of nanotubes in this image. (C) A 12 nm thick SWNT film indicating increased density and uniformity of overlapping bundles.

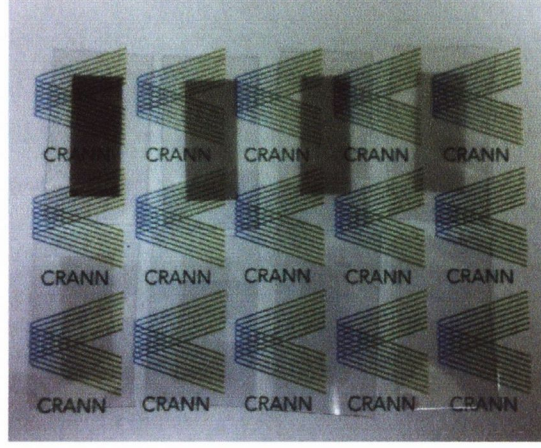


Figure 4.2: Photograph of single walled carbon nanotube transparent films on PET substrates. Different quantities of nanotubes were deposited, resulting in differing transmittance. The area of the transferred nanotube tubes films was 8 mm by 20 mm.

Optical transmittance measurements were performed for all films, and it was found that transmittance (at 550 nm) varied from 13% for the thickest film to 97% for very thin films. This M/A range spans the region of interest for the majority of transparent applications. Film thickness varies with transmittance for thin metallic films^{188;337} as indicated by Equation 4.1.

$$T = [1 + Z_0 \sigma_{Op} t / 2]^{-2} \quad (4.1)$$

Here, $Z_0 = 377 \text{ Ohm}$ is the impedance of free space and σ_{Op} is the optical conductivity. This expression has a virtually identical functional form as the Lambert-Beer law with $Z_0 \sigma_{Op} \approx \alpha$, the optical absorption coefficient. This can be seen by the first order Taylor expansion of Equation 4.1 and Equation 2.1. The optical conductivity of SWNTs is close to 170 S/cm ,^{191;220;338;339} enabling determination of film thickness from transmittance data, as shown in Figure 4.3A. Thus, the films prepared in this work have thicknesses spanning two orders of magnitude; from 5 nm to 530 nm.

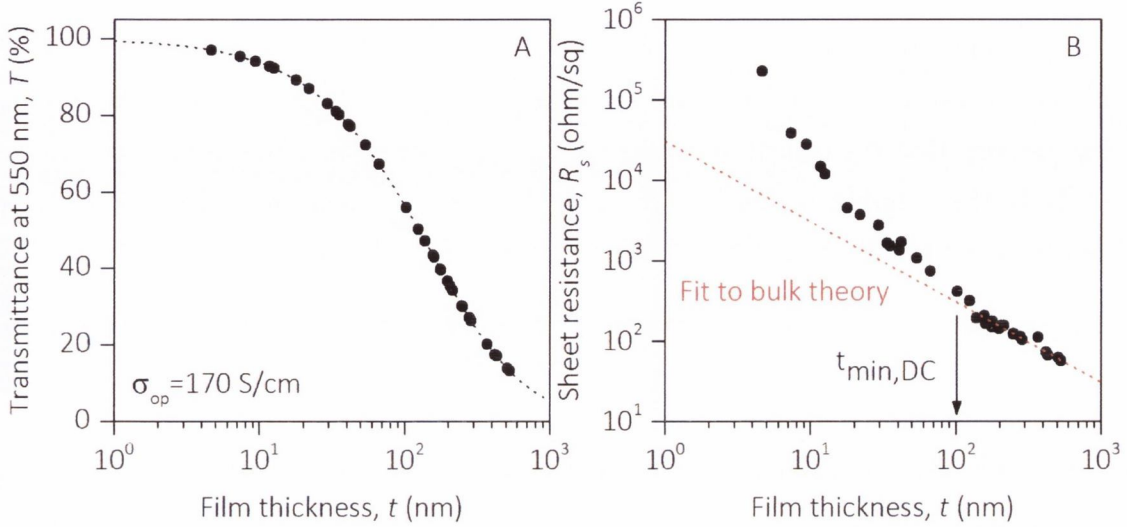


Figure 4.3: (A) Relationship between network transmittance (550 nm) and thickness, plotted using Equation 4.1 with $\sigma_{op} = 170 \text{ S.cm}^{-1}$. (B) Sheet resistance of P3-SWNT films plotted as a function of film thickness. The dashed line represents behaviour expected for bulk-like electrodes. The arrow indicates the thickness at which the electrical properties begin to deviate from bulk-like behaviour (100 nm).

Current voltage curves were obtained for all films using the four-point probe technique. Sheet resistance was calculated (Equation 2.3) for each film and plotted as a function of thickness as shown in Figure 4.3B. It was found that R_s varied from 10^2 up to 10^5 Ohm/sq as film thickness is reduced. For the thicker films, we observe that R_s scales inversely with film thickness, illustrated by the dashed red line, as expected for bulk-like films. However, below a critical thickness, $t_{min,DC} \approx 100 \text{ nm}$, the data began to deviate from this line as percolation effects become apparent. This behaviour has been observed for networks of other materials such as nanotubes,¹⁹¹ nanowires,⁹⁷ and graphene sheets.⁹⁶ Clearly, such percolation effects are detrimental to the electrical performance of these nanotube films. To emphasise this point, in the absence of percolation it would be expected that the thinnest film prepared here ($T=97\%$) would have a sheet resistance of 6.8 kOhm/sq, $30\times$ lower than the value realised. Such a large difference highlights the

importance of percolation effects on the properties of disordered nanostructured films.

In the field of transparent conductors, it is common to plot the transmittance as a function of sheet resistance. These data are presented in Figure 4.4 for these P3-SWNT films. It can be seen that the transition thickness, $t_{min,DC}$, corresponds to a film transmittance of 45%. In the bulk-like region ($t > t_{min,DC}$), the transmittance and sheet resistance data can be fitted to Equation 4.2, indicated by the red dotted line in Figure 4.4.

$$T = [1 + \frac{Z_0}{2R_S} \frac{\sigma_{Op}}{\sigma_{DC,B}})]^{-2} \quad (4.2)$$

This relation is formed by combining Equation 4.1 with $t = (\sigma_{DC,B} R_s)^{-1}$, where $\sigma_{DC,B}$ is the bulk-like DC conductivity of the network. The ratio of bulk-like DC to optical conductivity is often cited as a figure of merit (FoM) for bulk-like networks.¹⁶¹ We found that these films give a value $\sigma_{DC,B}/\sigma_{op} = 1.9$, similar to that observed for other carbon nanotube networks.⁹⁸ Using a value of 170 S/cm for the optical conductivity, we can estimate the bulk DC conductivity of the thicker networks as ≈ 300 S/cm. This value isn't particularly high considering that the best SWNT networks have $\sigma_{DC} = 12\,826$ S/cm.²²⁵

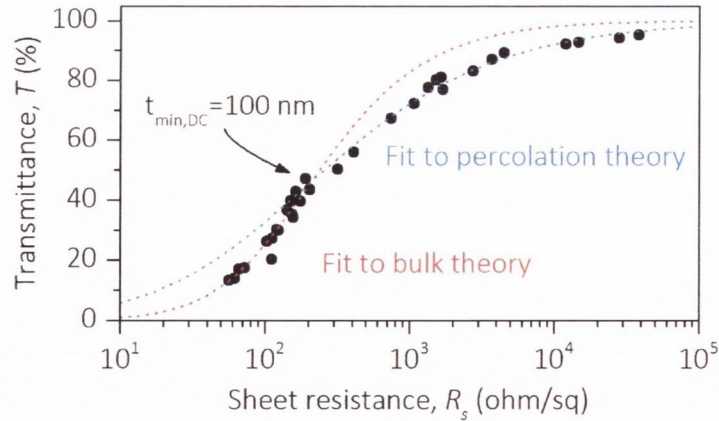


Figure 4.4: Optical transmittance (at 500 nm) plotted as a function of sheet resistance for P3-SWNT networks. The red and blue dashed lines are fits to Equations 4.2 and 4.3, respectively. The transition between these two regimes occurs at a film thickness of $t=100$ nm.

The presence of percolation effects means that the bulk-like electrical FoM does not enable a fair comparison between transparent conducting materials at the upper end of the transmittance range; the region of primary interest for transparent applications. In light of this, a previous study from our group¹⁶¹ has shown that in this percolation regime the transmittance and sheet resistance are related by Equation 4.3.

$$T = [1 + \frac{1}{\Pi} (\frac{Z_0}{R_s})^{1/(n_{DC}+1)}]^{-2} \quad (4.3)$$

Here Π is known as the percolative figure of merit and n_{DC} is the percolation exponent. When this relation is fitted to the data for $t < t_{min,DC}$, the data gives $\Pi = 3.1$ and $n_{DC} = 0.6$, as shown by the blue dotted line in Figure 4.4. These values are typical of nanotube films.⁹⁸ To qualify as a transparent EC, we would expect a device to have an overall transmittance $> 80\%$, with both electrodes having transmittance $> 89\%$. This requirement means that a transparent EC based on nanomaterial networks will operate well within the percolation regime.

4.3.2 Thickness Dependent Electrochemical Properties

Having established that percolation effects control the electrical properties of the SWNT networks studied here when they are thinner than 100 nm, we now turn to characterising their electrochemical properties over the same thickness range. Here we focus on two parameters; the equivalent series resistance (R_{ESR}) and electrode capacitance per unit area (C/A). Measurements to obtain these parameters were carried out in a three electrode electrochemical cell, with nanotube networks transferred directly onto PET as the working electrodes. We emphasise that no supporting current collector was used, thereby requiring that current collection occur through the network itself.

Electrochemical impedance spectroscopy was used to determine the R_{ESR} in 1 M H_2SO_4 for all electrode thicknesses. Figure 4.5A presents a complex plane plot of the impedance data obtained for selected films. The curves were extrapolated to the real impedance axis (Z') in the high frequency region to provide a measure of the equivalent series resistance of the cell. Plotting the obtained R_{ESR} as a function of thickness in Figure 4.5B reveals

a dependence almost identical to that observed for R_S in Figure 4.3B, with bulk-like behaviour above $t_{min,ESR} = 100$ nm and a marked deviation below. This similarity is made clearer in the inset of Figure 4.5, where R_{ESR} is plotted against R_S , giving a linear relationship. This is to be expected where the active material also acts as the current collector. Due to the large resistance associated with current collection through the network itself, the electrolyte resistance is relatively unimportant.

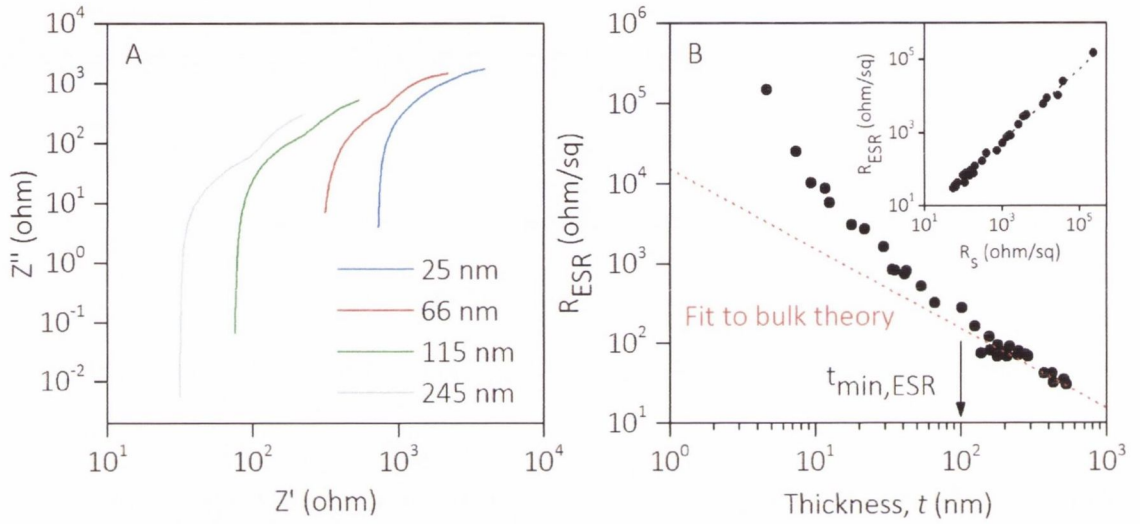


Figure 4.5: (A) EIS spectra of various P3-SWNT films with differing thickness. (B) High frequency real impedance intercepts extracted from (A) as a measure of electrode R_{ESR} plotted as a function of electrode thickness. The inset plots this quantity *vs.* the sheet resistance values shown in Figure 4.3B.

To more clearly demonstrate these observations, it is useful to plot a property that is normally thickness independent as a function of thickness, such as the DC conductivity. We calculated σ_{DC} from the sheet resistance using $\sigma_{DC} = (R_s t)^{-1}$, as well as an effective conductivity associated with the equivalent series resistance using $\sigma_{ESR} = (R_{ESR} t)^{-1}$. These were plotted against film thickness in the Figure 4.6 inset. We observed that for thickness above ~ 100 nm, within error, conductivity is independent of thickness as expected for bulk-like materials. Below this however, both conductivities fall non-linearly with decreasing thickness. Other thin conducting films of nanostructured materials display similar

behaviour, such as carbon nanotubes,^{191;340} graphene,²²⁹ and metallic nanowires.^{97;161} We emphasise that the effective conductivity based on the R_{ESR} displays similar behaviour because it is also dominated by the resistance of the electrode.

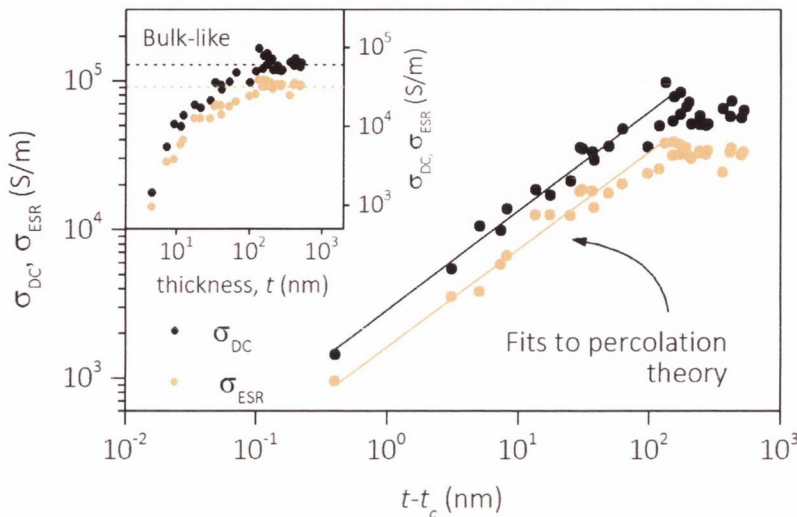


Figure 4.6: Percolation behaviour of the DC conductivity and an effective ESR conductivity for P3-SWNT films. The inset demonstrates onset of this deviation from bulk-like behaviour below ~ 100 nm for both quantities.

Confirmation that this behaviour is due to percolation is made by showing that the conductivity scales with thickness according to a percolation scaling law (Equation 2.6). This is demonstrated in the main Figure 4.6. Fits to the data find a percolation threshold of $t_c = 4.3$ nm in both cases, and percolation exponents $n_{DC} = 0.69$ and $n_{ESR} = 0.66$. These values are lower than the universal values of 1.3, expected for two dimensional systems. The reason for this discrepancy is unknown.

Cyclic voltammetry was similarly carried out on all network electrodes to investigate how capacitance varies with film thickness. CVs of selected films are presented in Figure 4.7A. It is clear that in addition to non-faradaic capacitive current passed due to the electrochemical double layer, there is appreciable faradaic activity occurring in this potential window; an oxidation wave at 0.5 V and corresponding reduction wave at 0.35 V *vs.*

Ag/AgCl. The nanotubes used in this study are known to possess oxygen containing functional groups such as carboxylic acids, likely to be responsible for this faradaic activity.²⁴⁵ In addition, these hydrophilic groups stabilise the nanotubes when dispersed in water and facilitate wetting of the network by the electrolyte. Capacitance normalised to the geometric electrode area (C/A) was calculated from the CVs by integrating the current over the potential window and these values were plotted as a function of film thickness, shown in Figure 4.7B. We observe that the capacitance increases linearly above a critical thickness, $t_{min,C} \approx 20$ nm, as expected for a bulk-like material that is effectively wetted by the electrolyte. However, below this critical thickness, linear behaviour is not maintained, with capacitance falling more quickly than expected. In fact, the thinnest film had a capacitance one order of magnitude lower than expected. Comparison to the behaviour observed for R_S and R_{ESR} strongly suggests that this behaviour may also be percolative in nature. To our best knowledge, this effect has not been reported previously.

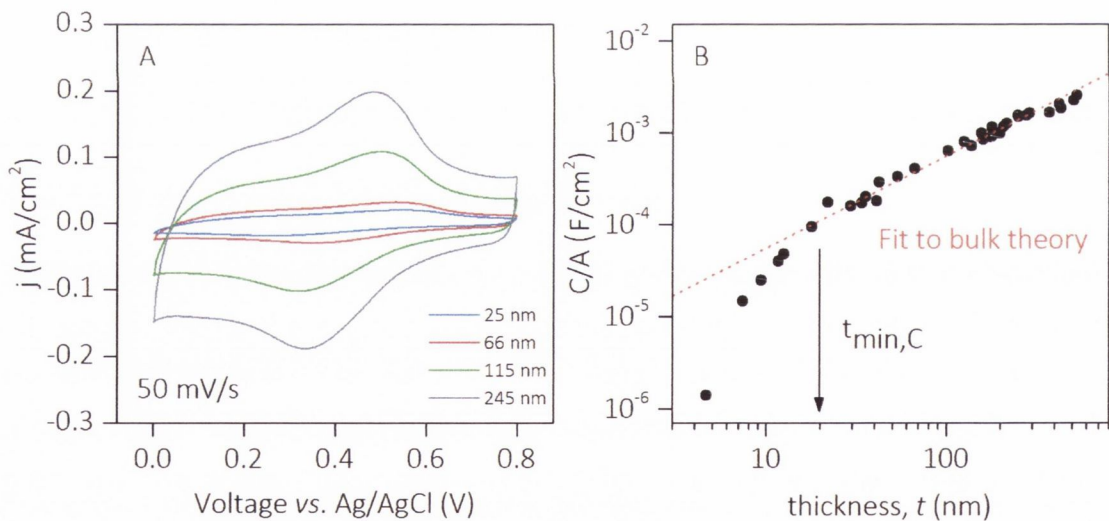


Figure 4.7: (A) Cyclic voltammograms of various P3-SWNT networks with various thickness using 1 M H₂SO₄ at 50 mV/s. (B) Capacitance per unit area was calculated from these CVs and plotted as a function of network thickness.

We can explore in more detail whether the deviation of capacitance values with decreasing film thickness can also be described by a percolation scaling law, by re-expressing the data capacitance per electrode volume ($C_V = C/At$). This quantity was plotted as a function of thickness in the Figure 4.8 inset. Assuming that thick networks have a well defined surface area per unit volume, the volumetric capacitance should be thickness independent for bulk-like films (in the absence of transport limitations). This is observed for calculated volumetric capacitance of films with thickness above 20 nm. We find a mean value for the bulk-like volumetric capacitance of $C_{V,B} = 55 \text{ F/cm}^3$ at a scan rate of 50 mV/s. Given an estimated nanotube density of 1000 kg/m^3 , measured for a thick free-standing film, we can obtain a value for the specific capacitance of our network, saturating at $\sim 55 \text{ F/g}$ for films in the bulk-like region. Similar values were reported in other studies featuring nanotube-based transparent supercapacitor electrodes.^{149;159} However, below the critical thickness, significant fall-off in capacitance is observed. If this fall-off is consistent with percolation, then we can expect the volumetric capacitance to scale with thickness in the thin film regime as per Equation 4.4.

$$C_V \propto (t - t_c)^{n_c} \quad (4.4)$$

We believe the capacitance will follow this form because a wide range of phenomena controlled by percolation can be modelled using this type of function.¹⁸⁹ The dashed blue line in main Figure 4.8 indicates that this model fits the data very well, giving $t_c = 4.3 \text{ nm}$ and $n_c = 0.83$. These values are similar to those obtained for sheet resistance and ESR.

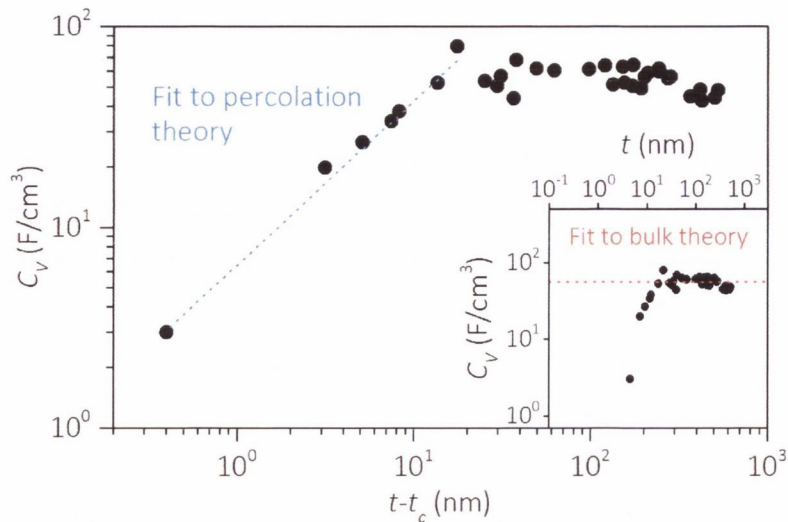


Figure 4.8: Percolation behaviour of the volumetric capacitance of P3-SWNT networks. The inset indicates that deviation from bulk-like behaviour begins at $t \sim 20$ nm. The data for thickness less than this value can be fitted to Equation 4.4, giving a percolation threshold of $t_c = 4.3$ nm and a percolation exponent of $n_c = 0.83$.

We expect that the percolation threshold determined from sheet resistance, equivalent series resistance and capacitance all agree ($t_c = 4.3$ nm), as in all cases they require current flow through the network. However, it is noted that the transition thickness from percolation to bulk-like behaviour differs considerably between the capacitance ($t_{min,C} \approx 20$ nm) and the sheet resistance or ESR ($t_{min,DC} \approx t_{min,ESR} \approx 100$ nm).

Understanding why can be found by considering what specific qualities of the network control these different properties. In the case of sheet resistance, it has been shown that the transition thickness can be correlated with a transition from spatial non-uniformity to a greater network uniformity.^{97;161;191} For rod-like objects, it has been shown that the transition occurs at a network thickness ~ 2.3 times the diameter of the rods making up the network.¹⁶¹ However, given that all the nanotubes present in the network form an electrochemical interface with the electrolyte, it is unlikely $t_{min,C}$ would be sensitive to spatial non-uniformity. It is more plausible that the capacitance would be sensitive to

the connectivity of the network. For sparse networks, not all nanotubes will be connected to the main network. Therefore, we can expect that the capacitance will depend on the number of nanotubes connected to the main network. The capacitance would then become thickness independent only when the last isolated cluster of nanotubes becomes connected to the main network and can contribute to the film capacitance. This transition is expected to occur well before the non-uniformity to uniformity transition, as is observed experimentally.

Capacitance scales with the surface area of the electrode, therefore we expect it to be proportional to the fraction of nanotubes connected to the network. Percolation theory suggests that the probability that an object is connected to a network (or fraction of objects connected, N_A) will scale as $P \propto (N_A - N_{A,C})^\beta$, where β is a scaling exponent.¹⁸⁹ This suggests that $C/A \propto P$, justifying the use of Equation 4.4.

This behaviour is illustrated schematically in Figure 4.9A, which depicts a sparse network of randomly arranged rods. The network is above the percolation threshold as seen by the unbroken path made by the rods coloured blue. It is thin enough to be spatially non-uniform, with the bottom left area having considerably less rods than other areas of the network. As discussed above, this non-uniformity is associated with thickness dependent DC conductivity. Indicated in red are clusters of nanotubes which aren't connected to the main network and therefore can't contribute to current flow or capacitance. Therefore we expect that this network has a thickness below both $t_{min,C}$ and $t_{min,ESR}$. In Figure 4.9B we present the same network though with another 50 rods added randomly. Now all rods are connected to the main network and therefore are able to contribute to the measured capacitance. However, in both cases, spatial non-uniformity is still present, representing a scenario whereby $t_{min,C} < t < t_{min,ESR}$, as suggested by these experiments.

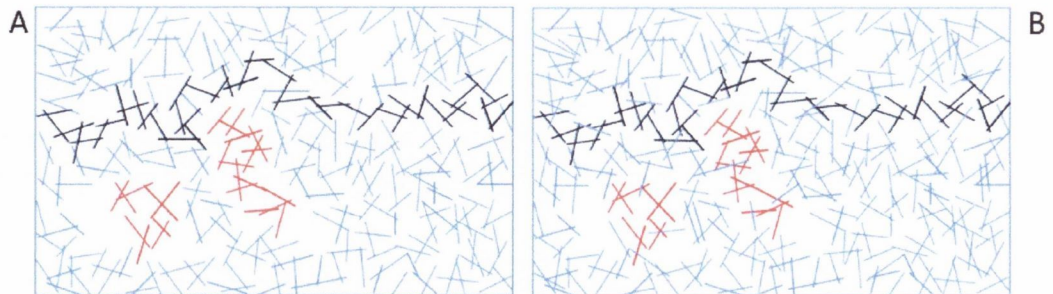


Figure 4.9: (A) A network of rods well above the percolation threshold, t_c , (highlighted by the black pathway). The red rods aren't connected to the main network and can't contribute to capacitance, therefore $t < t_{min,C}$. (B) When the number of rods per unit area (equivalent to M/A) is increased, the red clusters becomes connected to the main network, hence $t > t_{min,C}$. In both cases spatial non-uniformity is present, therefore $t < t_{min,DC} = t_{min,ESR}$.

4.3.3 Electrode Performance

We have established in the previous section that as electrode thickness is reduced to increase transmittance, the absolute capacitance falls not only because electrode mass scales with thickness but also due to percolation. This is important because the energy storage capability of the capacitor is proportional to the capacitance. We explore this trade-off between transmittance and capacitance by plotting the measured transmittance *vs.* areal capacitance in Figure 4.10. We see here that thicker films have high C/A and low T , while thin films display the opposite. For a bulk-like electrode, the areal capacitance is related to the thickness by $C/A = C_{V,B}t$, where $C_{V,B}$ is the bulk-like volumetric capacitance. Combining this with Equation 4.1 to eliminate t gives a relation between the transmittance and areal capacitance for bulk-like electrodes, shown in Equation 4.5.

$$T = [1 + \frac{Z_0 \sigma_{op} C}{2C_{V,B} A}]^{-2} \quad (4.5)$$

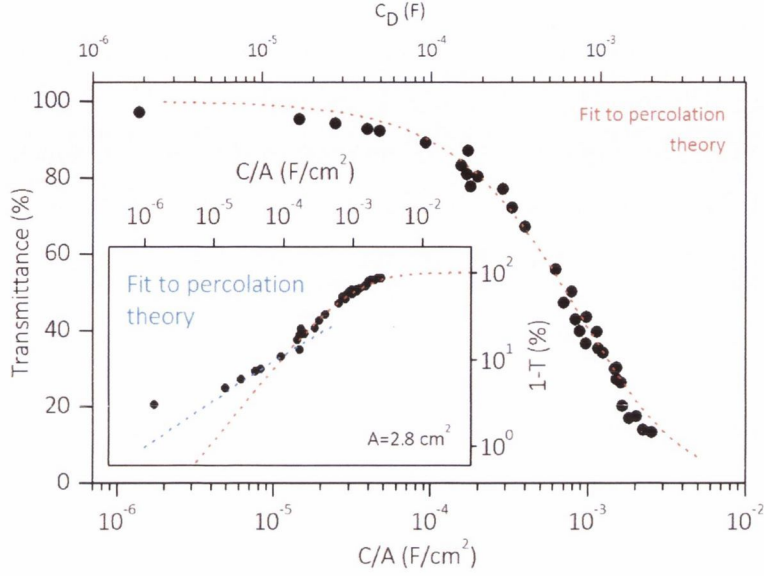


Figure 4.10: Measured transmittance (550 nm) of P3-SWNT films plotted as a function of areal capacitance. The dashed red line is a fit to Equation 4.5. For the inset the transmittance data is re-expressed as $1-T$ to better observe the presence of percolation. The dashed red line indicates bulk-like behaviour. The films transition to percolative behaviour below 20 nm, which can be fitted to Equation 4.6 indicated by the blue dashed line.

The blue dashed line in Figure 4.10 is a fit to data for these SWNTs networks using Equation 4.5. Very good agreement is observed for $C_{V,B}/\sigma_{op}=0.33$ F/S.cm². We note that the data begins to deviate from the fit for $C/A < 10^{-4}$ F/cm² due to percolation. This can be seen more clearly in the Figure 4.10 inset where we plot $1-T$ vs. C/A . We can use percolation theory to derive an expression for C/A for films with $t < t_{min,C}$, following the procedure described by De *et al.*¹⁶¹ Making the approximation that $t - t_c \approx t$, and given that at the bulk to percolation transition, $t = t_{min,C}$ and $C_V = C_{V,B}$, Equation 4.4 can be rewritten as $C_V = C_{V,B}(t/t_{min,C})^{n_C}$, where $C_{V,B}$ is the volumetric capacitance of the bulk-like film. Inserting this expression into $C/A = C_{V,B}t$, which we note is true for all thicknesses, gives an expression which can be substituted into 4.1 to produce Equation

4.6.

$$T = [1 + \frac{Z_0 \sigma_{Op} t_{min,C}}{2} (\frac{C/A}{C_{V,B} t_{min,C}})^{1/(n_c+1)}]^{-2} \quad (4.6)$$

All the parameters in the expression we have described previously; $\sigma_{Op} = 1.7 \times 10^4$ S/m, $t_{min,C} \approx 20$ nm (Figure 4.7B), $C_{V,B} \approx 55$ F/m³ and $n_c = 0.83$ (Figure 4.6). Using these parameters we can plot Equation 4.6 on the inset of Figure 4.10, which matches the data very well as indicated by the blue dotted line. Disagreement between the theoretical line and the lowest C/A datum is due to the approximation $t - t_c \approx t$.

It is useful to consider what capacitance may be achieved for a film with $T = 90\%$. Equation 4.6 can be rearranged and setting $T=90\%$, giving Equation 4.7.

$$(\frac{C}{A})_{T=90\%} = C_{V,B} t_{min,C} (\frac{0.11}{Z_0 \sigma_{Op} t_{min,C}})^{n_c+1} \quad (4.7)$$

This means that a high transmittance coupled with high C/A requires low σ_{op} and $t_{min,C}$ coupled with high $C_{V,B}$. We note that while σ_{op} is generally a materials property, both $t_{min,C}$ ¹⁶¹ and $C_{V,B}$ depend on nanotube bundle diameter, indicating that low diameter bundles should give better results. Additionally, high values of n_c are favourable for high C/A . It is known that for electrical percolation, n_{DC} is controlled by the distribution of junction resistances in the network^{341–343} and therefore scales with network non-uniformity.¹⁹² However, it is not yet clear what parameters control n_c . If we assume that it also scales with network non-uniformity, this would suggest that non-uniform networks are preferable for thin transparent supercapacitors. Given that the R_S and R_{ESR} scales with n_{DC} and n_{ESR} respectively,¹⁹² this would suggest that networks with high n_{ESR} and therefore presumably high n_C will have both higher C/A and higher R_{ESR} . Given that achievable power scales inversely with the equivalent series resistance (Equation 1.1), this trade-off will need to be considered for certain applications.

The energy density and power density of a symmetric supercapacitor³⁴⁴ can be calculated using the relations $E/M = C_D \Delta V / 2M$ and $P/M = \Delta V^2 / 4R_{ESR,D}M$, where ΔV is the operating voltage and M is twice the mass of SWNTs in the electrode. We note that the device capacitance C_D , is half the measured electrode capacitance, while the device ESR, $R_{ESR,D}$ is twice the measured electrode ESR (due to the fact that we have made

measurements in a three electrode cell³⁴⁴). We have plotted E/M and P/M , called a Ragone plot, in Figure 4.11. For comparison, we have also included data reported in the literature for other transparent supercapacitors. It is seen that the data for bulk-like networks prepared here cluster in the top right hand corner of the graph, similar to other EC electrodes published by others.^{141;149;157} However, if we focus on networks with $T > 90\%$, it is apparent that energy and power densities rapidly diminish due to percolation effects. In order to maximise power and energy density for high transmittance electrodes, it is necessary to shift the transition from bulk-like to percolation-like behaviour to lower thicknesses; that is, reduce $t_{min,ESR}$ and $t_{min,C}$. It is known that $t_{min,DC}$ scales linearly with the diameter of the rods making up the network, in this case, the nanotube bundle diameter, and it is reasonable to assume the same for $t_{min,ESR}$ and $t_{min,C}$. Therefore, it is possible to minimise or completely avoid percolation effects by using better exfoliated nanotubes. According to Figure 4.1A, $T=90\%$ can be achieved for $t=16$ nm. It was recently shown that $t_{min,DC} \approx 2.33D$, where D is the bundle diameter.⁹⁸ Thus, the onset of percolation could be suppressed to below this thickness if $D < 7$ nm.

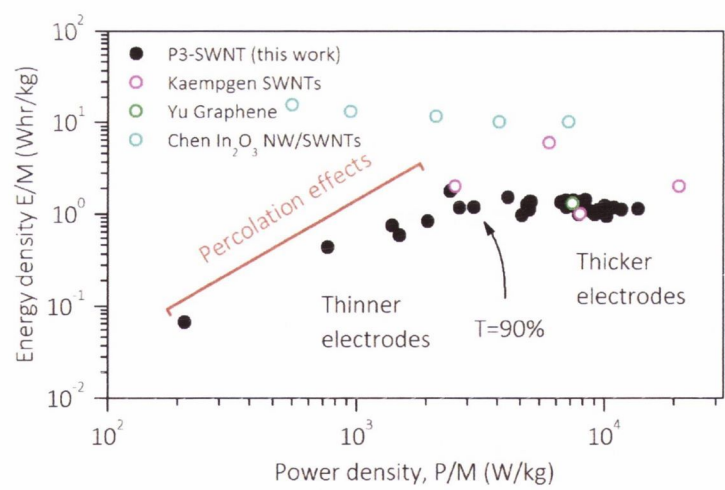


Figure 4.11: Ragone plot comparing the E/M and P/M for these P3-SWNT films and the available literature for thin film supercapacitors^{141;149;157}.

The data in Figure 4.10 show that for the SWNTs used here, a transmittance of 90% per electrode (80% per EC device, assuming perfectly transparent electrolyte) limits the attainable areal capacitance to $\sim 10^{-4}$ J per electrode or $\sim 1.5 \times 10^{-4}$ F for a two electrode device with an area of 2.8 cm^2 . It is difficult to assess whether these energies are enough for applications, as it is still unknown exactly what role transparent ECs will play in transparent electronics devices.

Today, considerable research is being conducted towards the creation of autonomous sensing and communication platforms.³⁴⁵ These miniature devices will incorporate sensors which communicate a detection event to the outside world using a radio frequency antenna. This communication event will likely be powered by an EC, which can be later recharged, possibly by photovoltaic technologies. Transparency may be an advantage for such integrated devices in order to provide camouflage or for aesthetic reasons. It has been estimated that the energy requirements for communication would be 10s of micro-joules per event.³⁴⁶ These requirements appear to be compatible with the transparent ECs described in this work. As was discussed in the introduction, if more energy is required, redox active materials such as RuO_2 or MnO_2 could be incorporated onto the nanotube network in order to impart additional pseudocapacitance.³⁴⁷ Although the volumetric capacitance will be increased, the percolation effects described here will still be present.

4.4 Conclusions

In this work, we have examined the effect of percolation on the charge storage properties of SWNT network electrodes. Measurements of the electrode transmittance and sheet resistance as a function of thickness reveal a distinct transition from bulk-like to percolative to behaviour as the thickness is decreased below 100 nm.

Characterisation of different thickness nanotube films as supercapacitor electrodes confirmed this behaviour. The equivalent series resistance also underwent a percolation to

bulk transition at electrode thickness of 100 nm. Interestingly, similar results were observed for the areal capacitance, albeit with a lower transition thickness of 20 nm. The DC conductivity, effective ESR conductivity and volumetric capacitance of thin films were all well described by percolation theory. All data could be described by percolation thresholds of 4.3 nm and critical exponents of $n_{DC}=0.66$, $n_{ESR}=0.69$ and $n_C=0.83$. We found the areal capacitance to be controlled by percolation for electrodes with $T>90\%$. At $T=90\%$, the capacitance was 10^{-4} F/cm², enough to power burst communication for an integrated sensing device. For bulk-like electrodes, the energy and power densities clustered in a well-defined area of the Ragone plot. However, the percolative data formed a long tail toward the bottom left corner of the graph, indicating severely impaired performance. This work illustrates that if high transparency is required when using nanomaterial networks, a severe penalty in both power and energy must be paid. However, that penalty can be estimated using percolation theory.

Chapter 5

Conducting Polymer Network Electrodes

5.1 Introduction

In this chapter, we seek to improve upon the performance of all previous transparent/flexible charge storage electrodes by using a molecular conductor, poly(3,4-ethylenedioxy thiophene):poly(styrene-4-sulfonate). Recent studies have shown that PEDOT:PSS can be used to produce transparent/flexible conductors with excellent properties, and it is known to possess very good capacitive electrochemical properties. Therefore, here we have prepared transparent films of this conducting polymer and analysed its suitability as a transparent capacitive layer.

By using a molecular conductor to produce thin networks (as opposed to using discrete nanoscale objects), it is hoped that detrimental percolation effects can be avoided. This would enable the production of transparent films whose properties remain bulk-like even at very low thicknesses. To help facilitate this we have used an airbrush spraying robot to provide greater control over the film deposition.

In addition, this spray system allows the production of large area films (max. 18 by 18 cm). Presently, little work has been done exploring the properties of transparent capacitive films larger than a few square centimeters. However, it is likely that larger area electrodes will be required for their application in transparent electronics. In the absence of an underlying current collector, charge must be collected through the plane of the film, which contributes appreciably to the R_{ESR} . As a result, it is likely that the absolute capacitance (and hence energy stored) will not scale linearly with film area, particularly when such films are discharged and recharged quickly.

Identifying and understanding the geometric effects that arise in this situation will be necessary for the application of transparent energy storage systems in future devices. Therefore, in this chapter, the charge storage properties of transparent conducting polymer networks are investigated, in particular, focusing on the effect of film lateral dimensions.

5.2 Experimental Methods

5.2.1 PEDOT:PSS Electrode Preparation

Heraeus supplied poly(3,4-ethylenedioxythiophene):poly(styrene-4-sulfonate) (PEDOT:PSS) solution, sold under the trademark Clevios, was diluted with water to concentration 0.75 mg/mL. PEDOT:PSS films were then produced using the method described by McCarthy *et al.*²⁷⁷ In brief, the diluted polymer solution was loaded into a graduated reservoir which was attached to a Harddner and Steenbeck Infinity airbrush spray system. Control over the airbrush was provided by a Janome JR2300N robot. The substrates were cleaned with surfactant solution and isopropanol prior to use and placed on the robot substrate stage, heated to 110°C.

PEDOT:PSS films were produced by spraying the dispersion (N₂ pressure: 45-55 psi) on the PET substrates using a raster pattern (line spacing: 0.5 cm, airbrush-substrate separation: 9 cm). The film area and geometry was controlled by the spraying program, limited by the dimensions of the substrate stage (here 18 cm by 18 cm). The thickness of the films was controlled by the number of repeated passes made by the spray, which delivers a greater total volume of polymer solution onto a given area of the substrate.

Films were subsequently exposed to a formic acid (FA) post treatment. This was achieved by dipping the films into a FA solution for 5 seconds then allowing the films to dry in air.

5.2.2 Electrode Characterisation

Optical transmittance spectra of the PEDOT:PSS films were obtained in the visible range (400-800 nm), subtracting the PET background absorbance. The four-point probe technique was used to characterise the DC electrical properties of the films. To do so, electrodes contacts were created on the film surface using an alcohol based conductive silver paint (Agar Scientific). The electrode separation and width were ~1 cm and ~0.5 cm, respectively. Current-voltage curves were obtained using a Keithley 2400 source meter.

PEDOT working electrodes were prepared for electrochemical testing by cutting strips from the main film and confining the electrolyte exposed area using adhesive tape. Silver paint was again used to form contacts to the external circuit. The electrode area exposed to the electrolyte varied by altering the length (L) while holding the width (W) constant or by altering W while holding L constant. Here we have defined W as the dimension parallel to the surface of the electrolyte solution and L as the perpendicular dimension (*i.e.* greater L are more distant from the electrical contact). For these experiments, a large electrode was prepared and sequentially cut to smaller dimensions after the necessary measurements were completed. The film dimensions were recorded in each case using a micrometer.

Electrochemical testing was carried out using a three electrode cell consisted of a carbon counter electrode and Ag/AgCl reference electrode. Electrochemical measurements performed on the electrode include cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The electrolyte used was 0.5 M $K_2SO_4(aq)$ in all cases. CVs were obtained between the potential limits of 0.1 to 0.7 V *vs.* the Ag/AgCl reference couple. The scan rate was varied between 50 and 5000 mV/s. Potentiostatic EIS was carried out at a DC bias of 0.4 V *vs.* Ag/AgCl using a 10 mV AC perturbation, varying between 0.1 Hz and 100 kHz. Immediately prior to acquiring the EIS spectra, working electrodes were conditioned at the as-mentioned DC bias for 180 seconds.

Symmetric two electrode measurements of large area films were performed in a large beaker containing 0.5 M $K_2SO_4(aq)$ electrolyte. For these measurements two films of equal dimensions and transmittance were positioned 1 mm apart. Here, CVs were performed while varying the film area. This was achieved by varying the film length ($L \leq 6$ cm) while holding the width constant ($W=18$ cm), giving a maximum measured area of 108 cm².

5.3 Results & Discussion

5.3.1 Optoelectronic Properties

Aqueous solutions of PEDOT:PSS (referred herein as simply PEDOT) were deposited onto flexible plastic substrates to form thin films using an automated airbrush spraying system (Figure 5.1 A and B). The maximum film area available using this system was 18 cm by 18 cm, limited by the dimensions of the substrate stage. For commercial applications this stage area could be extended to produce arbitrarily large films. For the initial part of this study samples were prepared with dimensions of 5 cm by 5 cm. Figure 5.1C presents a example film ($T=70\%$) alongside the diluted PEDOT stock solution. The chemical structural of the copolymer is also shown. (D) Photograph of a range of films produced with the same dimensions produced by varying the sprayed volume and hence film thickness.

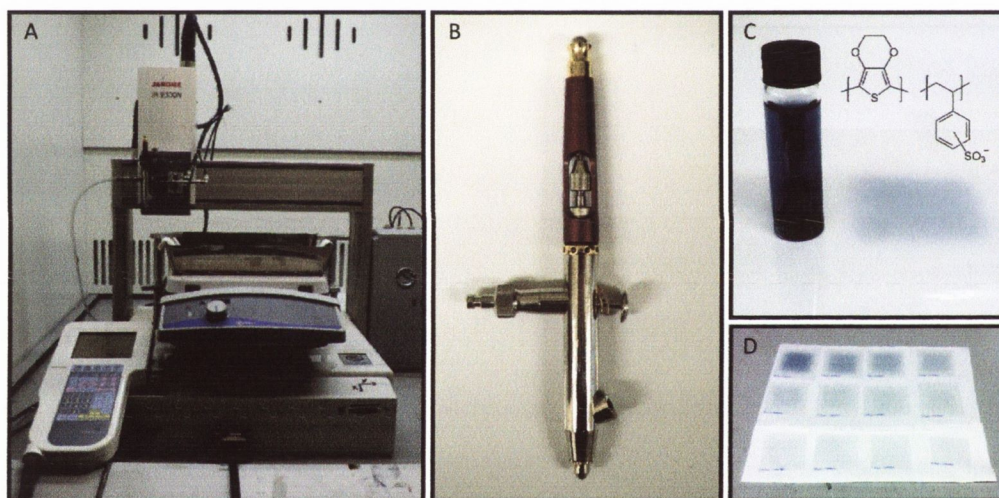


Figure 5.1: (A) Computer controlled spraying robot using (B) an airbrush spray system. (C) Photograph of an aqueous PEDOT dispersion and a film (5 cm by 5 cm, $T = 70\%$) produced by spraying the onto PET substrates. The chemical structural of the copolymer is also shown. (D) Photograph of a range of films produced with the same dimensions produced by varying the sprayed volume and hence film thickness.

The transmittance of the resulting films was readily controlled by the quantity of PEDOT solution sprayed onto the substrate, as indicated in Figure 5.1D and Figure ?? UV-visible transmittance spectra were obtained for a range these films, which are typically

broad and featureless (Figure 5.2A). As stated in Chapter 4, for metallic thin films³³⁷ the transmittance for a given thickness, t , is controlled by the optical conductivity, σ_{op} , *via* the Equation 5.1

$$T = (1 + \frac{Z_0 \sigma_{op} t}{2})^{-2} \quad (5.1)$$

σ_{op} is an important property of transparent SCs. To determine this parameter for PEDOT we measured the thickness of a number of sprayed films by profilometry (Dektak 6M, Veeco Instruments), finding values between 470 and 1600 nm. These films were sprayed onto glass substrates rather than PET, to obtain more accurate thickness measurements. Plotting the data as $T^{-1/2} - 1$ *vs.* t (Figure 5.2B) and fitting Equation 5.1, we obtained a value of $\sigma_{op}=24$ S/cm (at 550 nm) for these PEDOT films. For comparison, we have also included data for spin-coated PEDOT films³⁴⁸ (unfilled points), which fall close to our fitted curve. Using this value, the thickness of films sprayed on PET could then be determined from the transmittance spectra, which were found to vary between 17 and 432 nm. We note that this value of σ_{op} is extremely low compared to other conducting materials: Silver nanowires display values in the range 38-65 S/cm,^{97;192} SWNTs have 150-200 S/cm,^{191;220;338} and graphene has 100-2000 S/cm.⁹⁶ We believe this low optical conductivity will be critical to their success as transparent SCs (or conductors).

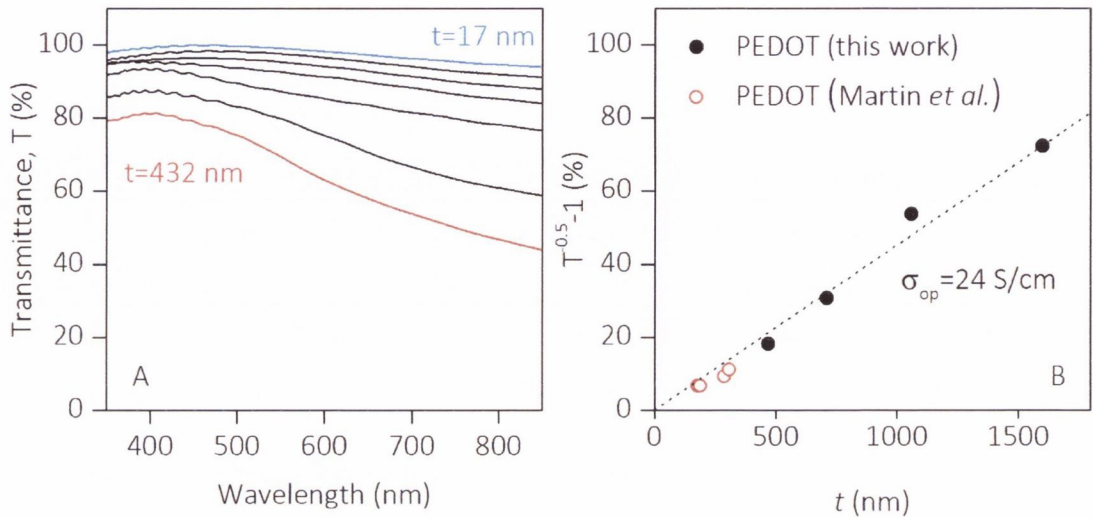


Figure 5.2: (A) Visible transmission spectra of PEDOT films with various sprayed volumes and hence thickness. (B) Plot of $T^{-0.5} - 1$ vs. film thickness measured by profilometry, for PEDOT films sprayed on glass substrates. Fitting Equation 5.1 to these data allowed the optical conductivity of PEDOT to be found; $\sigma_{op}=24$ S/cm (550 nm). Unfilled points are for spin coated PEDOT films described by Martin *et al.*³⁴⁸

As for traditional EC electrodes, in order for a transparent EC electrode to operate with high power, electronic transport to and from the electrochemical interface must occur efficiently. In light of this, next we characterised the electrical properties of these PEDOT films to evaluate their suitability as transparent current collectors.

Recent studies have found that although the electrical conductivity of as-prepared PEDOT films are poor, dramatic improvements are easily obtained by exposing the films to a variety of species such as sorbitol,²⁷⁴ ethylene glycol,²⁷⁵ methanol,³⁴⁹ and H_2SO_4 .^{276;350} Here we have used the simple and effective treatment reported recently by McCarthy *et al.*, which involves dipping the PEDOT films in concentrated formic acid (FA) for ~5 seconds.

The effect of this post processing treatment on the electrical properties of these films was determined using the four point-probe method. We measured sheet resistance, R_s , of a

number of films before and after exposure to the FA. The resulting R_s data is plotted as a function of film transmittance in Figure 5.3A. Clearly, the treatment dramatically improves the electrical properties of our transparent films, consistent with previous reports.²⁷⁷ At high transmittance (e.g. $T=90\%$), the sheet resistance is reduced by 3 orders of magnitude, falling from an untreated value of $R_s=1.5 \times 10^5$ Ohm/sq to 102 Ohm/sq after treatment.

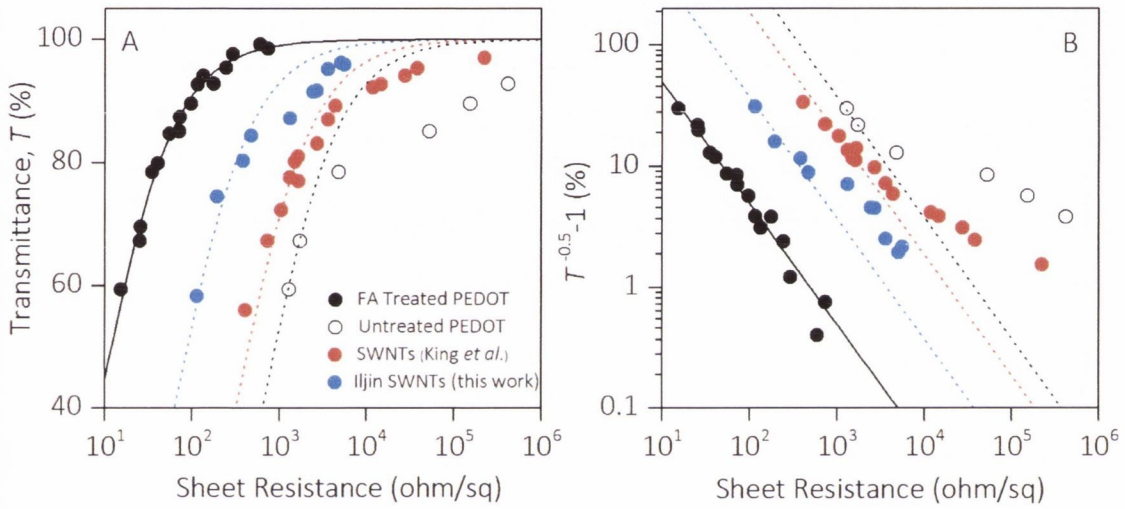


Figure 5.3: (A) Film transmittance (at 550 nm) as a function of sheet resistance for the as-prepared PEDOT films (unfilled black circles) and after treatment with formic acid (filled black circles). Also shown are data for disordered networks prepared using two different types of nanotubes. (B) The same data replotted to emphasise that the FA treated PEDOT films remain bulk-like (indicated by the linear plots) to very high transmittance ($T=99\%$).

For bulk-like films ($R_s = (\sigma_{DC}t)^{-1}$) the transmittance is related to sheet resistance *via* Equation 4.2. Here, the ratio σ_{DC}/σ_{Op} can be used as an electrical figure of merit (FoM_e) for transparent conductors. The black dashed line in Figure 5.3 is a fit to this relation, indicating that the as-prepared films have $\sigma_{DC}/\sigma_{Op} < 1$, making them unsuitable for use as transparent current collectors. However, the FA treatment causes an exceptional improvement; the FoM_e increases to $\sigma_{DC}/\sigma_{Op} = 39$ (shown by the black line), a value

that is hardly surpassed by any nanostructured electrode material bar silver nanowires.⁹⁸ For comparison, Figure 5.3 also includes data for transparent current collectors formed by disordered networks of two different types of SWNTs; P3 nanotubes characterised in Chapter 4 and Iljin nanotubes that are featured in Chapter 6. Fitting Equation 4.2 to these data sets yields $\sigma_{DC}/\sigma_{Op}=1$ and 5, respectively, both inferior to the FA-treated PEDOT films.

We note that the transmittance spectra were largely unchanged by the FA post-treatment (see Figure ??), indicating that increased σ_{DC} is responsible for the improved FoM_e rather than due to substantial changes in σ_{Op} . This was also observed by Xia et al. when treating spin coated films treated with H₂SO₄.²⁷⁰ As the optical conductivity is known (Figure 5.2B), we can calculate the DC conductivity of the treated PEDOT films as $\sigma_{DC}=936$ S/cm. This value is quite high for polymeric conductors, albeit not as high as some other recent values; PEDOT films have been demonstrated with a DC conductivity of 1418 S/cm when treated with ethylene glycol³⁵¹ and 3000 S/cm when treated with 1.5 M H₂SO₄ at 160°C.²⁷⁰

Considering Figure 5.3A, for both the SWNT-based networks and the untreated PEDOT data there is marked deviation from the fits described by Equation 4.2 at higher transmittance values. This can be seen more closely by replotting the data as $T^{-0.5} - 1$ vs. R_s , shown in Figure 5.3B. Here the linearised fits correspond to bulk-like behaviour. Deviation from linearity has been explained as a manifestation of percolation-type phenomena.¹⁶¹ While this is probably the case for the nanotube films, in the case of PEDOT, it is probably due to the presence of thickness non-uniformities in the thinnest films, which can mimic percolation behaviour. In any case, no such deviation is observed for the FA treated PEDOT films, indicating a good deal of uniformity even for the thinnest films ($T=99\%$).

The lack of deviation from bulk-like behaviour is significant as such deviations always diminish the performance of transparent SCs at high T (Chapter 4). These effects should be minimised, or if possible, eliminated by nanoconductor selection and processing control.¹⁹² We suggest that spraying this molecular conductor onto our substrates and the subsequent FA treatment enables the production of films that remain highly confluent

even at extremely low loadings. In contrast, networks formed from typical discrete nano-sized objects such as carbon nanotubes, graphene or metallic wires will almost always show percolation effects as film thickness is reduced.¹⁹³

Thus, FA treated PEDOT films make excellent transparent current collectors. Percolation effects are completely absent even for the thinnest films we produced ($T=99\%$). As is the case for all transparent conductors, larger R_s values accompany higher transmittance. Despite this, the FoM_e for these films is very high; $\sigma_{DC}/\sigma_{Op} = 39$. This consideration will also come into play regarding the energy able to be stored and retrieved by transparent electrodes of different geometries and under varying charge/discharge timescales. These aspects are discussed in the sections following.

5.3.2 Electrochemical Properties of Small Area Electrodes

The superlative optical and electrical properties of FA treated PEDOT films make this material ideal for the production of transparent supercapacitor electrodes. The low optical conductivity means that for a given transmittance (e.g. $T=95\%$) the electrode can be relatively thick. For a given intrinsic volumetric capacitance, C_V this will result in a larger areal capacitance, C_A (where $C_A = C_V t$). Additionally, high DC conductivity will facilitate transport of stored charge to the external circuit even for thin electrodes.

The charge storage properties of PEDOT films were characterised in a three electrode cell by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). All electrochemical measurements were performed using 0.5 M K₂SO₄ aqueous electrolyte. First, we investigated the effect of the FA treatment on the electrochemical response of PEDOT films. Shown in Figure 5.4A are CV scans for a PEDOT film ($T=67\%$, $t=490$ nm, $\dot{V}=100$ mV/s) before and after the FA treatment. This indicates a dramatic improvement in current response after the treatment, consistent with the large reduction in sheet resistance. We consider a series resistor and capacitor circuit as a simple model of the current response of these films to a linear potential scan,¹⁹⁶ shown in Equation 5.2.

This is the same as Equation 2.10 but has been normalised to film geometric area, A .

$$j = C_A \dot{V} (1 - e^{-t/\tau}) \quad (5.2)$$

where j is the current density, $\dot{V} = dV/dt$ is the scan rate, intrinsic C_A is the electrode capacitance per unit area charged as a function of time, t , according to a time constant $\tau = R_{ESR}C$. The rapid current response of the FA treated film indicates a dramatic reduction in the time constant compared with the as-prepared films. It is known that for transparent EC electrodes R_{ESR} scales linearly with R_s (Chapter 4). Considering that the FA treatment dramatically reduces the R_s of this film (from 1730 to 25 Ohm/sq), we suggest the observed change in CV behaviour is predominately due to improved current collection through the plane of the film.

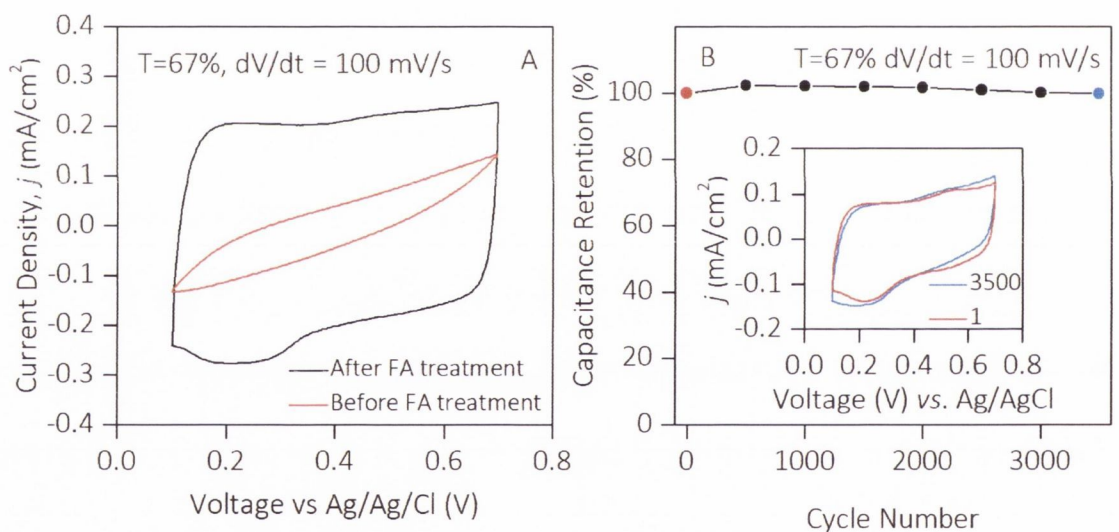


Figure 5.4: (A) Comparison of CV response of PEDOT films response before (red) and after (black) FA treatment ($\dot{V} = 100$ mV/s). (B) Capacitance retention upon repeated cycling of a treated film. Inset compares the CV response at cycle 1 and 3500 ($\dot{V} = 100$ mV/s).

Next, we assessed the stability of the treated films under multiple charge/discharge cycles. To explore this we carried out 3500 repeated CV cycles on a film between 0.1 to 0.7 V

vs. Ag/AgCl (voltage window is $\Delta V=0.6$ V, $\dot{V}=100$ mV/s). By integrating the current passed per cycle, a capacitance retention ratio was calculated, and this has been plotted as a function of the number of CV cycles in Figure 5.4B. With $>99\%$ retention, the charge/discharge process is stable over this duration of cycling. The Figure 5.4B inset compares the CV trace of the 1st and the 3500th cycle, indicating some minor changes in features of the CV. Alongside the well-known stability of PEDOT,^{259;264} these results suggest excellent cyclability of this material, a prerequisite of any promising EC electrode.

We then examined the charge storage properties of the FA treated film in more detail. For this characterisation the exposed electrochemical area of all films was fixed to squares; 1 cm by 1 cm. This active area is typical for transparent supercapacitor electrodes appearing in the literature.^{149;151;160} Here we refer explicitly to film dimensions rather than simply the film area, as electrode aspect ratio influences charge storage behaviour, a point that will be discussed in the following sections.

It's important to ascertain the charge and discharge conditions over which these small area PEDOT films behave as a capacitor. This can be determined using CV measurements by examining the relationship between the measured current density and scan rate;⁵² capacitive behaviour predominates when $j = C_A \dot{V}$. Equation 5.2 shows that this is approximately the case when the time constant, $\tau = R_{ESR}C$, is small relative to the charging or discharging time (*i.e.* $\tau \ll \Delta v/\dot{V}$). Under these conditions, Equation 5.2 can be re-expressed as $\log j = \log C_A + \log \dot{V}$ indicating that capacitive behaviour can be identified from CV data when the current density at some potential varies linearly with scan rate, having a slope of 1. Extrapolating these data to the y-intercept allows extraction of C_A . Note that this quantity differs from C/A , the available capacitance per unit area measured by integration of the CV. This difference arises due to the exponential term in Equation 5.2, and will be discussed later in this section.

Figure 5.5A shows CV measurements of films with different transmittance ($T=80\%$ to 99% , $t=10$ - 260 nm at 100 mV/s). Using these data, the current density at mid-voltage (0.4 V *vs.* Ag/AgCl), was evaluated and plotted as a function of scan rate for films with different transmittance, shown in Figure 5.5B. Clearly, near ideal capacitive behaviour

predominates over a wide range of scan rates for all the films. Only above ~ 1000 mV/s does deviation from a slope of 1 become apparent, corresponding to charge and discharge times less than ~ 0.6 seconds. Similar behaviour for PEDOT based SCs without an underlying current collector was observed by Carlberg *et al.*²⁶⁴ Close inspection of Figure 5.5B reveals that for thicker films (with lower R_s and T), the onset of this deviation shifts slightly to greater scan rates. This provides a subtle indication that the transport limitations which determine R_{ESR} are likely to be due to the sheet resistance as opposed to ionic diffusion. If this weren't the case we would expect the onset of this deviation to be independent of film transmittance.

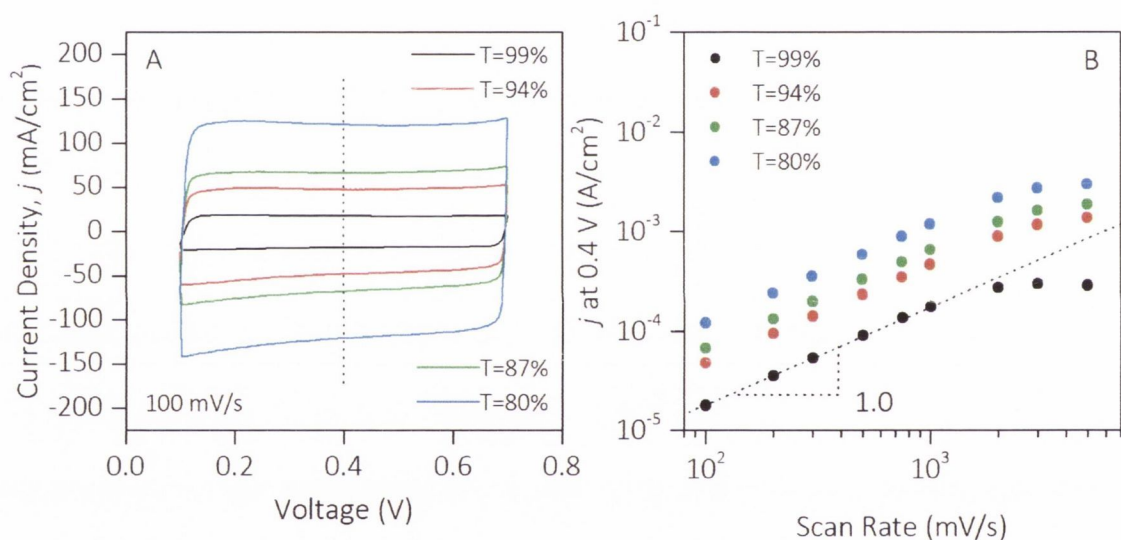


Figure 5.5: (A) CV of various PEDOT films with differing transmittance at 100 mV/s. (B) Current density evaluated at 0.4 V *vs.* Ag/AgCl from the CVs for various FA treated films with differing transmittance over a wide scan rate range ($\dot{V}$ =100-5000 mV/s). Black dashed line indicates capacitive behaviour (slope=1). Intercepts with y-axis enable extraction of the intrinsic (i.e. rate independent) areal capacitance, C_A .

Using the scan rate range over which the behaviour is near ideally capacitive ($\dot{V} < 1000$ mV/s), we extracted the rate-independent C_A for each film from intercept with the y-axis. These data have been plotted as a function of film transmittance in Figure 5.6. As

expected, films with greater transmittance store less charge for a given geometric area because less capacitive material is present on the surface. We measured $C_A=1.9 \text{ mF/cm}^2$ for a low transmittance film ($T=70\%$), which decreased to $C_A=0.18 \text{ mF/cm}^2$ for the most transparent film produced in this work ($T=99\%$).

Provided C_V is constant for all of film thickness, these data should be described by Equation 4.5. Fitting this equation to the data in Figure 5.6 gives $C_V/\sigma_{Op} = 1.7 \text{ F/S.cm}^2$ for these films, which can be considered a figure of merit for transparent capacitive electrodes (FoM_c). Alongside these PEDOT data we have also included the results from transparent EC literature. Note that this excludes work done in this field where underlying ITO current collectors have been used^{147;148;150;152;154;156–159;352}; due to its brittleness and the need for high processing temperatures, ITO films aren't compatible with flexible plastic electronics applications. We highlight that other than this work and the work described in Chapter 4 (blue circle), to our knowledge no other data has been presented for electrodes with $T > 90\%$, the region of interest for transparent devices. These treated PEDOT films have a much higher FoM_c than the disordered SWNT networks which display $C_V/\sigma_{Op} = 0.3 \text{ F/S.cm}^2$ (blue dashed line). In addition, while the capacitance of the nanotube networks deviate substantially from this line at $T > 90\%$, the PEDOT films remain bulk-like even at very high transmittance ($T=99\%$). As discussed above, the absence of percolation effects is a key advantage of these sprayed PEDOT films compared with disordered nanomaterial network electrodes.

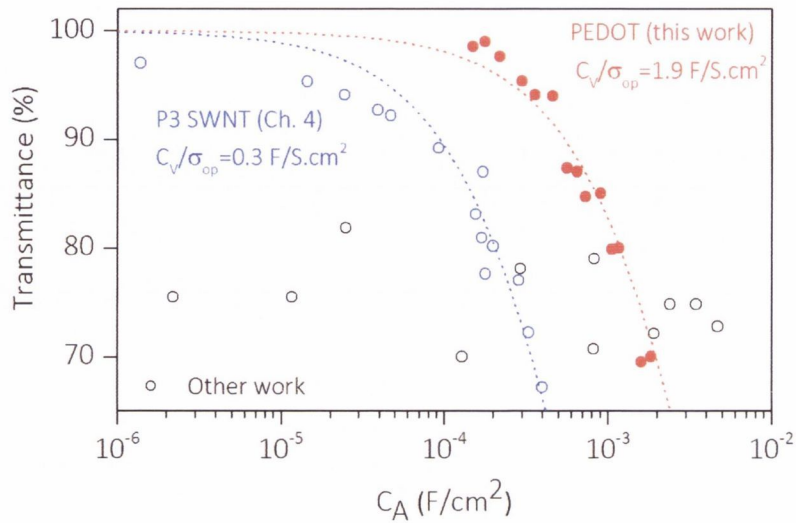


Figure 5.6: PEDOT film transmittance plotted as a function of the C_A values obtained in Figure 5.5. Unfilled blue points are data from Chapter 4 (SWNT films) and unfilled black points are from the literature. Fits are made using Equation 4.5. Figure ?? contains a detailed version of this figure indicating the authors of literature data.

Equation 4.10 indicates that the capacitive performance of transparent EC electrodes depends strongly on C_V ; however is rarely calculated explicitly for transparent EC electrodes. As was done in the previous section for FoM_e, we can determine the volumetric capacitance of this material using the fitted FoM_c and the known σ_{Op} of this material, yielding $C_V=41 \text{ F/cm}^3$. In light of the disparity between the FoM_c of these PEDOT films (1.7 F/S.cm^2) and the SWNT films described in Chapter 4 (0.3 F/S.cm^2), it's interesting to note that these two materials have reasonably similar volumetric capacitances (55 F/cm^3 for the carboxylic acid functionalised SWNTs, using $1 \text{ M H}_2\text{SO}_4$ as the electrolyte). Therefore, again we can attribute the superior performance of PEDOT as a transparent EC charge storage film to its very low optical conductivity (24 S/cm compared with 167 S/cm for the SWNTs).

Many electrode materials have been reported with substantially higher volumetric capacitance; Carlberg *et al.* reported 100 F/cm^3 for PEDOT films,²⁶⁴ Ghaffari *et al.* measured

84 F/cm³ for PEDOT coated nanotubes²⁴⁸, Largeot *et al.* reported values ~100 F/cm³ for nanotubes,²⁷ Heon *et al.* measured 180 F/cm³ for carbide derived carbon³⁵³ and values as high as 1160 F/cm³ have been achieved using MnO₂ composites.³⁵⁴ The literature data in Figure 5.6 which sits ahead of our PEDOT data for low transmittance films suggests that higher FoM_c are possible, which could yield better capacitance at high transmittance values (T>90%), provided films of these materials could be produced thin enough, while also avoiding percolation effects. We suggest this may be achieved by composite formation of this FA treated PEDOT with other highly pseudocapacitive materials such as MnO₂ or RuO₂,^{57,355} to boost C_V without substantially increasing σ_{Op} .

Considering Figure 5.5B, when the scan rate is too fast, the capacitance that is realised becomes impaired compared to the intrinsic areal capacitance, *i.e.* $C/A < C_A$. We can examine the scan rate dependence of the CV data more effectively by normalising the measured current density to the scan rate, yielding a differential capacitance (*i.e.* $dq/dV)/A = j/\dot{V}$).¹⁸⁰ Figure 5.7A shows CV data expressed in this manner for a film with $T=99\%$ at a variety of scan rates (100 to 5000 mV/s). Equation 5.2 can be modified similarly, as shown by Equation 5.3

$$j/\dot{V} = (dq/dV)/A = C_A(1 - e^{-t/\tau}) \quad (5.3)$$

This demonstrates the reduction in charge storage with scan rate when the time constant becomes comparable to the time available to accumulate or dispense charge. Although Figure 5.5B allowed extraction of the intrinsic areal capacitance (at 0.4 V *vs.* Ag/AgCl), the realised capacitance at a given scan rate is given by the total charge passed over the voltage window, (*i.e.* $C/A = (\Delta q/\Delta V)/A$). This can be found at each scan rate by integrating the data in Figure 5.7A using Equation 2.11. The calculated data is shown in Figure 5.7B for a number of different transmittance films. Here the dashed lines are the rate-independent C_A values obtained from Figure 5.5B. Crucially, the integrated capacitance values approach this intrinsic quantity at low scan rates. The ratio of these values ($(C/A)/C_A$) provides a measure of the capacitance that is accessible at a given scan rate. For example, for the $T=99\%$ film, 92% of C_A is available at 300 mV/s, which decreases to 75% at 1000 mV/s. Although these deviations aren't terrible, these films are

small (1 cm by 1 cm). Given that real devices are likely to require electrodes with larger dimensions, it is important to characterise this behaviour for larger area films.

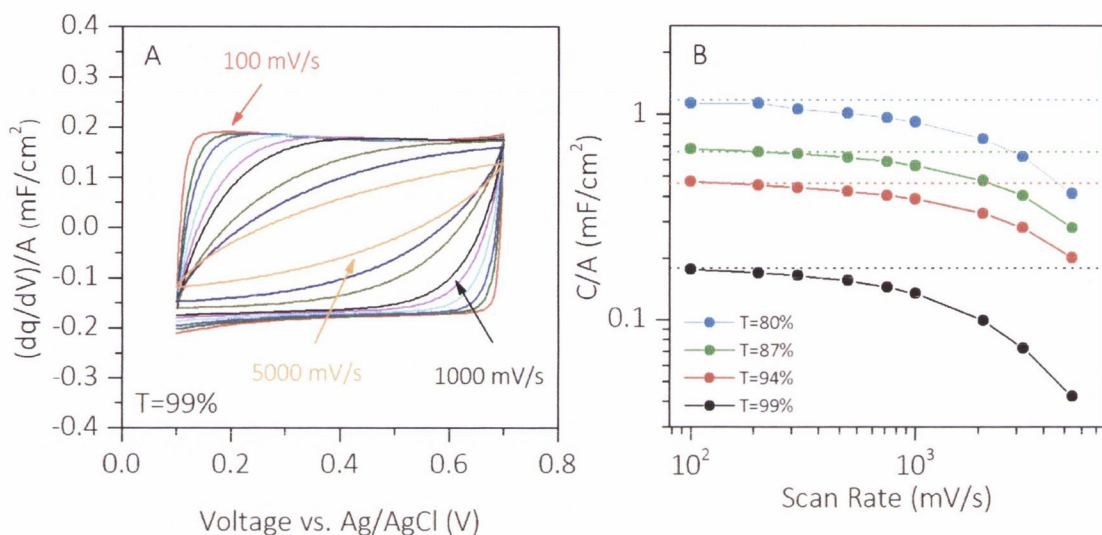


Figure 5.7: (A) CVs for a number of FA treated samples with varying film transmittance ($dV/dt=100$ mV/s). (B) Available areal capacitance determined by integration of CVs for four films ($T=80\%$ to 99%) plotted as a function of scan rate. All electrodes have square dimensions; 1 cm by 1 cm.

5.3.3 Effect of Film Size and Geometry on Charge Storage Properties

5.3.3.1 Cyclic Voltammetry

For a transparent charge storage material with a given C_V , when film thickness is constrained to provide some transmittance (say $T=90\%$), the only way to store more charge is by extending the lateral dimensions of the film. However, in the literature the majority of transparent EC electrodes are tested with small active areas and data presented either on a per mass or per area basis. No attempt has been made to explore the properties of

transparent capacitive electrodes as a function of film area, in particular, the scaling of absolute capacitance.

Here we perform such a study, exploring the effect of both electrode length and width on the absolute capacitance. We define the electrode width, W , as the dimension parallel to the electrode contact at the upper film edge, and electrode length, L , as the perpendicular dimension (Figure 5.8A). Initially, we measured CVs for electrodes as a function of film length (and so area) while keeping the width constant ($W=0.5$ cm). This was achieved by first characterising the largest area film, then cutting off a small bottom section to reduce L (and therefore A). Figures 5.8B and C show the length dependence of the CVs at two scan rates, 100 mV/s and 1000 mV/s, respectively ($T = 70\%$). Here L was varied from 3.6 cm to 1.2 cm, resulting in a variation in film area from 1.8 cm² to 0.6 cm². As was done for Figure 5.7A, the measured current density has been normalised to scan rate to express as a differential capacitance per unit area ($dq/dV/A$).

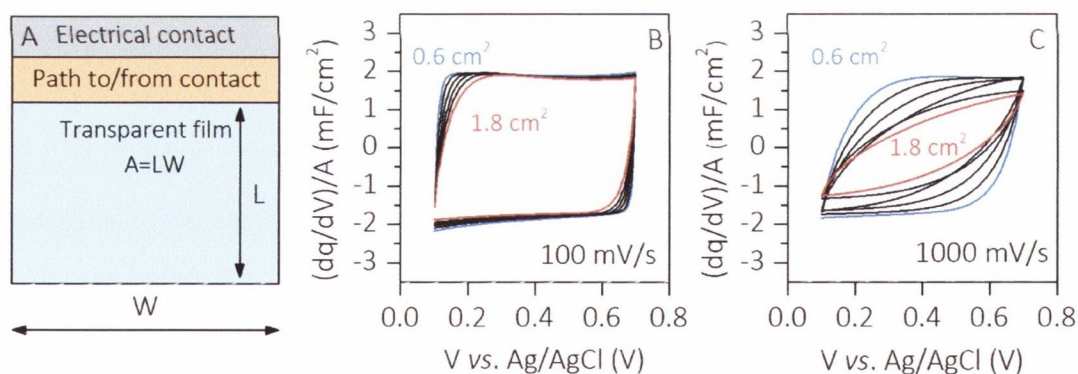


Figure 5.8: (A) Diagram of electrode indicating length (L) and width (W) dimensions with relation to the electrical contact (along top edge). (B) CVs at 100 mV/s and (C) 1000 mV/s a $T=70\%$ film with areas varying L from 0.6 cm² to 1.8 cm², achieved by altering by length between 1.2 cm and 3.6 cm while keeping the width constant ($W=0.5$ cm). The measured CV current density has been normalised by the scan rate, yielding a differential capacitance; $j/\dot{V} = (dq/dV)/A$.

These CV results highlight the effect of both sample length and scan rate on capacitance. At the relatively slow scan rate of 100 mV/s, there is a small but noticeable increase in time constant as the sample length is increased, consistent with the increased in plane electrode resistance contributing to the R_{ESR} . This will manifest itself as a slight reduction in the achievable areal capacitance (C/A). However, at the higher scan rate of 1000 mV/s, this effect is more pronounced. As the sample length is increased, very large increases in time constant can be seen. These results imply that long electrodes display significant reductions in areal capacitance compared to that expected for short ones, especially at high scan rates. This is an important result as it illustrates that the absolute capacitance cannot simply be projected from the areal capacitance measured for a small area samples.

We can quantify this behaviour by calculating C/A from the CV scans by integration using Equation 5.4. We performed this analysis on samples with a range of lengths (with $W=0.5$ cm) at a variety of scan rates, shown in Figure 5.9A and B. It is clear from these results that the apparent areal capacitance falls dramatically as both length and scan rate are increased, as suggested above. These effects can be significant; when increasing electrode length from 1.2 cm to 3.6 cm the apparent areal capacitance at 1000 mV/s is a factor of three less than expected.

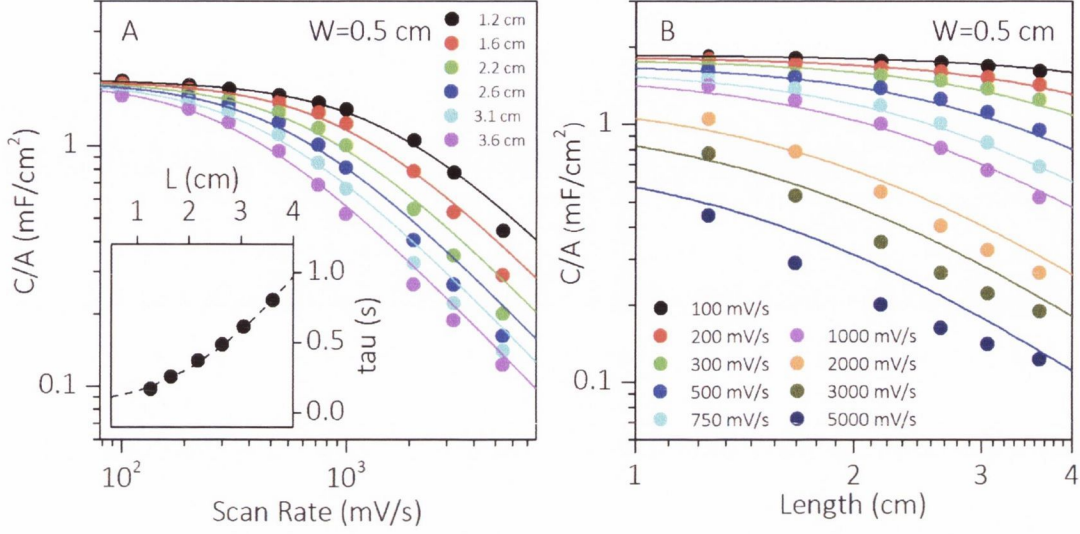


Figure 5.9: (A) Capacitance data (C/A) obtained by integrating CV data shown in Figure 5.8) plotted as a function of scan rate for the various sample length ($L=1.2$ to 3.6 cm). Fits of Equation 5.5 to the data were used to determine the time constant, τ , as a function of length, which plotted as the inset. Fitting Equation 5.6 to these data gave $C_A=1.9$ mF/cm², $R_s=29$ Ohm/sq and $G_A=18.6$ S/cm². (B) The same capacitance data plotted as a function of sample length (L) at various scan rates. Using the parameters found in (A), Equation 5.8 has been plotted with alongside these data showing good agreement until ~ 1000 mV/s.

The decrease in apparent areal capacitance with increasing L can be understood as follows: As the electrode gets longer, the average resistance felt by electrons moving from the current collector into the PEDOT increases. This in turn increases the time constant ($\tau = R_{ESR}C$), causing a slower current rise on voltage reversal. Because the capacitance is calculated by integration of the CV curve, this results in lower apparent areal capacitance than the intrinsic value (*i.e.* $C/A < C_A$). We can model this quantitatively by combining Equations 5.3 and 2.11 to give Equation 5.4:

$$\frac{C}{A} = \frac{1}{\Delta V} \int_{V_1}^{V_1+\Delta V} (C_A(1 - e^{-t/\tau}))dV \quad (5.4)$$

All the terms appearing here have been described earlier. Changing variable from V to t

($dV = \dot{V} dt$) and integrating gives Equation 5.5.

$$\frac{C}{A} = C_A \left(1 - \frac{\dot{V} \tau}{\Delta V} (1 - e^{-\Delta V / \dot{V} \tau}) \right) \quad (5.5)$$

This describes the dependence of the experimentally measured areal capacitance, C/A , on the intrinsic areal capacitance, C_A , the scan rate, $\dot{V}$ and the time constant, τ .

We can use Equation 5.5 to fit the C/A vs. $\dot{V}$ data shown in Figure 5.9A, finding very good agreement. From the fits we find that for this particular thickness of PEDOT ($T=70\%$) the intrinsic areal capacitance is $C_A=1.9$ mF/cm², close to the expected a value of 1.8 mF/cm² based on FoM_c (Figure 5.6). In addition we find that the time constant varies considerably with sample length, as shown in the Figure 5.9A inset. We can understand this by noting that the time constant is given by $\tau = R_{ESR}C$, where C reflects the capacitance of the electrode and R_{ESR} reflects the series combination of electrode and electrolyte resistances ($R_{electrode} + R_{electrolyte}$). We can express these three parameters in terms of the electrode geometry; the capacitance as $C_A LW$, the electrolyte resistance as the inverse of the electrolyte conductance per unit area multiplied by area, $1/G_A LW$ and the electrode resistance as the sheet resistance multiplied by electrode aspect ratio $R_s L/W$. Note that $G_A = l \sigma_{electrolyte}$, where l is the electrode separation. When combined, these give an expression for the time constant which is a function of electrolyte length, L , given by Equation 5.6.

$$\tau = C(R_{electrode} + R_{electrolyte}) = C_A LW \left(R_s \frac{L}{W} + \frac{1}{G_A LW} \right) = C_A R_s L^2 + \frac{C_A}{G_A} \quad (5.6)$$

As shown in Figure 5.9 inset, Equation 5.6 fits the experimental data extremely well allowing us to extract values of $R_s=29$ Ohm/sq and $G_A=19$ S/cm². Note that we expect a value of 25 Ohm/sq for a sample with this transmittance based on FoM_e (Figure 5.3). G_A can be converted to an approximate conductivity using the electrode separation (~ 2 cm) giving ~ 40 S/cm. This is a little lower than expected for 0.5 M K₂SO₄ due to additional electrode resistance that hasn't been taken into account for this analysis. Given that the area capacitance and sheet resistance are related to film thickness *via* $C_A = C_V t$ and $R_s = (\sigma_{DC} t)^{-1}$, it can be seen that for a given electrode length the time constant

should increase linearly for thicker films as shown by Equation 5.7.

$$\tau = \frac{C_V}{\sigma_{DC}} L^2 + \frac{C_V}{G_A} t \quad (5.7)$$

We can also apply this model to the data for apparent areal capacitance as a function of sample length. To do this we combine Equations 5.5 and 5.6 to give Equation 5.8.

$$\frac{C}{A} = C_A \left[1 - \frac{\dot{V}}{\Delta V} (C_A R_s L^2 + \frac{C_A}{G_A}) (1 - \exp[\frac{-\Delta V / \dot{V}}{(C_A R_s L^2 + C_A / G_A)}]) \right] \quad (5.8)$$

Because all parameters in this expression (C_A , R_s , G_A , Δv) are known, we can plot this expression as a function of L for different scan rates, $\dot{V}$, shown in Figure 5.9B. The agreement is good, however it disimproves as scan rate is increase, *i.e.* for scan rates > 1000 mV/s. This point that will be discussed in the section following.

The same characterisation was also performed for the converse situation; with length kept constant ($L=0.5$ cm), while varying the width ($W=0.8$ cm to 4.5 cm). As shown in Figure 5.10A and B, the resulting behaviour is completely different. Although the measured areal capacitance falls with scan rate in line with Equation 5.5, it is invariant with sample width, W , at all rates. This is as expected because the sample width does not appear in Equation 5.8. These observations are intuitive given that the capacitance of longer films must be charged through a growing resistance ($R = R_s L / W$). This feature arises due to the absence of an underlying current collector, necessary for these films to be suitable for printed transparent/flexible electronics applications. This insight is important for the design of transparent energy storage devices.

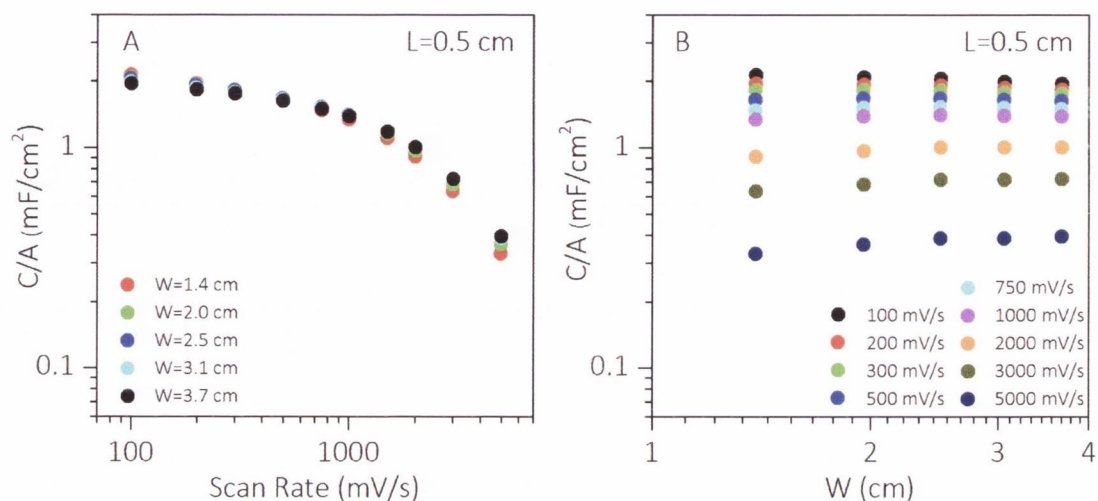


Figure 5.10: (A) Equivalent CV data to Figure 5.9 where W has been varied between 1.4 and 3.7 cm while keeping length constant ($L=0.5$ cm), plotted as a function scan rate, and (B) W and different scan rates.

5.3.3.2 Electrochemical Impedance Spectroscopy

Using the CV analysis, it was clearly shown that the finite resistance of the active material results in geometric effects which limit the available C/A for longer films and higher discharge and recharge rates. Here this behaviour is explored in more detail.

Electrochemical impedance spectroscopy was also used to examine L dependence of charge storage properties of the PEDOT transparent films. Here a sinusoidal excitation potential of 10 mV (rms) was applied with a DC bias of 0.4 V *vs.* Ag/AgCl at frequencies spanning from 0.1 Hz to 100 kHz. Figure 5.11A presents a series of complex plane plots obtained for different electrode lengths (with $W=0.5$ cm² and $T=70\%$). Figures 5.11B and C present the real (Z') and imaginary ($-Z''$) components of the impedance plotted as a function of excitation frequency, ω , focusing on the range of interest ($\omega < 100$ Hz, where spectra differ as a function of sample length). Qualitatively, the spectra in Figure 5.11A

consist of a region with phase angle close to $\pi/2$ at low frequencies which transitions to a region with phase angle of $\pi/4$ section at high frequencies. We denote the critical frequency separating these two distinct regimes as ω_c . These characteristics resemble the EIS spectra obtained for a variety of electrode systems which possess spatially distributed capacitance and resistance, such as porous network electrodes and brush electrodes. A variety of transmission line equivalent circuits have been developed to account for this behaviour.²⁸

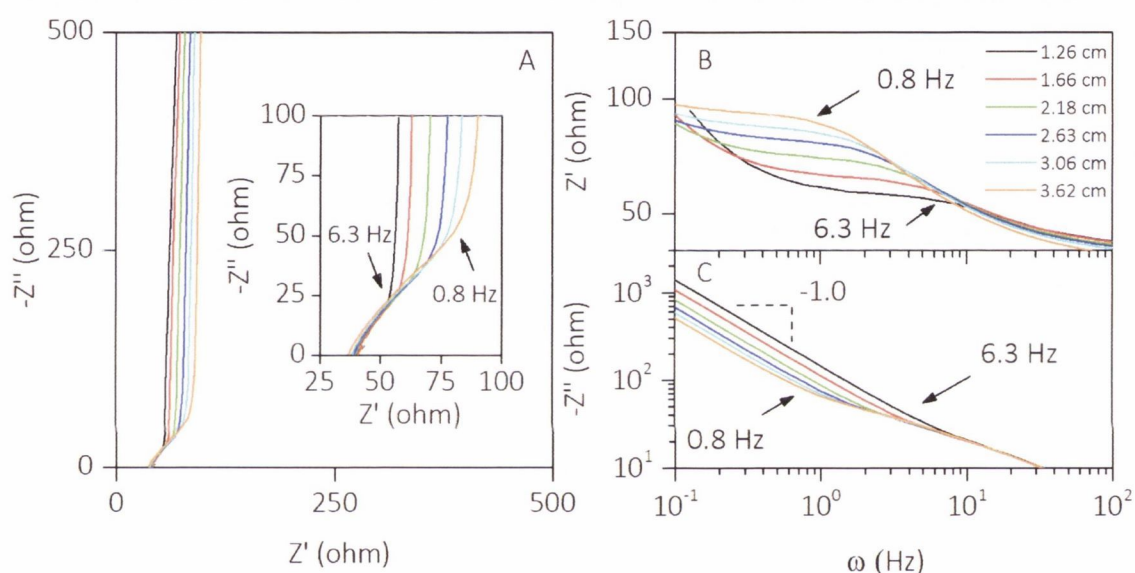


Figure 5.11: (A) Complex plane plot obtained for a $T=70\%$ films with various lengths from 1.2 cm to 3.6 cm with constant width ($W=0.5$ cm). Spectra were obtained using an excitation potential of 10 mV (rms) at a DC bias of 0.4 V *vs.* Ag/AgCl at frequencies, ω , ranging from 0.1 Hz to 100 kHz. The real (Z') and imaginary ($-Z''$) components of these data are plotted as a function of frequency in (B) and (C) respectively. All spectra have marked the characteristic frequency (ω_c) for the longest and shortest samples shown.

We have taken a similar approach in this work, modelling the AC behaviour of these transparent electrodes using a single-arm transmission line model. A diagram indicating the features of this model is provided in Figure 5.12. Transmission line models are employed where the electrode properties are spatially distributed along the some dimension. Although this is the thickness dimension for porous electrodes (between the current col-

lector and the porous film surface), in this case the capacitance is distributed laterally along the length of the film due to the absence of an underlying current collector. Thus, an appropriate model consists of a resistance running along the length of the film (L), to represent the flux of electrons to and from the electrochemical interface *via* the external circuit. This resistive arm branches continuously to an interfacial element which we have treated as an ideal capacitor. This is the simplest possible transmission line model which we may provide a more realistic representation of the behaviour of these films as a function of sample length than the series resistor-capacitor model used in the previous section.

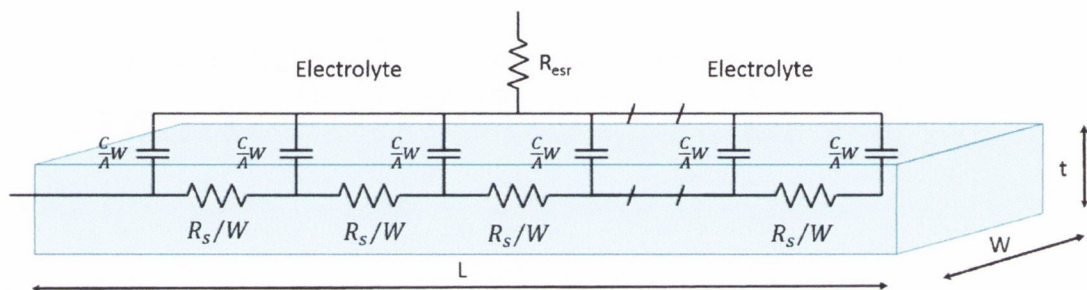


Figure 5.12: Single-arm transmission line circuit used to model the impedance behaviour of these PEDOT films as a function of sample length.

Using the analytical solution to a model of this form²⁸ and substituting in the terms relevant to this system yields an expression for the AC impedance as a function of excitation frequency, shown in Equation 5.9:

$$Z = \frac{1}{W} \left(\frac{R_s}{i\omega C_A} \right)^{1/2} \coth[L(i\omega C_A R_s)^{1/2}] \quad (5.9)$$

The details of how this expression was obtained from the general form of this model appears in the Appendix. All the same electrode properties are present as for the CV analysis described in the previous section. Equation 5.9 can be simplified under conditions where ($\omega < \omega_c$) to yield an expression for the impedance in terms of real and imaginary components, appearing in Equation 5.10.

$$Z \sim \frac{L}{3W} R_s - \frac{i}{\omega C_A L W} \quad (5.10)$$

This expression indicates that the low-frequency portion of Z' should be frequency independent. Figure 5.11B shows that this is approximately the case over a certain range. The thinner samples in particular show an additional unexplained increase in Z' at very low frequencies (e.g. at $\omega < 1$ Hz for the $L=1.2$ cm sample) which weren't considered in this analysis. Therefore, the frequency independent portions of the spectra were extrapolated to the real axis intercept and plotted as a function of electrode aspect ratio (L/W) for various transmittance samples ($T=70$ to 99%) in Figure 5.13A. As expected from Equation 5.10, the data varies linearly with L/W , and the slopes were determined to calculate values for the sheet resistance of each film. These data are plotted as a function of the electrode transmittance in Figure 5.13B. Also presented is data measured directly by the four point probe method from Figure 5.3. These data sets overlay extremely well, providing evidence for the validity of this transmission line model for this electrode system.

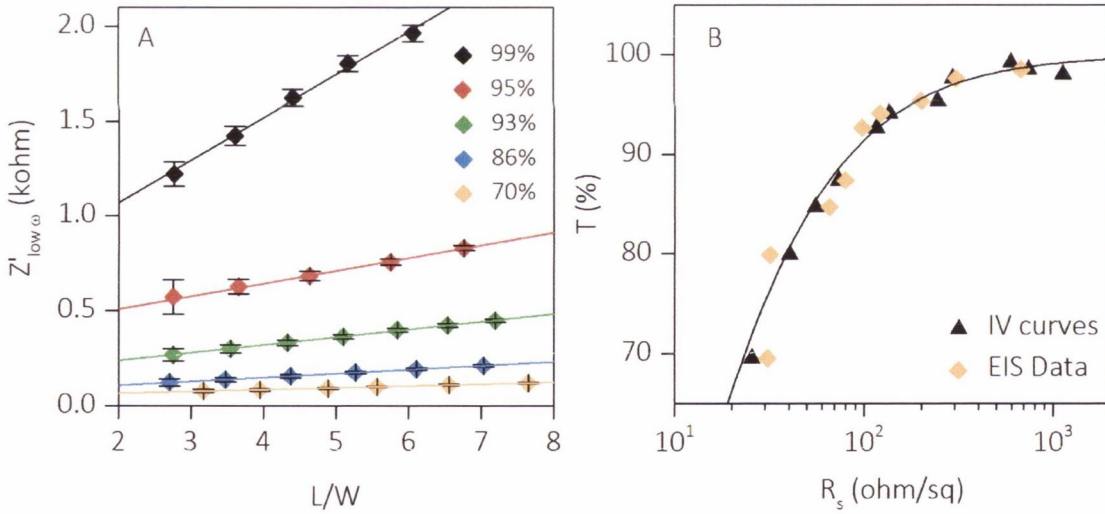


Figure 5.13: Derived EIS data. (A) Z' intercepts obtained by extrapolating the linear portion of spectra when $\omega < \omega_c$, plotted as a function of film aspect ratio (L/W). These data enabled extraction of the sample sheet resistance using $Z' = R_s L / 3W$. (B) The obtained sheet resistance data plotted as a function of films transmittance. Also shown are the sheet resistance values obtained from four point probe measurements.

As described above, at any instant, the current flowing in the electrode decays as the distance from the current collector is increased. We note that the approximation in Equation 5.10 can be written as $Z' = R_s L/3W$ for $\omega < \omega_c$. This indicates that in this frequency region the electrode behaves like a normal resistor with length one third of its normal length. This is an advantage of this impedance model as this information cannot be extracted from the model describing the CV data. As the sample length is increased, additional contributions are made to the R_{ESR} , arising from need to charge and discharge the films capacitance through the plane of the film.

We now turn to the imaginary part of the impedance spectrum. Equation 5.10 shows that when $\omega < \omega_c$ these electrode should behave as ordinary capacitors, *i.e.* $Z = i/\omega C$. This behaviour can be seen in Figure 5.11C, where the low-frequency data scales inversely with frequency. To analyse this portion of the spectra we extract the relevant low-frequency regime and have plotted $-Z''$ *vs.* $1/\omega$, presented in Figure 5.14A for a $T=70\%$ electrode at a range of lengths ($L=1.5$ cm to 3.7 cm). The capacitance, C , was determined from the slope of these data and plotted *vs.* electrode area ($A=LW$) in Figure 5.14B along with the capacitance data for a number of other films obtained similarly ($T=70\%$ to 99%). The intrinsic areal capacitance, C_A , of each film was determined from the slopes of these graphs and were plotted as a function of electrode transmittance in Figure 5.14C. Alongside these results are the intrinsic areal capacitance values obtained using CV analysis (Figure 5.5B). These datasets obtained using different experimental techniques overlap very well, providing further evidence for the validity of this impedance model.

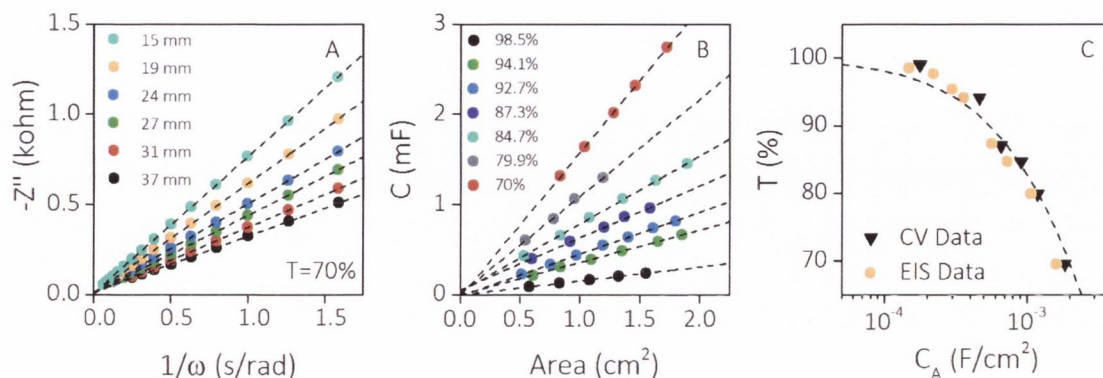


Figure 5.14: (A) $-Z''$ data obtained at a variety of sample lengths plotted *vs.* inverse frequency. These data were obtained for a range of films and used to determine capacitance using $Z'' = i/\omega C$, plotted in (B). (C) The film transmittance plotted as a function of these C_A values, showing the comparison to values obtained from the CV analysis presented in Figure 5.5B.

5.3.4 Limitations of Length and Scan Rate (or Frequency)

As indicated by Figure 5.9A and B, the available areal capacitance begins to fall once either the sample length or the scan rate increases above a certain value. The design of real large-area EC electrodes would be facilitated by an understanding of the relationship between sample length and scan rate when the effective capacitance begins to deviate from the intrinsic value. We can obtain such a relationship using either of the models described above.

Using the impedance model, it is possible to obtain such a relationship using the concept of penetration depth.²⁸ The characteristic frequency marks the transition from capacitive behaviour to a Warburg-like response when either the electrode is too long (at a given excitation frequency) or the excitation frequency is too fast (for a given length). For this single-arm transmission line model²⁸, the characteristic frequency is given by Equation 5.11, which we can express in terms of the intrinsic areal capacitance and sheet resistance

of the electrode, or more generally, the volumetric capacitance and DC conductivity:

$$\omega_c = \frac{1}{C_A R_s} L^{-2} = \frac{\sigma_{DC}}{C_V} L^{-2} \quad (5.11)$$

This relation is plotted in Figure 5.15 using the parameters relevant for this system ($\sigma_{DC}=936$ S/cm, $C_V=41$ F/cm³). Here the frequency has been expressed in hertz, $\omega_c = 2\pi f_c$. For example, when $L=1.0$ cm these electrodes will operate as an ideal capacitor for $f < 3.7$ Hz, however when $L=5.0$ cm, ideal behaviour occurs when $f < 0.14$ Hz.

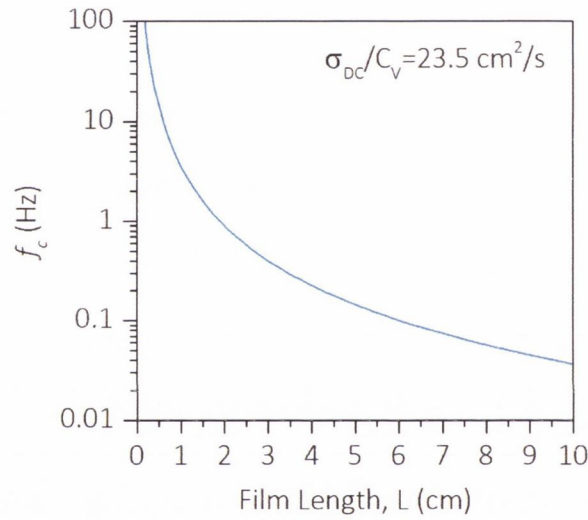


Figure 5.15: Characteristic frequency plotted as a function of sample length for PEDOT:PSS films.

Similar information can be obtained using the CV model. The areal capacitance as obtained from Equation 5.5 is essentially constant for a low values of $\dot{V}\tau/\Delta V$. It can be shown very simply that the areal capacitance begins to fall off approximately when $\dot{V}\tau/\Delta V = 0.5$. Using Equation 5.6 we can demonstrate that for a given sample length, the maximum scan rate before the experimental capacitance begins to fall off is given by Equation 5.12.

$$\dot{V}_{max} = \frac{\Delta V/2}{(C_A R_s L^2 + C_A/G_A)} \quad (5.12)$$

Alternatively, if the capacitor must be operated at a given rate the maximum sample length before the experimental capacitance begins to fall off is given by Equation 5.13.

$$L_{max} = \sqrt{\frac{1}{C_A R_s} \left(\frac{\Delta V/2}{\dot{V}} - \frac{C_A}{G_A} \right)} \quad (5.13)$$

Both of these expressions contain parameters (*i.e.* R_s and C_A) which depend on electrode thickness (and hence transmittance). Using $R_s = (\sigma_{DC} t)^{-1}$ and $C_A = C_V t$, we can find the thickness dependence of these two expressions, shown in Equations 5.14 and 5.15.

$$\dot{V}_{max} = \frac{\Delta V/2}{(C_V L^2 / \sigma_{DC} + C_V t / G_A)} \quad (5.14)$$

$$L_{max} = \sqrt{\frac{\sigma_{DC}}{C_V} \left(\frac{\Delta V/2}{\dot{V}} - \frac{C_V t}{G_A} \right)} \quad (5.15)$$

We note that these expressions can alternatively be expressed as a function of transmittance rather than thickness using Equation 5.1. However, for the sake of simplicity they have been left in the current form. We can plot graphs showing the relationship between maximum rate and sample length and maximum sample length and rate (Figure 5.16), using the parameters established above for PEDOT combined with the electrolyte used here ($\sigma_{DC}=936$ S/cm, $C_V=41$ F/cm³, $\Delta V=0.6$ V, $G_A=19$ S/m²). These graphs clearly show the limitations of large area transparent supercapacitors. For example, if the electrode transparency is set at 90% and a maximum scan rate of 1 V/s is required, the sample length can be no more than 1 cm before the effective areal capacitance start falling off from its intrinsic value.

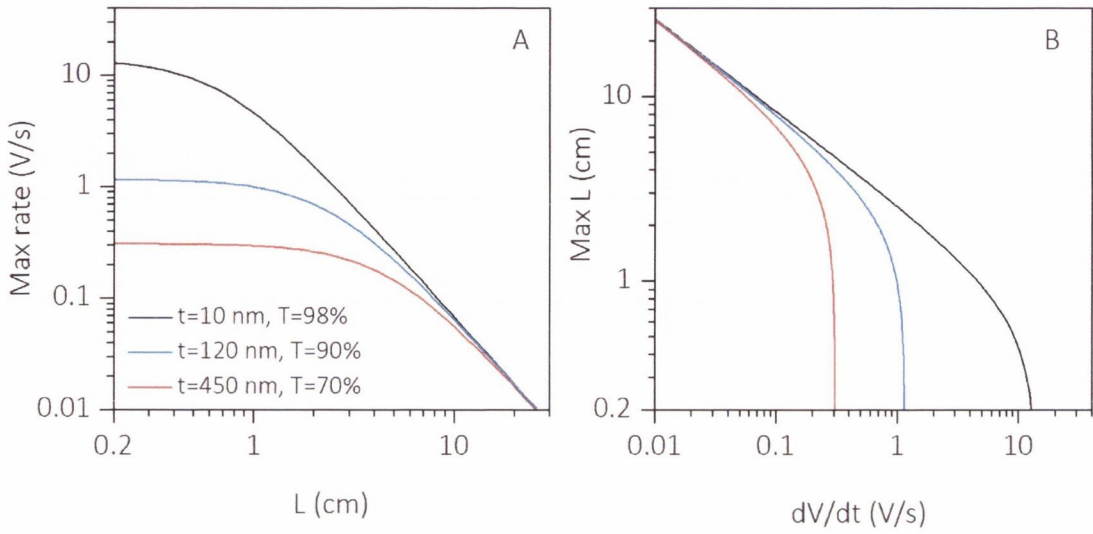


Figure 5.16: (A) Maximum scan rate at which transparent EC electrodes remain approximately capacitive for a given length and (B) the same information plotted to provide the maximum length for a given scan rate.

It is worth highlighting that despite the differences in the origin of CV and impedance models, Equation 5.11 and 5.14 can be considered equivalent, as they both indicate that the maximum rate of discharge or recharge (by either a linear potential sweep or AC potential perturbation) depends on the ratio σ_{DC}/C_V and varies as L^{-2} . The additional term in the denominator of Equation 5.14 is due to inclusion of the effect of the electrolyte. Although this is not taken into account by the impedance model, it more accurately describes the processes occurring within the film during charge and discharge, that is, the distributed nature of capacitance along the length of the film. Despite the simplified treatment of the physical processes taking place, the CV model is of more practical use as it provides the available capacitance for a given sample length and scan rate (up to around $V' = 1000$ mV/s). Clearly this understanding will be important for EC design.

5.3.5 Large Area Device Measurements

Presently, the largest transparent EC device¹⁵¹ in literature is only 4.5 cm². Given that applications will no doubt require larger area devices capable of greater absolute charge storage, it is necessary to demonstrate what kind of performance is possible. The spray system used in this work is capable of producing films with dimensions of 18 cm by 18 cm, potentially giving a device area of 324 cm². However, given the geometric effects described above, the absolute capacitance of devices with an L dimension greater than ~ 5 cm are not able to store significantly more charge at the charge/discharge rates of interest for EC applications (~ 100 s of mV/s). Accordingly, here we present measurements for devices with dimensions of $W=18$ cm and $L \leq 6$ cm), giving a maximum electrode footprint of 108 cm². A photograph of these films are presented in Figure 5.17A. We emphasise that this is substantially larger than any transparent EC device published previously.

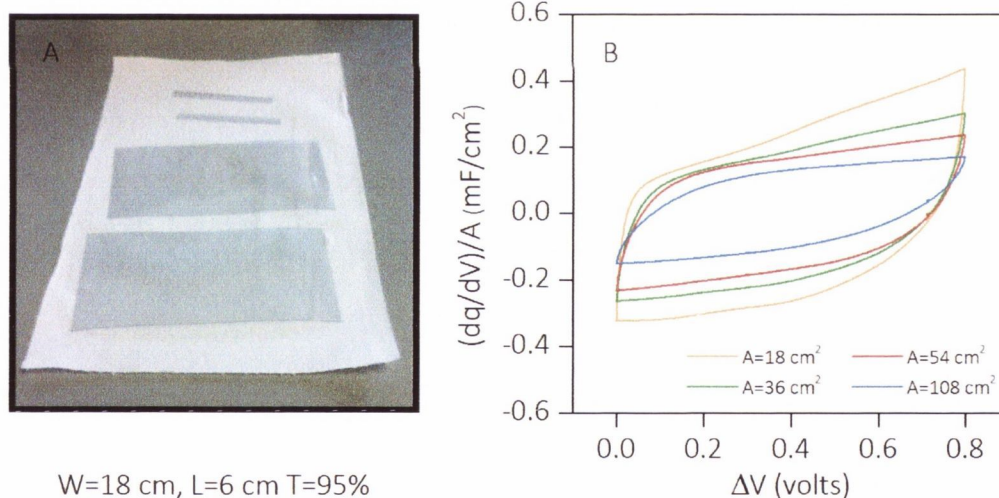


Figure 5.17: (A) Large area sprayed PEDOT films ($W=18$ cm, $L=6$ cm, $T=95\%$) used to form a two electrode cell. (B) CVs were obtained of this large area device configuration and the film length was sequentially reduced, to decrease the film area.

Using a two electrode configuration, these electrodes were tested in a large beaker by cyclic voltammetry at a variety of scan rates (50 to 1500 mV/s). Figure 5.17B shows CVs obtained at 50 mV/s for different sample lengths, and hence electrode areas varying from $A=18\text{ cm}^2$ to 108 cm^2 . These were expressed as differential capacitance $((dq/dV)/A)$. Areal capacitances were found by integrating the current passed over the potential window, and are these data plotted *vs.* device length for a range of scan rates (Figure 5.18A). In all cases, C/A falls with sample length, although this phenomenon is less severe for a low scan rates. Presented in Figure 5.18B is the absolute capacitance plotted *vs.* electrode length. For the largest area device we measured 12.5 mF at 50 mV/s.

In comparison, Jung *et al.* reported a transparent EC device using electrodes with $T=71\%$ and $A=4.5\text{ cm}^2$, which gave a capacitance of 2.1 mF by constant current charge discharge measurements ($j=5\text{ }\mu\text{F}/\text{cm}^2$). Although this value is 5x less than reported here, it is difficult to make a fair comparison. This is because the two devices possess different aspect ratio, different transmittance and were characterised by different electrochemical techniques. To facilitate comparison between different transparent EC devices in the future it is suggested that either some standards be agreed upon in terms of device geometry, film transmittance and test conditions used by researchers. However, it is probably easier if the intrinsic material properties of relevance for transparent ECs be reported, as has been done in this work (i.e. σ_{DC} , σ_{Op} , and C_V). Once known, these can be used to indicate the performance that would be obtained for any device geometry and test conditions using the theory developed here.

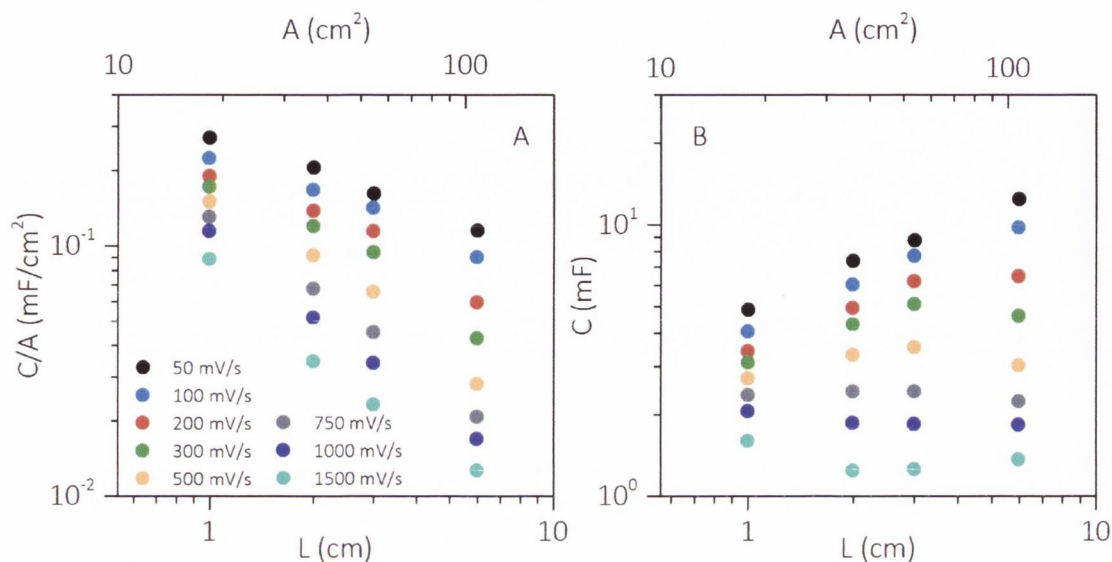


Figure 5.18: (A) Areal capacitance as a function of device length and area found by integration of CVs at various scan rates (50 to 1500 mV/s). (B) Absolute capacitance as a function of device length at area at various scan rates, showing a maximum capacitance of 12.5 mF for the largest area device at 50 mV/s.

5.4 Conclusions

In this work, we have examined the capacitive charge storage properties of transparent PEDOT:PSS films. Films were prepared on flexible PET substrates using a robot controlled airbrush spraying method. This enabled the production of high quality samples with lateral dimensions to 18 by 18 cm with a range of transmittance values (70% to 99% at 550 nm).

The optical and electrical properties were studied to evaluate their use as transparent current collectors. Through the use of a simple formic acid post-treatment, these films were shown to possess a DC conductivity of 936 S/cm and low optical conductivity of 24 S/cm (at 550 nm). In combination these provide an impressive electrical figure of

merit, $\sigma_{DC}/\sigma_{Op} = 39$. Importantly, percolation effects were not observed even for the most transparent films we prepared ($T=99\%$).

The capacitive charge storage properties of small area (1 cm by 1 cm) films were examined by cyclic voltammetry, demonstrating ideal capacitive behaviour up to high scan rates of 1000 mV/s, providing intrinsic volumetric capacitance of 41 F/cm³. This provides an areal capacitance 0.18 mF/cm² for a $T=99\%$ film. To characterise their performance as transparent electrochemical capacitors we found a capacitive figure of merit of $C_V/\sigma_{Op} = 1.7$ F/S.cm². Repeated CV cycling found a 99% capacitance retention after 3500 cycles.

As transparent electronic devices are likely to require energy storage electrodes with areas larger than 1 cm², the effect of film lateral dimensions on charge storage properties were also examined. It was found that absolute capacitance does not scale linearly with sample area when it is increased *via* the length dimension (*i.e.* greater distance from the electrical contact). This results in lower areal capacitance than expected. To our knowledge this effect has not been studied previously. Some simple models were proposed to account for this length-dependent behaviour on the CV as well as the electrochemical impedance response of these films, using a single-arm transmission line model. On the other hand, absolute capacitance scaled linearly with the width dimension (parallel to the electrical contact). Device measurements were obtained for large area films (footprint area 108 cm², $T=95\%$), for which we measured a capacitance of 12.5 mF at 50 mV/s. To our knowledge this is the highest value recorded for a transparent ECs using electrodes with $T>90\%$.

Chapter 6

SWNT:MnO₂-Nanoplatelet Network Electrodes

6.1 Introduction

A growing number of redox active materials have been identified that display impressive pseudocapacitive behaviour. These have the potential to greatly enhance the energy storage capabilities of EC electrodes beyond those which solely employ the electrochemical double layer.

However, many of the most promising candidates also possess poor electrical conductivity. This was observed in the previous chapter for electrodes without an underling current collector. However, even with a current collector electrodes can be limited by current flow in the perpendicular direction (*i.e.* parallel the the film thickness). As a result, experimentally determined specific pseudocapacitance seldom approach theoretical values, with the exception of ultra-thin film electrodes when they are charged and discharged slowly.^{57;318;356} This means that the available capacitance falls dramatically at high charge/discharge rates required for many EC applications.

A common solution to this problem is to combine the pseudocapacitive material with a nanoconductor such as carbon-black, acetylene black, carbon nanotubes or graphene to form a composite electrode.^{58–64} Numerous researchers have shown that this strategy can result in increased the utilization of pseudocapacitive materials by facilitating transport of charge from redox sites to the external circuit.^{58;60;309;357;358} However, as was indicated in Chapter 3, the nanoconductor content is often poorly justified and therefore likely sub-optimal. Presently, there is a paucity of detailed studies exploring the effect of carbon filler content on the resulting electrical and electrochemical properties of composite faradaic EC electrodes. This situation has likely arisen due to the extensive characterisation required for a large number electrode compositions. Therefore, the challenge remains to build a genuine understanding of factors that influence transport of charge from the redox site to the external circuit *via* the nanoconductor material.

The aim of this work is to address this problem by combining MnO₂-nanoplatelets with single-walled carbon nanotubes using solution processing techniques. This approach affords fine control over electrode composition, enabling a detailed study into the effect

of nanotube content on composite properties by forming a spatially extended current collector, potentially enabling maximal use of the pseudocapacitive component.

6.2 Experimental Methods

6.2.1 MnO₂ Dispersion Preparation

A dispersion of MnO₂-nanoplatelets in isopropanol was prepared in Prof. Valeria Nicolosi's lab for collaborative purposes. This involved taking 1.7 g of Mn(NO₃)₂ and 0.5 g of poly(ethylene glycol)poly(propylene glycol) poly(ethylene glycol) triblock copolymer (P123) and dissolving them together in 100 mL of distilled water. The solution was heated to 45°C and 100 mL of 0.1 M KMnO₄(aq) was added drop-wise under vigorous stirring. The obtained precipitate was filtered under pressure, washed with distilled water and allowed to dry for 24 hours. All chemicals involved in the synthesis of MnO₂ material were supplied by Sigma-Aldrich (99.99% purity).

The resulting MnO₂ powder was then exfoliated by bath sonication to form a stable dispersion in isopropanol (starting concentration, 10 mg/mL). Sonication was carried out for 3 hours using a FisherBrand 11207 sonic bath (37 kHz, 200 W). The dispersion was then centrifuged for 30 min at 1500 rpm using a Heraeus Multifuge X1 Centrifuge to remove any unstable material.

A stock solution of ethyl cellulose (Sigma-Aldrich) was prepared by dissolving this polymer in isopropyl alcohol (IPA) while heating at 75°C (concentration, 5 mg/mL). This solution was then added to the stock MnO₂ solution, such that the binder:MnO₂ mass ratio was 1:10. Although ethyl cellulose was required as a binder for neat MnO₂ films, it wasn't required for composite films formed with SWNTs.

6.2.2 SWNT Dispersion Preparation

A stock solution of sodium dodecyl sulfate, SDS (Sigma-Aldrich), was prepared by adding the surfactant to Millipore deionised water to a concentration of 5 mg/mL. This solution was then added to arc-discharge produced single-walled carbon nanotube powder (SWNTs, Iljin Nanotech Co.) in 20 mL batches such that the surfactant/SWNT mass ratio in the resultant dispersions was 5:1 (SWNT concentration, 1 mg/mL). Each dispersion received 5 min of high power tip sonication (VibraCell CVX; 750W, 20% 60 kHz), before being placed in a sonic bath (Branson 1510-MT sonic bath, 20 kHz) for 1 h, followed by another 5 min of tip sonication. The dispersions were then centrifuged at 5500 rpm for 90 min. The supernatant of each dispersion was carefully decanted and combined. The concentration of the resulting stock dispersion was then determined by absorbance spectroscopy (Varian Cary 6000i spectrophotometer), using Equation 2.1 (Beer-Lambert relation) with the known extinction coefficient of the SWNT ($3389 \text{ mLmg}^{-1}\text{m}^{-1}$ at 660 nm²¹⁹).

6.2.3 Film Preparation

All films were prepared by vacuum filtration of select volumes of the stock dispersions using porous mixed cellulose ester filter membranes (MF-Millipore membrane, hydrophilic, 0.025 μm pore size, 47 mm diameter). In this work, we prepared MnO₂-only and SWNT-only films, as well as composite films by combining the two stock dispersions prior to filtration. The resulting films (diameter, 36 mm) were cut to the desired dimensions and transferred to either polyethylene terephthalate (PET) for electrical testing, indium tin oxide (ITO) coated glass for electrochemical testing, or Au-sputtered silicon substrates for SEM imaging. Here the cellulose filter membrane was removed by treatment with acetone vapor and subsequent acetone liquid baths.

6.2.4 Film Characterisation

Film thickness was measured by profilometry using a Dektak 6M, Veeco Instruments. Step profiles were obtained at three locations on the film and the average calculated. Electrical conductivity values were calculated from current-voltage measurements made using the four-point probe technique using a Keithley 2400 source meter (Keithley Instruments, Inc.) and LabView interface (National Instruments, Inc.). Silver electrodes were painted onto the surface of the films using Agar Scientific supplied silver paint. The electrode width (~ 0.5 cm) and separation (~ 1 cm) were recorded.

SEM was performed using a ZEISS Ultra Plus (Carl Zeiss Group). Imaging was performed using an accelerating voltage of 5 kV, a 30 μm aperture and a working distance of approximately 5 mm.

X-ray photoelectron spectroscopy was performed under ultra-high vacuum conditions ($<5.10\text{-}10$ mbar) using monochromated Al $K\alpha$ X-rays (1486.6 eV) from an Omicron XM1000 MkII X-ray source and an Omicron EA125 energy analyser. An Omicron CN10 electron flood gun was used for charge compensation and the binding energy scale was referenced to the C 1s core-level of the adventitious carbon at 285 eV. The O 1s and Mn 2p core-levels were recorded at an analyzer pass energy of 20 eV and with slit widths of 6 mm (entry) and 3 mm $\times$ 10 mm (exit). After subtraction of a Shirley background, the spectra were fitted with Gaussian Lorentzian line shapes. XPS testing and analysis was performed by Dr. Nina Berner.

Raman analysis was performed using a Witec Alpha 300 R using a 532 nm excitation wavelength and a 1800 lines/mm grating. Average spectra were obtained for each sample from line scans consisting of 50 discrete spectra, each with an integration time of 5 min, taken over a line 200 μm in length. A laser power of 400 μW , as measured using a LaserCheck power meter, was employed to minimise sample damage. Raman testing and analysis was performed by Dr. Niall McEvoy.

Electrochemical properties of the films were examined using cyclic voltammetry in a three electrode electrochemical cell. The cell consisted of a Ag/AgCl reference electrode

and an amorphous carbon counter electrode with 0.5 M K_2SO_4 electrolyte. Test electrodes were first cycled at 100 mV/s for 50 cycles between 0.1 and 0.8 V to ensure stable charge/discharge behavior, followed by 20 cycles each at various scan rates from 10 to 5000 mV/s (corresponding to charge/discharge times from 0.14 to 70 s). Film capacitance was estimated from the cyclic voltammograms by integrating the current passed during the positive and negative potential sweeps, which were averaged. The film geometric area was kept constant at 0.25 cm².

6.3 Results & Discussion

6.3.1 Single component films of MnO_2 or SWNT

Layered manganese dioxide was prepared by a modified version¹⁷⁰ of the co-precipitation method reported by Jiang *et al.*⁶³ The material was received as a brown dispersion with concentration of ~ 0.2 mg/ml in IPA (Figure 6.1A). TEM analysis showed the dispersed material to be in the form of thin nanosheets with mean lateral size of ~ 200 nm (Figure 6.1B & C). We note that such samples always contain a small population of relatively large crumpled objects such as the one at the bottom of Figure 6.1C.

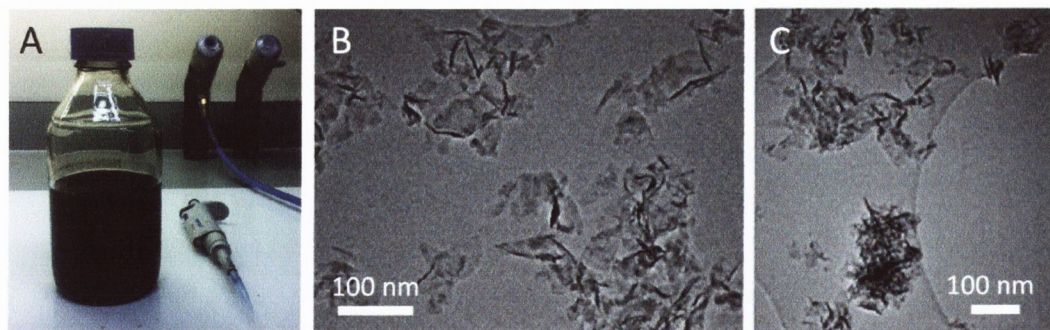


Figure 6.1: (A) Photograph of stock MnO_2 /IPA dispersion. (B) and (C) TEM images of MnO_2 -nanoplatelets.

Thin films of MnO_2 nanosheets were produced by vacuum filtration for Raman and XPS analysis. A typical Raman spectrum is presented in Figure 6.2A and displays a dominant feature at $\sim 645 \text{ cm}^{-1}$, which we attribute to the symmetric stretching vibration $\nu_2(\text{Mn-O})$ of MnO_2 , as expected for layered MnO_2 .^{359–361} The shoulder observed on the left hand side of this primary peak ($\sim 575 \text{ cm}^{-1}$) can be attributed to the $\nu_3(\text{Mn-O})$ stretching vibration associated with MnO_6 octahedra.³⁶²

XPS measurements of the Mn 2p and O 1s core-levels (Figure 6.2B and C, respectively) show the expected MnO_2 components in the correct stoichiometry, with a ratio of manganese to oxygen very close to 50 %. The Mn 2p 3/2 peak has been fitted with five multiplet components in accordance with the parameters established for MnO_2 by Biesinger *et al.*³⁶³ The additional Mn^{3+} component can be attributed to X-ray damage and/or other oxide species like Mn_2O_3 , but this constitutes a very minor part of the spectrum. Apart from the main MnO_2 component, the deconvoluted O 1s peak also shows contributions from the SiO_2 substrate, nitrates, which are most likely associated with the $\text{Mn}(\text{NO}_3)_2$ starting material, as well as minor contribution from adventitious carbonates. This analysis indicates that the synthesised material to be predominately layered MnO_2 .

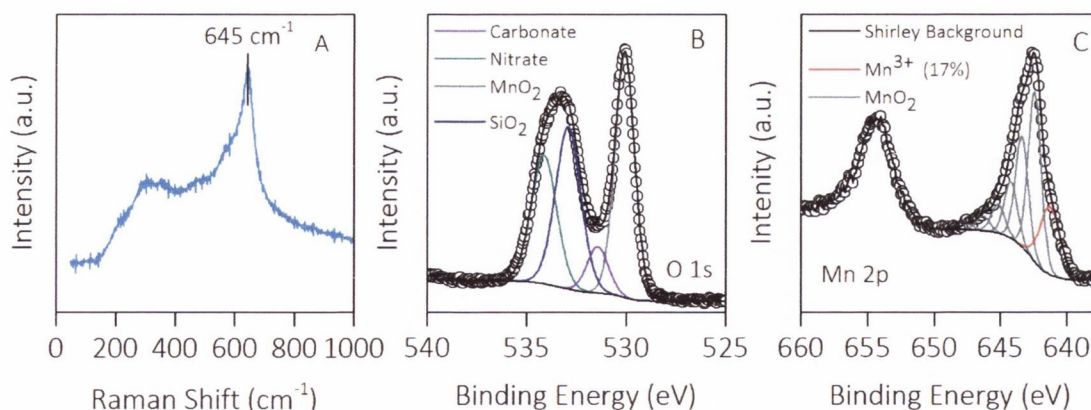


Figure 6.2: Characterisation of MnO_2 -nanoplatelets measured on vacuum filtered thin films of MnO_2 . XPS spectra showing (A) Mn 2p peaks and (B) O 1s peaks. (C) Raman spectrum

Subsequently we used vacuum filtration to prepare a range of MnO_2 thin films with varying mass per unit area (M/A). This quantity was controlled *via* the volume of dispersion filtered. A small quantity (10 wt%) of ethyl cellulose (EC) was added as a binder. The film M/A varied from 2 to $160 \mu\text{g}/\text{cm}^2$, a relatively broad range as compared to previous work (*i.e.* Pang *et al.*,³¹⁸ $1\text{--}14 \mu\text{g}/\text{cm}^2$, Hu *et al.*,³⁶⁴ $130\text{--}150 \mu\text{g}/\text{cm}^2$). After filtration, pieces of the films ($A \sim 0.25 \text{ cm}^2$) were transferred from the nitrocellulose filter membranes onto ITO-coated glass current collectors using acetone to dissolve the membrane.¹⁸³

Film thicknesses were determined using profilometry, revealing that the M/A loading range corresponds to thicknesses varying from 40 nm to $1.7 \mu\text{m}$ (Figure 6.3). Despite the inclusion of the ethyl cellulose, we found it impossible to prepare electrodes of the MnO_2 thicker than $1.7 \mu\text{m}$, due to poor mechanical properties leading to difficulties in transfer. We measured the film density as $0.95 \text{ g}/\text{cm}^3$ suggesting a high film porosity of $\sim 80 \%$ (using $\rho_{\text{MnO}_2} = 5 \text{ g}/\text{cm}^3$). This morphology is attractive for electrochemical capacitor applications due to the combination of high surface to bulk atomic ratio and porosity, which allows for ready access of electrolyte counter ions to the internal surface area of the electrode.

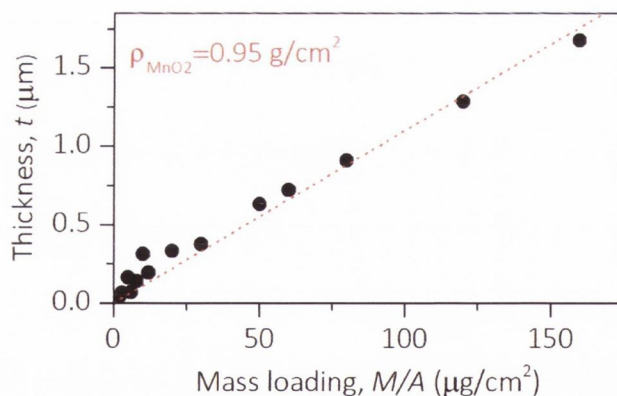


Figure 6.3: Thickness of MnO_2 thin films plotted as a function of sample loading (M/A). Calculated film density was $0.95 \text{ mg}/\text{cm}^3$.

Electrochemical experiments were performed on prepared electrodes to investigate the charge storage properties of the MnO_2 films. Cyclic voltammetry (CV) was carried out using 0.5 M K_2SO_4 electrolyte in a three electrode configuration. Before measurement, each film was conditioned by applying 50 CV cycles between 0.1 and 0.8 V *vs.* Ag/AgCl ($dV/dt=100$ mV/s) to ensure a stable electrochemical response. Following the electrode conditioning, CVs were recorded at a variety of scan rates from 10 to 5000 mV/s. The slowest and fastest scan rates correspond to charging/discharging times of 70 sec and 0.14 sec respectively. These charging/discharging times are suitable for many supercapacitor applications.³⁶⁵

The typical CV response of an ultra-thin MnO_2 electrode ($t=40$ nm) at two scan rates (50 and 5000 mV/s) is presented in Figure 6.4A. To facilitate comparison, we normalised the current response to both scan rate and the mass of active material, yielding a differential gravimetric capacitance. The shape of the CV curves are broad and near-rectangular, typical of the pseudocapacitive response of this material.⁶² At the lower rate of 50 mV/s, faradaic features can be discerned centered at 0.5 V on the oxidation sweep and 0.4 V on the reductive sweep. These features disappear at higher rates and the current is slow indicates resistive character even for this thin film electrode. The capacitance was calculated by integrating the current passed within the potential window. We calculated a relatively high specific capacitance (C/M) for this material (~ 200 F/g at 50 mV/s), typical for a thin film of MnO_2 charged relatively slowly.^{304;366} This value decreases at higher rates, to ~ 90 F/g at 5000 mV/s.

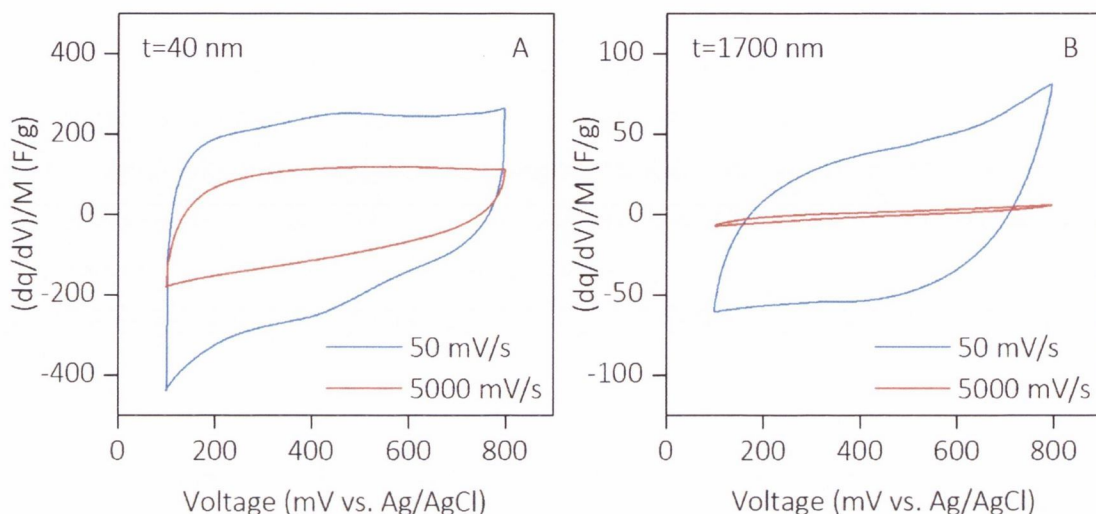


Figure 6.4: Cyclic voltammograms of MnO_2 -only films with measured thickness of (A) 40 nm and 1700 nm (B) at 50 and 5000 mV/s. Measured current density is normalised to scan rate to yield a differential capacitance. Electrolyte was 0.5 M K_2SO_4 .

Characterisation of films with thickness in the nanometer range is useful to evaluate the quality of the material. However, for many applications where greater absolute capacitance is required, the electrode thickness needs to be scaled up. Therefore it is important to evaluate how capacitance varies with electrode thickness. To investigate this we have prepared thicker electrodes and evaluated their charge storage behaviour in a similar manner. Figure 6.4B shows CVs for a 1.7 μm thick MnO_2 film. We observe that C/M has decreased by a factor of ~ 10 at 50 mV/s and a factor of ~ 100 at 5000 mV/s, compared with the 40 nm thick film. The CV shape exhibits a more resistor-like behaviour for thicker films, and the faradaic features observed for the thin films are no longer perceivable. We emphasise that these thicker MnO_2 films are still relatively thin; commercial supercapacitor electrodes based on porous carbon typically have thicknesses of 10-100's of microns.¹⁸⁰

To demonstrate this behaviour more clearly we have plotted C/M as a function of scan rate for three different electrode thicknesses (Figure 6.5A) and as a function of thickness

for three different scan rates (Figure 6.5B). In both cases we observe impaired specific capacitance for thicker films and faster charge/discharge rates, indicating that a diminishing proportion of active redox sites are being utilised. Such results are consistent with electrodes which are limited by poor electrical performance.^{10;58;309;318;334;357} In particular, the symmetry between these temporal and spatial dependencies suggests they are determined by the same underlying electrode properties, namely those determining the transport of charge between active sites and the external circuit. Using the four-probe technique, we measured the electrical conductivity of the thin films of MnO_2 nanosheets used here to be $\sim 1.7 \times 10^{-5} \text{ S/m}$. This low conductivity is similar to values reported by others^{332;333} and would be expected to limit supercapacitor performance. Understanding how these effects can be overcome is crucial for the design of supercapacitor electrodes that overcome the problem of underwhelming absolute capacitance, particularly at high power.

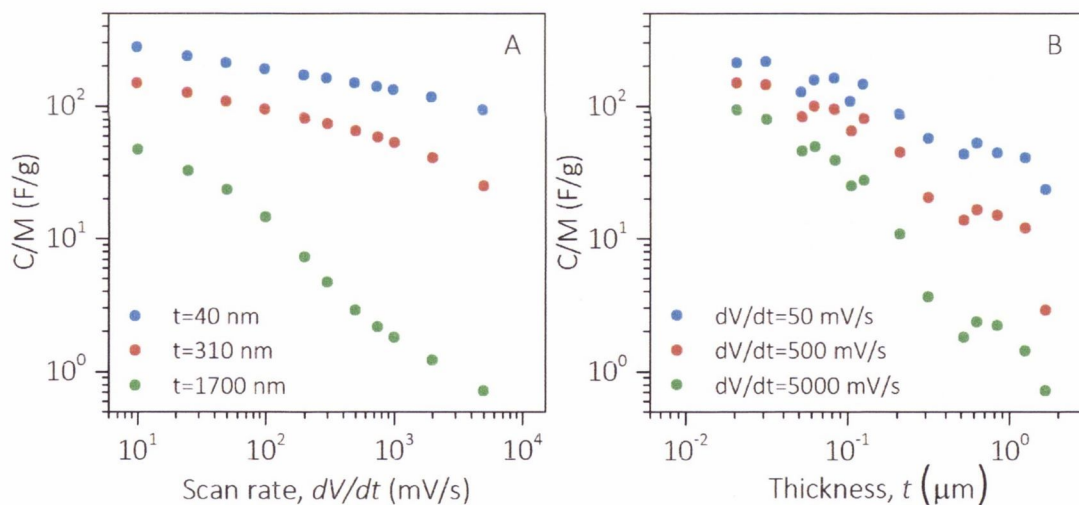


Figure 6.5: Specific capacitance of MnO_2 -only films (A) as a function of scan rate for three film thicknesses and (B) thickness for three scan rates.

In contrast to the observed poor electrical properties of these MnO_2 films, the high electrical conductivity of many carbon-based materials makes them excellent candidates as

high performance supercapacitor electrodes. To compare with the MnO_2 data described above, we prepared disordered network films of single-walled carbon nanotubes (SWNTs) of various thicknesses. We measured the film conductivity to be $\sim 2 \times 10^5 \text{ S/m}$, which is in agreement with previous reports.¹⁹¹ Cyclic voltammetry carried out under the same conditions as for MnO_2 showed highly rectangular behaviour (Figure 6.6A), indicating a close to ideal capacitive response with a small time constant. The gravimetric capacitance determined by integration of the CVs was virtually invariant with both thickness and scan rate at $\approx 10 \text{ F/g}$ (Figure 6.6B and C) as has been reported by others.³⁶⁷ The slightly raised apparent capacitance for the thinnest film is due to the contribution of the underlying ITO current collector, which becomes significant for very thin films.

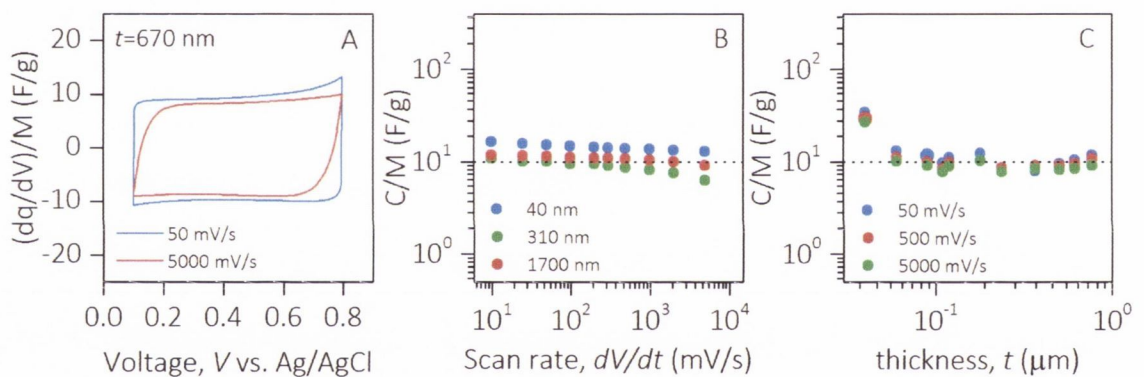


Figure 6.6: Cyclic voltammograms of (A) SWNT-only film with $t=670 \text{ nm}$ at two scan rates. Specific capacitance of SWNT-only films (B) as a function of scan rate at three film thicknesses and (C) thickness at three scan rates.

It is clear from this work that thin films of MnO_2 have great potential as supercapacitor electrodes, but they are limited by poor conductivity resulting in disappointing performance at high scan rates and for thicker electrodes. Indeed, overcoming electronic transport limitations of pseudocapacitive materials in general is key to achieving high performance electrodes. As discussed by a number of authors,^{334;358} a simple solution is to add carbon nanotubes to the MnO_2 electrode, forming a conducting network to facilitate charge transport from redox sites to the external circuit. Furthermore, this strategy

is known to improve mechanical properties of films containing layered materials and assist with electrolyte accessibility by preventing restacking of adjacent sheets.^{368;369}

6.3.2 Composite Films of MnO₂ and SWNTs

In order to test the effect of adding carbon nanotubes to films of MnO₂ nanosheets, we prepared composite films with a range of SWNT:MnO₂ mass ratios. This was achieved by simple mixing of appropriate volumes of the two component dispersions followed by vacuum filtration and film transfer (see Methods). In this study, we chose a fixed MnO₂ mass loading of 160 $\mu\text{g}/\text{cm}^2$. We then added increasing quantities of SWNTs to this fixed quantity of MnO₂ forming composites with nanotube mass fractions of up to 40 wt%. As indicated in Figure 3.10, this maximum carbon loading is likely to be well above the optimum conducting filler content for composite electrochemical capacitor electrodes. The chosen method of composition study differs somewhat from others^{312;370} where the total film mass is kept constant and the masses of both components are altered simultaneously. Keeping the MnO₂ mass constant for all films, our approach greatly simplifies analysis of the way MnO₂ pseudocapacitance varies with film composition. While the film thickness is relatively constant at $\sim 1.5 \mu\text{m}$ up to $M_f=20 \text{ wt}\%$, the addition of SWNTs beyond this loading caused the film thickness to increase. At the maximum mass fraction ($\sim 40 \text{ wt}\%$) tested the film thickness was $\sim 3 \mu\text{m}$. (Figure 6.7A). The fixed MnO₂ M/A of 160 $\mu\text{g}/\text{cm}^2$ was chosen because it corresponds to the greatest thickness at which we could produce mechanically robust MnO₂-only films for comparison. Considering Figure 6.5A & B, it is clearly a thickness where the capacitance of MnO₂ is transport limited. Additionally, while remaining relatively thin we minimised the influence of ionic transport which cannot be ignored for thick electrodes.

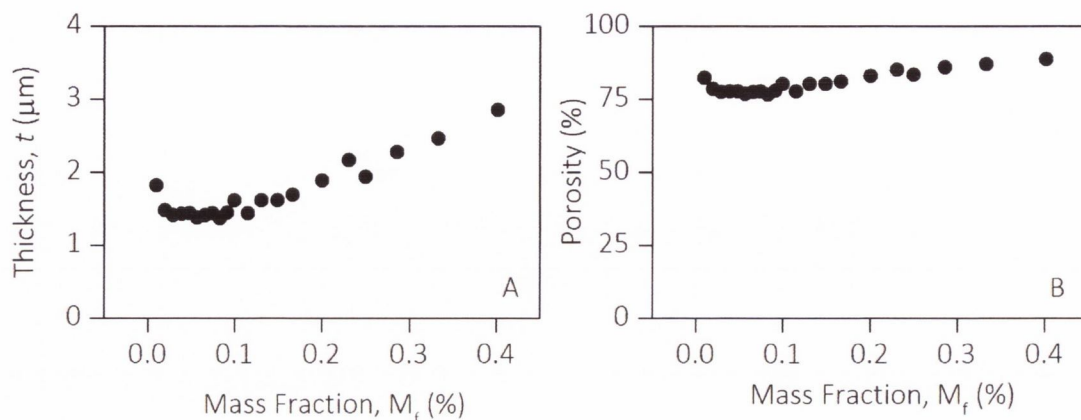


Figure 6.7: SWNT: MnO_2 composite film thickness (A) and calculated porosity (B) plotted as a function of SWNT mass fraction.

SEM images of an MnO_2 -only film and two composite films ($M_f=1$ and 25 wt%) are presented in Figure 6.8. Even at 1 wt% loading, the presence of the nanotubes is apparent. The images at higher loadings suggest effective mixing of the two components, with the MnO_2 intimately incorporated within the nanotube network. Importantly, we found that the addition of any amount of SWNTs greatly improved the film's mechanical integrity, making the inclusion of ethyl cellulose binder unnecessary. This is not unexpected as we have previously observed films of exfoliated nanosheets to be very brittle but become much more robust on addition of nanotubes.^{94;370} The opportunity to discard the polymeric binder is of significant benefit as the 10 wt% ethyl cellulose is an otherwise poor use of mass (and volume) within an electrode material, imparting no intrinsic capacitance or electrical transport pathways. This contrasts with previously reported composite electrodes where the conductive additive has not also acted as a binder.^{62;371} In addition, the composite films are extremely porous containing free volumes of $>75\%$ for all mass fractions (Figure 6.7B). This is advantageous as it should allow free access of the electrolyte to the internal surface of the electrode. Conversely, very high porosity will ultimately reduce the scope for high volumetric capacitance.

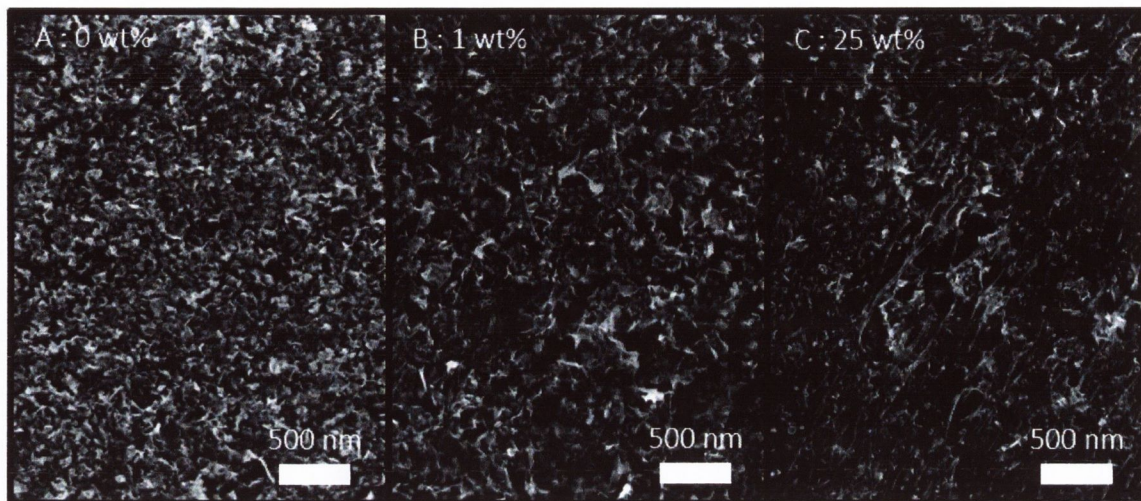


Figure 6.8: SEM images of MnO_2 -only (A) and SWNT: MnO_2 nanotubes films at 1 wt% SWNTs (B) and 25 wt% nanotubes (C). All films had thickness of ~ 100 nm

Using the four-probe technique we measured the in-plane electrical conductivity for SWNT: MnO_2 composites with a range of nanotube contents. The conductivity data is plotted in Figure 6.9, where the nanotube content is represented as a volume fraction, ϕ . We found that the DC conductivity increases rapidly with the addition of small amounts of nanotubes, reaching ~ 100 S/m for $\phi=1$ vol% and approaching 10^5 S/m for $\phi=25$ vol%. This behaviour is qualitatively similar to that observed previously for composites of MoS_2 nanosheets mixed with carbon nanotubes.^{94;184} The electrical properties of such insulator/nanoconductor composites is described by percolation theory.³⁷² In this framework the film conductivity is expected to be very low until a critical volume fraction of nanoconductors is reached, called the electrical percolation threshold, $\phi_{c,e}$. Above the percolation threshold, the electrical conductivity is described by:¹⁸⁹

$$\sigma = \sigma_0(\phi - \phi_c)^n \quad (6.1)$$

where σ_0 is related to the conductivity of the nanoconductor and n is the percolation exponent.¹⁹⁴ Fitting our data to equation 6.1 (Figure 6.9) gives a very low electrical percolation threshold of $\phi_{c,e}=0.16$ vol%, $\sigma_0=1.4 \times 10^6$ S/m and a percolation exponent of 1.82. We note that the percolation threshold for composites with 1D fillers is thought

to scale with the diameter to length ratio of the filler particles.³⁷³ Accordingly, very low percolation thresholds such as that found here are often observed for composites based on carbon nanotubes.¹⁹⁴ This is a significant advantage for our purpose as a small percolation threshold means significant conductivities can be achieved at relatively low ϕ , meaning very little capacitive material has to be sacrificed to introduce the conductive paths.

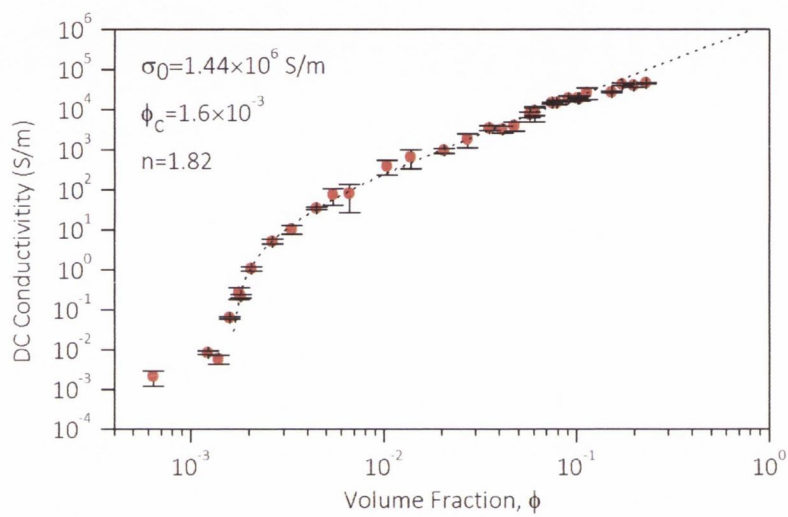


Figure 6.9: In-plane electrical conductivity of SWNT:MnO₂ composite thin films plotted as a function of nanotube volume fraction. The dotted line is a fit using Equation 6.1 with fit constants given in the graph. In all cases the films were 1.5 to 3 μm thick.

6.3.3 Composite Electrochemical Capacitor Electrodes

If relatively thick MnO_2 -only electrodes display capacitances which are limited by electrical conductivity, the data in Figure 6.9 would lead us to expect the addition of nanotubes to result in significant capacitance enhancements. To test this, we measured CVs for a range of composites and compared their response to the MnO_2 -only film. Shown in Figure 6.10A are the current responses of three composite films to linear potential sweeps with $dV/dt=1000$ mV/s. The first thing to note is a considerable increase in current density as nanotube content is increased. This strongly supports the idea that the introduction of conductive paths facilitates the accessibility of redox sites. However, the shape of the CV curves is also of interest. Considering the current response of a simple series resistor-capacitor model (Equation 5.2), it is clear that increasing the SWNT content results in reduced τ , suggesting a substantial reduction of R_{ESR} due to the presence of the nanotubes. Similar observations regarding CV shape were made by Lee *et al.*⁵⁸ and Kim *et al.*³⁰⁹ on adding carbon black to MnO_2 . This effect is also evident, though less pronounced, at slow scan rates (Figure 6.10B). Subtle faradaic features of the MnO_2 can still be discerned even with 33 wt% nanotubes. This observation is important; if the capacitance increase were imparted by the added nanotubes themselves, these MnO_2 redox features would likely be obscured, especially at higher nanotube loadings. This suggests that the capacitance increase of the composites is predominately due to the action of the nanotubes providing electrical access to the MnO_2 , rather than *via* their intrinsic capacitance.

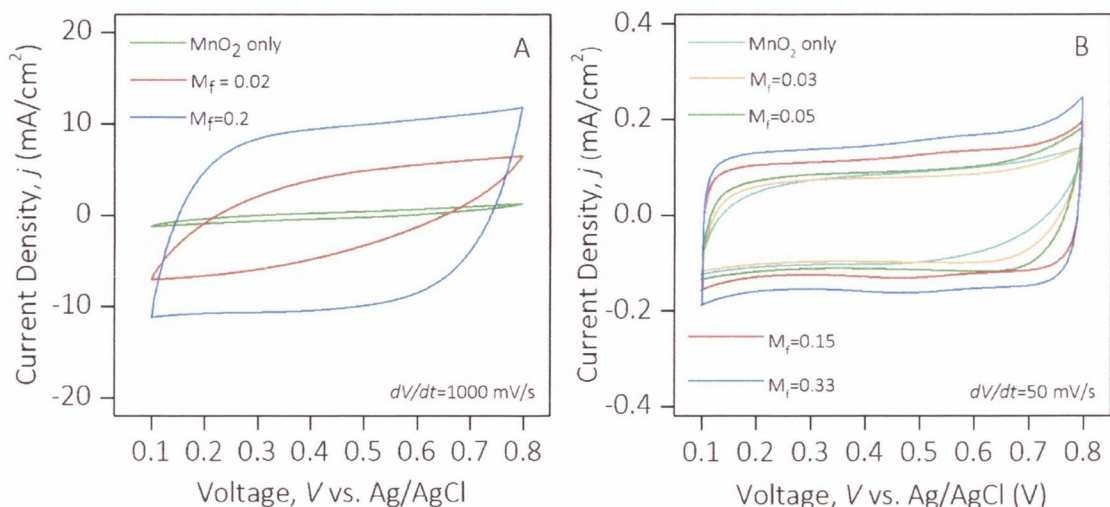


Figure 6.10: Cyclic voltammograms of MnO_2 -only and SWNT: MnO_2 composite films at 50 mV/s (A) and 1000 mV/s (B) with various nanotube loadings.

We can quantify this capacitance increase by plotting the measured capacitance of the composite film normalised to total film mass, (C_T/M_T) as a function of nanotube mass fraction. These data are shown in Figure 6.11 for three scan rates. (N.B. $M_T = M_{\text{MnO}_2} + M_{\text{NT}}$ and assuming both MnO_2 and SWNTs contribute to the capacitance, $C_T = C_{\text{MnO}_2} + C_{\text{NT}}$). It is clear that for all scan rates the capacitance increases dramatically upon addition of even a few percent of nanotubes before falling off at higher mass fraction. The SWNT loading providing maximum capacitance falls in the range of 5-15 wt%, shifting slightly to higher loadings with increasing scan rate. In some cases, the improvements are large: for the 500 mV/s data a $\times 15$ increase in C_T/M_T was observed at $M_f = 11$ wt% compared to the MnO_2 -only electrode. Beyond the optimised values, the specific capacitance decreases as the relative nanotube content in the films increases, presumably approaching the nanotube-only value of ~ 10 F/g. This behaviour would not be expected if the MnO_2 and SWNTs were both contributing to the capacitance only as per their individual specific capacitances (*i.e.* the rule of mixtures: $C_T/M_T = (C/M)_{\text{MnO}_2}(1 - M_f) + (C/M)_{\text{NT}}M_f$). To contrast this behaviour with our data, RoM-type behaviour is also indicated in Figure 6.11 as the dashed lines.

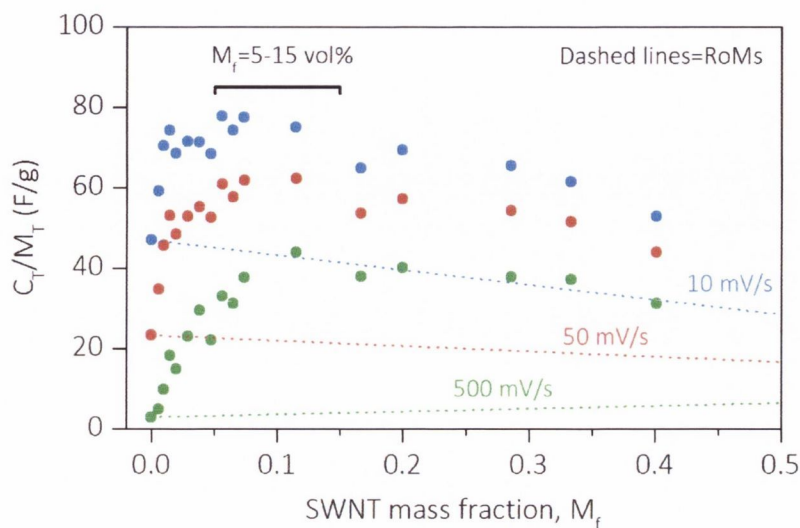


Figure 6.11: Measured total capacitance ($C_T = C_{MnO_2} + C_{NT}$) of SWNT:MnO₂ composite films as a function of nanotube mass fraction at CV three scan rates. The dotted lines indicate are the expected total capacitance for rule of mixtures (RoM) behaviour.

A similar peak to that observed in Figure 6.11 has been reported previously for supercapacitors formed from mixtures of activated carbon/carbon black³⁷⁴ and carbon aerogels filled with nanoconductors such as carbon black, nanotubes and carbon fibres.³⁷⁵ In these publications it was suggested that the peak capacitance occurred at the percolation threshold. However, comparing the results in Figure 6.11 and Figure 6.9 indicates that the peak capacitance occurs at volume fractions substantially above the electrical percolation threshold. This optimum loading of carbon nanotubes (5-15 wt%) is relatively low compared to the literature where (often unoptimised and therefore poorly justified) conductor contents tend to fall in the range 15-25%^{58;62;309;311;358;367;376-378} (see Figure 3.10). Lower conductor contents are desirable from an economic standpoint given the present relative cost of these two materials in addition to the fact that the nanotubes provide little intrinsic capacitance.

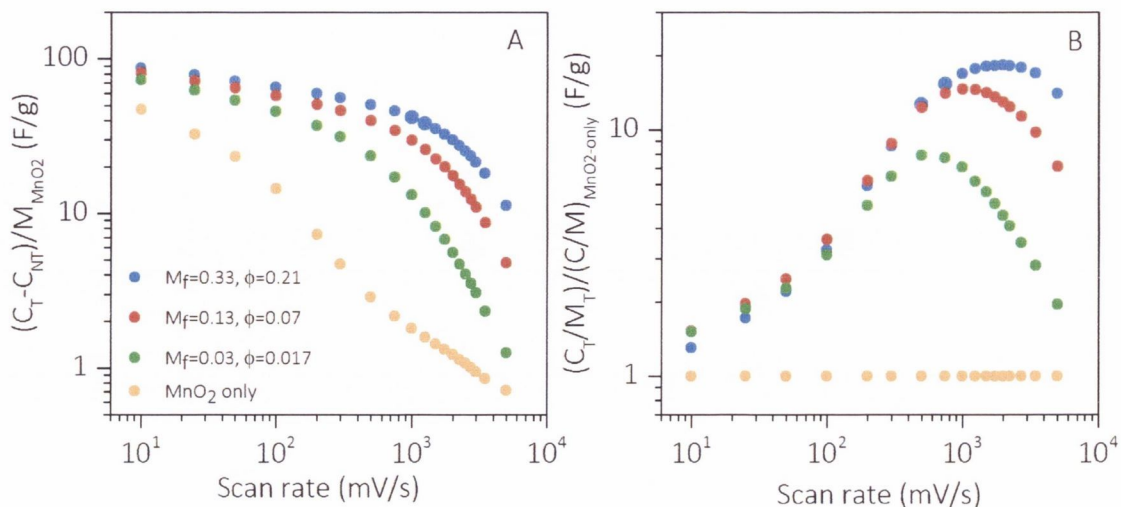


Figure 6.12: (A) Specific capacitance associated only with the MnO_2 (*i.e.* with the SWNT component removed) measured for various composite electrode compositions plotted *vs.* scan rate. (B) Increase in specific capacitance due to the presence of the SWNTs relative to MnO_2 -only electrode plotted *vs.* scan rate, for various electrode compositions (see (A) for legend). In all cases films were 1.5 to 2 μm thick.

The fact that the capacitance data in Figure 6.11 does not follow the rule of mixtures also suggests the increase in capacitance is due to the addition of conducting paths to the MnO_2 electrode. The presence of these paths seemingly “activates” the nearby MnO_2 by enabling the transport of stored charge to and from the current collector. To examine this hypothesis, we should consider the effect of nanotube content on the specific capacitance due only to the MnO_2 . To do this, we subtract the capacitance contribution due to the nanotubes (*i.e.* 10 F/g), and normalise to the mass of MnO_2 (*i.e.* we calculate $(C_T - C_{NT})/M_{MnO_2}$). These data are presented in Figure 6.12A, plotted *vs.* scan rate for a number of composite electrodes with differing nanotube contents. Included for comparison is the equivalent data for a MnO_2 -only film of with the same M/A ($160 \mu g/cm^2$). These data indicate that the presence of nanotubes considerably increases the capacitance associated with the MnO_2 at all scan rates. However, the effect is particularly apparent at high scan rates with the MnO_2 capacitance at 1000 mV/s increasing from ~ 2 F/g in the MnO_2 -only film to ~ 42 F/g for the film with 33 wt% SWNT.

In practical terms, what is important is the increase in specific electrode capacitance which can be achieved by adding nanotubes. This can be examined by plotting the ratio of the specific capacitance of a composite electrode to that for an MnO_2 -only electrode (*i.e.* $(C_T/M_T)/(C/M)_{\text{MnO}_2}$) *vs.* scan rate (Figure 6.12B) for a number of mass fractions. While a two-fold increase is found at low scan rates, much larger increases are found at higher scan rates; the relative capacitance increase peaks at scan rates in the 600-2000 mV/s range, with a twenty-fold increase observed at 2000 mV/s for the 33 wt% sample. The decrease which occurs at scan rates beyond this maximum is likely due to ionic diffusion becoming the rate limiting step for electrode charge and discharge.

6.3.4 Percolation of Capacitance in Composite Films

To allow future optimisation of solution-processed nanostructured supercapacitor electrodes, it will be necessary to understand the nature of these capacitance increases. The increase in MnO_2 capacitance compared to an MnO_2 -only electrode, normalised by MnO_2 mass is given by equation 6.2

$$(\Delta C/M)_{\text{MnO}_2} = \frac{C_T - C_{NT} - C_{\text{MnO}_2\text{-only}}}{M_{\text{MnO}_2}} \quad (6.2)$$

We note that calculation of this parameter is facilitated by the fact that all films have identical MnO_2 mass as described above and in the Experimental Methods. Presented in Figure 6.13A is $(\Delta C/M)_{\text{MnO}_2}$ plotted *vs.* nanotube volume fraction, ϕ , for data collected at two representative scan rates. As illustrated by these plots, data collected at all scan rates display the same features: at low ϕ , $(\Delta C/M)_{\text{MnO}_2}$ increases non-linearly with ϕ up to $\phi = \phi_{\text{sat}}$, after which it reaches a constant value which we denote $(\Delta C/M)_{\text{sat}}$. We will first discuss the behaviour at low ϕ before turning to the saturation regime.

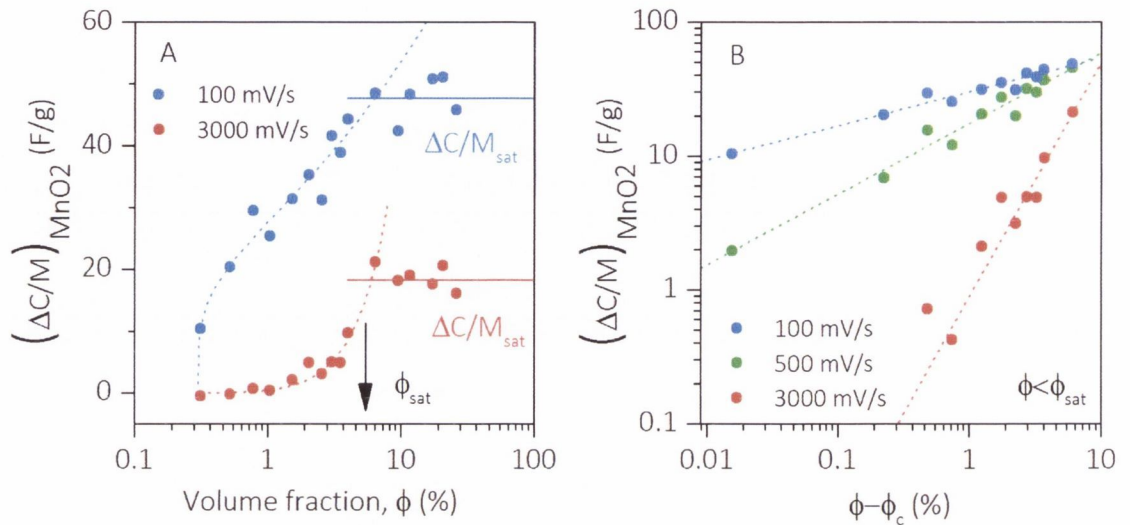


Figure 6.13: Percolation analysis of composite thin film electrochemical capacitor electrodes. (A) Increase in specific capacitance of MnO₂ due to percolative effect $(\Delta C/M)_{\text{MnO}_2} = (C_T - C_{NT} - C_{\text{MnO}_2\text{only}})$ (*i.e.* with capacitance contribution of nanotubes equivalent MnO₂-only film subtracted off), plotted *vs.* nanotube volume fraction for two scan rates. At all scan rates the increase in this quantity saturated at the same volume fraction ϕ_{sat} . The dashed lines are fits to percolation theory equation 6.3, while solid lines indicate capacitance in the saturation region. (B) Percolation scaling graphs for the specific capacitance increase. Only data with $\phi < \phi_{\text{sat}}$ are shown. In all cases the percolation threshold was $\phi_c = 0.3$ vol%.

As discussed previously, it is likely that the observed increases in capacitance are associated with the introduction of conducting paths to the electrode. The conductivity of the overall network is controlled by percolation theory (Figure 6.9). However, it has previously been shown that, for supercapacitor electrodes based on percolating nanotube networks, the resulting capacitance is also described by percolation theory.¹⁶⁰ This occurs because the capacitance is directly proportional to the number of nanotubes connected to the network; a parameter which is controlled by percolation theory.^{160;189} It is likely that similar phenomena are present in the SWNT:MnO₂ composites under study here. We propose that, as the nanotube volume fraction increases and the network becomes more extensive, the volume of MnO₂ within close proximity of the network increases. This

proximate MnO_2 can easily transfer charge to the current collector *via* the nanotube network, and as such it becomes “activated”. Thus, we expect the capacitance to scale with network size and propose that the capacitance increase can be described by a percolative scaling law of the form:

$$(\Delta C/M)_{\text{MnO}_2} = (\Delta C/M)_0(\phi - \phi_{c,c})^{n_c} \quad (6.3)$$

where $(\Delta C/M)_{\text{sat}}$ is a constant, $\phi_{c,c}$ is the capacitive percolation threshold and n_c is the capacitive percolation exponent. We note that, in general, the $(\Delta C/M)_{\text{MnO}_2}$ *vs.* ϕ data is quite scattered making it difficult to accurately fit a three-unknown function such as equation 6.3 to the data. To address this, we fixed $\phi_{c,c}$ at a constant value for all scan rates. Initial trials found that setting $\phi_{c,c} = \phi_{c,e} = 0.0016$ (the in-plane electrical percolation threshold) gave reasonable fits for all scan rates. However, it was found that using $\phi_{c,c} = 0.003$ gave clearly better fits, especially at low ϕ (15 out of 19 scan rates displayed $R^2 > 0.9$). This can be seen by plotting $(\Delta C/M)_{\text{MnO}_2}$ *vs.* $\phi - \phi_c$ as shown in Figure 6.13B. This justifies our proposal to use equation 6.3 and suggests the capacitance is indeed described by percolation theory. The fact that $\phi_{c,c} > \phi_{c,e}$ is perhaps not unexpected. The electrical measurements were associated with current flowing in the plane of the composite. However, in the capacitance measurements the composite electrode sits on top of an ITO current collector, with the electrolyte in contact with the top composite surface. In this case, current flow from ITO to redox sites is, on average, out of plane. In thin film composites, we expect the nanotubes to be randomly arranged in the plane of the film but partially aligned with the film surface making in-plane and out-of-plane charge transport non-equivalent. In fact, it has been shown that the percolation threshold for aligned rods is higher than that for randomly arranged rods³⁷⁹ making the difference between $\phi_{c,c}$ and $\phi_{c,e}$ perhaps unsurprising.

Fitting gave n_c and $(\Delta C/M_0)$ with reasonably low uncertainties for a range of scan rates between 10 and 5000 mV/s. These data are presented in Figure 6.14A and B. The capacitive percolation exponent increases monotonically with scan rate from $n_c \sim 0.2$ for $dV/dt = 10$ mV/s to $n_c \sim 3$ for $dV/dt = 5000$ mV/s. This is somewhat unexpected; for electrical percolation the percolation exponent tends to be a property of the network, scaling

with parameters such as network uniformity¹⁹² or width of the junction resistance distribution.³⁴¹ Such network properties would not be expected to vary with scan rate. The scan rate dependence of $(\Delta C/M)_0$ is also poorly understood. It follows a similar form as the n_c *vs.* scan rate data, increasing continuously with rate. By analogy with electrical percolation³⁷³ we would expect this parameter to reflect the material properties of the system. We suggest that to some extent these variations in the fit parameters with scan rate reflect an influence of ionic diffusion constraints which becomes important at higher rates (see Figure 6.12; in particular, where capacitance decreases beyond ~ 1000 mV/s). Thorough examination of these effects will require future characterisation of how ionic diffusion within the electrode vary with nanotube loading in these composites. However, it is clear that the relative capacitance increase associated with MnO_2 is consistent with percolation theory.

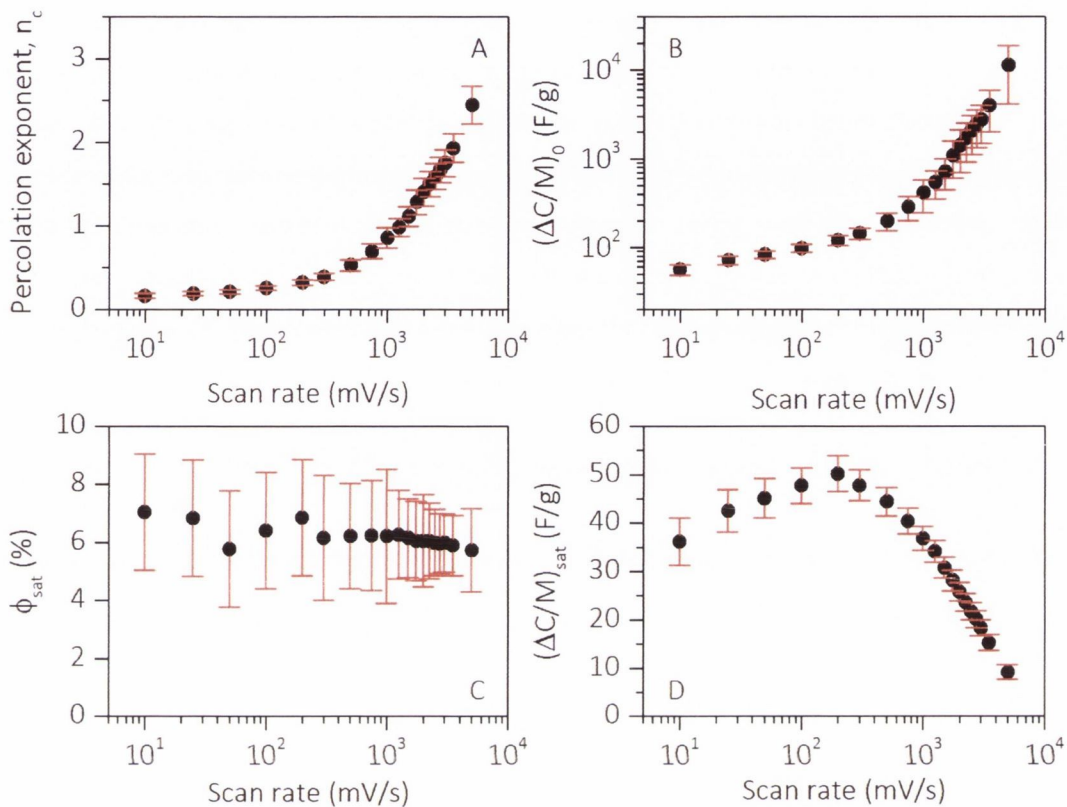


Figure 6.14: Percolation fit parameters plotted *vs.* scan rate: the percolation exponent, c_n (A), $(\Delta C/M)_0$ (B), the saturation volume fraction, ϕ_{sat} (C), the saturation capacitance, $(\Delta C/M_{MnO_2})_{sat}$ (D).

The saturated regime indicated in Figure 6.13A is perhaps more intuitive. As ϕ is increased the network becomes more extensive, bringing increasingly more MnO_2 within proximity of nanotubes. However, at some critical volume fraction, ϕ_{sat} , all MnO_2 in the electrode will be close enough to a nanotube to effectively exchange charge with the network. After this, the capacitance cannot be increased by increasing the volume fraction and it saturates at a value of $(\Delta C/M)_{sat}$. The saturated volume fraction, ϕ_{sat} , is plotted *vs.* scan rate in Figure 6.14C, remaining constant at ~ 6 vol%. This invariance implies that the maximum distance (R) over which MnO_2 can exchange charge with the network is scan rate independent. This maximum range defines a shell, of thickness R ,

which surrounds the nanotube network and defines the volume of activated MnO_2 *i.e.* the MnO_2 which can effectively transfer charge to the nanotube network. The saturation volume fraction is then the lowest volume fraction where the shell encloses all the MnO_2 in the electrode. Considering a local section of shell associated with a straight section of nanotube (radius r), both of which we model as cylinders, the saturation volume fraction is approximately the nanotube volume divided by the volume enclosed by the shell: $\phi_{sat} = r^2/(r + R)^2$. Taking $\phi_{sat} = 6 \text{ vol}\%$ gives $R \approx 3r$. Assuming that the nanotubes are in the form of bundles of diameter $\sim 20 \text{ nm}$ (as observed previously¹⁹¹), with $r \sim 10 \text{ nm}$, it follows that $R \sim 30 \text{ nm}$.

The dependence of $(\Delta C/M)_{sat}$ on scan rate is presented in Figure 6.14D. Interestingly, $(\Delta C/M)_{sat}$ increases at low scan rate before reaching a maximum at $\sim 200 \text{ mV/s}$. We note that the position of this maximum is controlled by the details of the rate dependence of both n_c and $(\Delta C/M)_0$. However, it is the presence of this maximum that results in the shape of the curves given in Figure 6.12B.

This work demonstrates the importance of percolation in composite supercapacitors. While a number of papers have suggested percolation plays a role in the operation of composite supercapacitors,^{374;375;380} even indicating the onset of capacitance at the electrical percolation threshold,⁵⁹ percolation scaling of capacitance has not been observed. When studying a nanotube/activated carbon composite, Pico *et al.* observed a rule of mixtures rather than percolative behaviour.³⁸⁰ However, it is likely that this was due to the relatively high conductivity of the capacitive phase and the moderate difference in conductivities between the components of the composite ($\times 1000$ compared with $> \times 10^8$ here). We believe the current study is the first demonstration of percolation of capacitance in composite supercapacitor electrodes (although percolation scaling of capacitance has been observed in single-component nanotube networks¹⁶⁰). Understanding the nature of such percolation effects will be critical for the optimisation of capacitive composites.

6.3.5 Thick Composite Films

Electrochemical capacitors must display large areal capacitances, C/A , to maximise their energy storage capacity. Because $C/A = \rho t C_T/M_T$, where ρ and t are electrode density and thickness respectively, maximisation of areal capacitance requires C_T/M_T to remain high even as the film thickness is increased. However, as discussed, electrodes of MnO_2 nanosheets display two significant problems. Firstly, the specific capacitance C_T/M_T tends to fall with increasing thickness for resistive electrode materials. The second issue is the problem of poor mechanical integrity of MnO_2 electrodes. As described previously, we found it impossible to prepare MnO_2 -only electrodes with $t > 1.7 \mu\text{m}$ due to their severe brittleness. We expect both of these problems to be addressed by the production of MnO_2 -nanotube composites. To test this, we produced a set of composite electrodes ($\phi = 15 \text{ vol}\%$, well in the saturated regime) with thicknesses between 1.6 and 17 μm . In all cases the electrodes were mechanically robust with no problems associated with brittleness.

We performed CV measurements to determine the capacitance of these electrodes for a number of scan rates. Shown in Figure 6.15A is the specific capacitance, C_T/M_T , measured at two scan rates and plotted as a function of thickness (filled symbols). For comparison, the equivalent data is also shown for MnO_2 -only electrodes (unfilled symbols). While the MnO_2 -only capacitance tends to fall off with increasing thickness, it is clear that the composites have higher capacitance for a given thickness. In addition, for the 100 mV/s data, the measured values of C_T/M_T remain roughly constant as thickness is increased. For the 1000 mV/s data, C_T/M_T falls with increasing thickness, probably because at this high rate the capacitance becomes diffusion limited. However, even at 1000 mV/s the capacitance is much higher in the composite than would be likely be achieved for thicker MnO_2 -only films, if such films could be made.

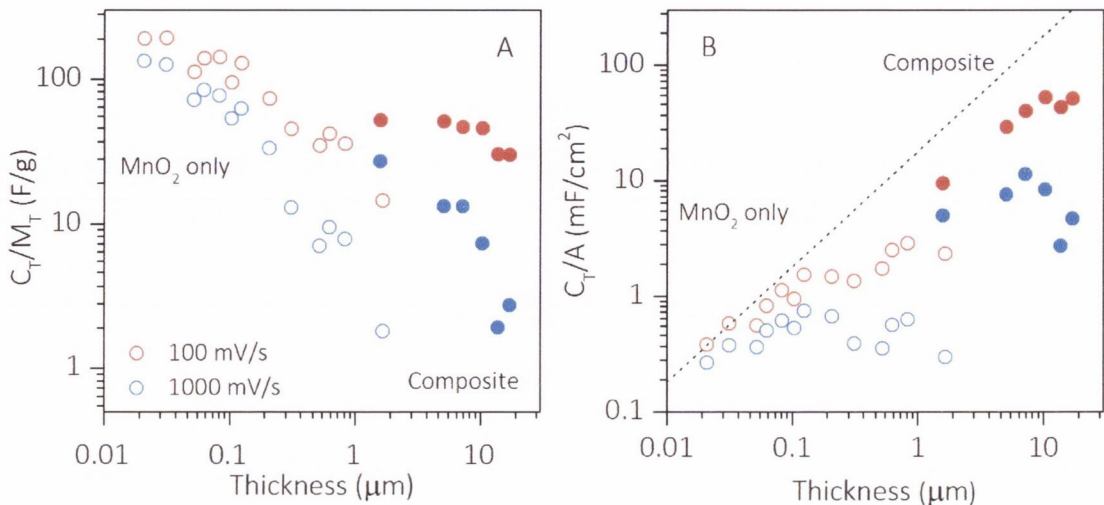


Figure 6.15: Specific capacitance (A) and areal capacitance (B) plotted as a function of electrode thickness for two scan rates. The unfilled points are MnO₂-only films up to the maximum thickness able to be prepared. The filled points are SWNT:MnO₂ composite films with 15 vol% to a maximum thickness of 10.3 μm .

A more intuitive representation of the data is found by plotting C_T/A as we have done in Figure 6.15B. Here, the MnO₂-only data increases sub-linearly (linearity indicated by dashed line) with t . However, for the composite, the 100 mV/s data increases linearly, reaching 52 mF/cm² at $t=10.3$ μm . In addition, even though the 1000 mV/s composite data increases sub-linearly, the best composite still displays 11.4 mF/cm², considerably larger than the best MnO₂ film. Similar values were obtained by Okamura *et al.*³⁸¹ who prepared Mn/Mo mixed oxide composite electrodes with carbon nanotubes, measuring 20.4 mF/cm² for a 4.1 μm film (100 mV/s in 0.5 M Na₂SO₄ electrolyte) and Wen *et al.*³⁸² who prepared MnO₂ composites with carbon black, measuring 20 mF/cm² for a 20 μm film (10 mV/s, 0.1 M KCl).

In Figure 6.16A, we compare the areal capacitance for the thickest MnO₂-only film ($t=1.7$ μm) with that of the best performing composite film ($t=10.3$ μm). The data indicates that the composite substantially outperforms the MnO₂-only film at all scan rates. We

can quantify the improvement shown in Figure 6.16B by plotting the ratio of composite to MnO_2 -only capacitances *vs.* scan rate. This graph shows a better than tenfold improvement in areal capacitance at all scan rates below ~ 3000 mV/s. Indeed, at scan rates close to 500 mV/s enhancements of $\times 40$ are achieved. We note that these improvements are due to the combination of enhanced MnO_2 capacitance resulting from better electrical transport and the ability to prepare thicker electrodes due improved the mechanical properties also afforded by the presence of the tubes.

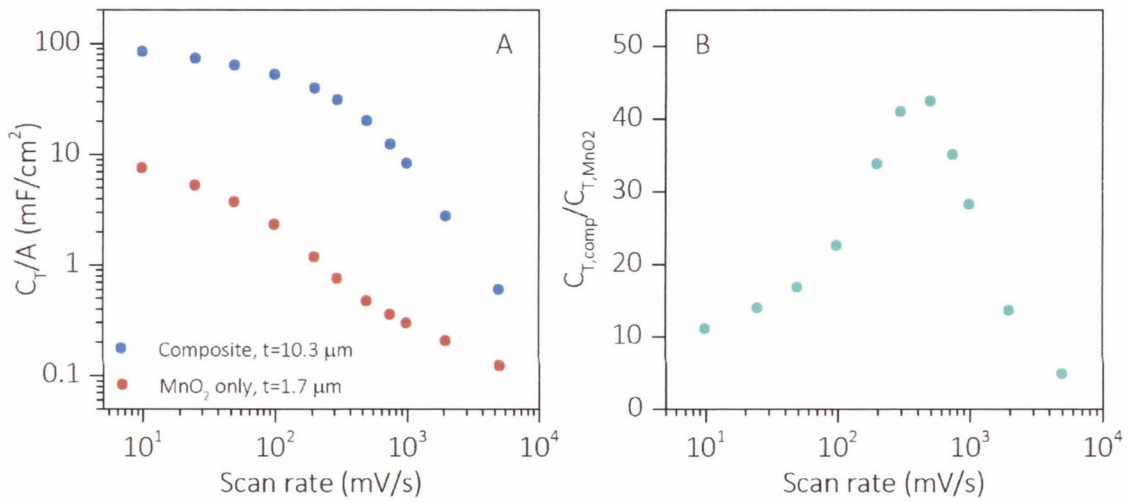


Figure 6.16: (A) Comparison between the maximum MnO_2 -only film able to be produced (using 10 et% ethyl cellulose) compared with a thick SWNT: MnO_2 composite film ($t=10.3 \mu\text{m}$, 15 wt% SWNT) plotted as a function of scan rate.

6.4 Conclusions

We have demonstrated that supercapacitor electrodes can be easily fabricated by solution processing methods from MnO_2 nanosheets and SWNT: MnO_2 composites. The MnO_2 -only electrodes displayed specific capacitance which decreased rapidly with increasing charge/discharge rate and electrode thickness. This is consistent with observations by other authors and is due to the poor electrical conductivity of the MnO_2 . However, on addition of nanotubes we found the electrode conductivity increased by eight orders of magnitude in a manner described by percolation theory. Because of the increased conductivity, we observed large increases in capacitance especially at high scan rates where a >10 -fold increase in specific capacitance was observed. This capacitance increase is due to the nanotube network facilitating charge transport from redox sites to the external circuit. We found that the increase in specific capacitance associated with MnO_2 alone increased with nanotube volume fraction as described by percolation theory. However, the percolation fit parameters varied with scan rate in a manner that is currently not understood. At high nanotube content, the specific capacitance associated with MnO_2 alone saturated. The saturation volume fraction was ~ 6 vol%, a value we associate with the nanotube network activating the entire MnO_2 volume. We tested the applicability of these results by preparing thick, binder-free SWNT: MnO_2 composites. We found the areal capacitance to be up to 40 times higher than the best MnO_2 -only electrode we could prepare.

To translate the excellent charge storage properties of pseudocapacitive material into real applications requires they be processed into macroscopic structures. However, for these to be useful the problem of poor electrical conductivity must be addressed. Here we show that when a nanoconductor is added to form composites, percolation theory applies not only to the way electrical properties vary with composition, but also the extent to which interfacial processes can occur due to the creation new electrical pathways. These insights pertain not only to the design of nanostructured EC electrodes, but any electrochemical application requiring charge transport between interfacial sites and the external circuit through a nanostructured network current collector.

Chapter 7

Summary and Future Work

This thesis has presented steps towards the creation of electrochemical energy storage systems for use within printed electronic devices that are flexible and transparent. Three electrode systems have been explored; single-walled carbon nanotube networks, conducting polymer networks produced using PEDOT:PSS and composite networks of single-walled carbon nanotubes combined with manganese dioxide nanoplatelets.

The electrochemical charge storage properties of ultra-thin carbon nanotube networks were investigated first as these have been the subject of many studies for use as transparent conductors, and they are known to possess excellent properties for electrochemical capacitors generally.

This study focused on the electrical and electrochemical properties of carbon nanotube networks as a function of the electrode thickness and hence the transmittance. It was found that when the thickness of single-walled carbon nanotube networks are reduced to provide greater optical transmittance, the electrical transport properties are simultaneously impaired. This is due to a reduction in the number of current pathways spanning from one part of the network to the other. Initially, this behaviour scales with thickness in accordance with the bulk-like DC conductivity of the network (*i.e.* $R_s = (\sigma_{DC,B}t)^{-1}$). However, as film thickness is further reduced, at some critical value called $t_{min, DC}$ this transitions to a power-law behaviour that can be understood using percolation theory (*i.e.* $\sigma_{DC} \propto (t - t_c)^{n_{DC}}$). In this percolative regime the electrical properties of the network diminish with reduced thickness much faster than for the bulk-like.

This phenomenon is crucial to the performance of transparent electrochemical capacitors as through-plane electrical transport determines the ability of these nanotube networks to act as a current collector within electrochemical capacitors, that is, deliver charge to and from the electrochemical interface *via* the external circuit. This was confirmed using electrochemical impedance measurements which showed that the equivalent series resistance of these networks, R_{ESR} , scales in the same manner as the sheet resistance, R_s , and therefore is also controlled by percolation effects. This has ramifications for the power capabilities of transparent nanomaterial networks (because $P \propto R_{ESR}^{-1}$).

For any electrochemical capacitor electrode, the measured capacitance scales with the spatial extent of interface that is available to the electrolyte. Since this property is sensitive to the connectivity of disordered nanomaterial networks, it is likely that the capacitance of these networks will also vary non-linearly as the electrode thickness is reduced. Accordingly, the capacitive properties of transparent carbon nanotube networks were also investigated.

Cyclic voltammetry was used to measure the capacitance per unit area, C/A , of these networks at a scan rate of 50 mV/s. These measurements found that for thicker films, C/A also varied linearly with thickness in accordance with the bulk-like volumetric capacitance of the networks (*i.e.* $C/A = (C/V)t$). However, as for the electrical properties, below a certain thickness, $t_{min, C}$, this behaviour also transitions to a power-law type behaviour. This is not unexpected as percolation theory also suggests that the spatial extent of disordered networks (as measured by the capacitance) should scale as a power law such as $C_V \propto (t - t_c)^{n_c}$. This has ramification for the energy capabilities of transparent nanomaterial networks (because $E \propto C$). In spite of these effects, to our knowledge, the capacitance of these films were superior to all other reports from the literature in the technologically relevant transmittance range ($T > 90\%$). Further improvements could be obtained by the deposition of a thin layer of pseudocapacitive oxides on the surface of the nanotubes to produce a composite materials with enhanced intrinsic capacitance. This deposition process would have to be carried out judiciously to preserve the conductivity through the nanotubes themselves, as well as at the junctions between nanotubes.

Identical percolation thresholds were found for both the sheet resistance and the capacitance ($t_c = 4.3\text{nm}$), which is to be expected as both these properties require current flow through the network. Interestingly, the transition thickness from bulk-like to percolative behaviour for these two properties differed; $t_{min, DC} \approx 100\text{ nm}$ while $t_{min, C} \approx 20\text{ nm}$. This has been rationalised qualitatively using simple geometric arguments.

It was found that these transparent networks occupy similar positions on a plot of energy *vs.* power in the bulk-like regime. However, for thicknesses necessary for high transmittance electrodes ($T > 90\%$), percolation effects cause greatly reduced performance, ob-

served as a tail towards low energy and power. Therefore, this work has important implications for the design of electrochemical capacitors using ultra-thin networks of nanomaterials such as carbon nanotubes, nanowires or graphene, that require high transparency and do not make use of an underlying current collector.

Having identified the detrimental effects of these percolation-based phenomena on transparent electrochemical capacitors, the next part of this thesis aimed toward minimising or avoiding these, if possible. Recent studies on nanomaterial networks found that $t_{min,DC}$ scales with the diameter of the nanotube bundles that constitute the network. Therefore, one strategy to improve these networks could involve optimising the nanotube exfoliation process to achieve smaller bundles. This could then shift the transition from bulk-like to percolative behaviour to lower thicknesses (and higher transmittance). This being the case, instead of using discrete nanoobjects to form nanomaterial networks, in the work following, a molecular conductor has been employed. A single chain of conducting polymer has the lowest possible diameter of any conducting element, therefore presents an opportunity to avoid percolation effects.

Like single-walled carbon nanotubes, the chosen conducting polymer, PEDOT:PSS, has also shown excellent performance as a transparent conductor, as well as within emerging electrochemical capacitor electrodes. Due to its solubility in water, this copolymer can be readily converted into mechanically flexible films by liquid phase processing. As the thickness is reduced, greater transparency is achieved and therefore this material is also an attractive candidate for use as a transparent energy storage electrode.

By using a robot-controlled airbrush spraying system, highly uniform films were produced with controllable transparency. As for the nanotube networks, the electrical and electrochemical properties of these films were measured as a function of thickness in the technologically relevant range for transparent devices ($T=70\%$ to 99% at 550 nm). Formic acid was employed as a secondary dopant, improving the electrical properties of these films by 2-3 orders of magnitude. Most importantly, through the use of the spraying film production technique and the formic acid treatment, percolation effects were not observed, demonstrating a significant advantage of this approach.

Other than their ease of processing, and lack of percolation effects, an important factor for the superiority of these PEDOT:PSS networks was their very low optical conductivity ($\sigma_{op} = 24 \text{ S/cm}$ at 550 nm). This value is much lower than other candidate transparent/flexible conductor components such as carbon nanotubes, graphene and metallic nanowires, presenting an important advantage for this application.

The ability to produce large area films by this approach presented an opportunity to study the charge storage properties of films much larger than has been done previously in the literature. For a given material (with some C_V), if the film thickness is fixed to provide some necessary transmittance, the only remaining way to increase the absolute energy storage is by extending the lateral dimensions of the electrode. Therefore it will be necessary to know the dependence of the charge storage properties on the lateral dimensions of the film. With this in mind, the fact that the film itself is acting as the sole current collector for the electrode means that capacitive elements more distant from the external contacts can only be accessed through an increased resistance.

These geometric dependencies were examined using cyclic voltammetry and electrochemical impedance spectroscopy. Indeed, it was found that while capacitance increases linearly with the electrode width (dimension parallel to the device contact) it increases sub linearly for electrode length (dimension perpendicular to the device contact). A simple RC circuit model was proposed to account for this behaviour for the CV measurements and a single-arm transmission line model for the impedance measurements. This work highlights that the properties of small area electrodes cannot be simply scaled linearly to project the capabilities of larger area electrodes. Significantly reduced performance was observed due to increasing the electrode length by only a few centimeters, particularly at fast discharge and recharge times. This understanding is crucial for the design of larger area transparent electrochemical capacitors. Large area two-electrode measurements were performed for electrodes with $T=95\%$, providing a device capacitance of 12.5 mF for a geometric area of 108 cm^2 when charged at 50 mV/s. To our knowledge this is the largest capacitance measured for any transparent electrochemical capacitor device with technologically relevant transmittance ($T>90\%$).

Future studies are necessary to try and improve the volumetric capacitance of the electrode through the use of Faradaic redox processes available to the PEDOT electrochemically reduced. Alternatively, high pseudocapacitance materials such as ruthenium dioxide or manganese dioxide could be added, forming composite transparent electrodes. In addition, it is likely that transparent electrochemical capacitor devices will require gel or solid state electrolyte materials separating the two electrodes. Therefore, subsequent studies are necessary to determine the performance that can be obtained using more realistic electrolyte systems. PEDOT has shown some susceptibility to environmental factors such as temperature, UV-light and oxygen. Further studies are necessary to assess the extent of these effects on the performance of transparent devices.

Increasing the specific or volumetric capacitance of an electrochemical capacitor electrode is probably the most frequently pursued strategy for improved performance. This may be achieved by employing materials that are capable of Faradaic reactions of a capacitive-like nature, as opposed to solely using the electrochemical double layer.

However, a downside of many otherwise promising candidate materials is limited electrical conductivity. To overcome this problem, much research is being carried out exploring the properties of composite electrodes by combining a high capacitive material with a smaller quantity of a conducting additive. In many cases this approach is providing encouraging results. However, often the ratio of these two components is poorly justified and therefore unlikely to provide the best possible performance. In addition, the principles which dictate the improvement that may be obtained by composite formation is not well understood at present.

Therefore, in the final part of this thesis, composite nanomaterial networks have been created by mixing different quantities of single-walled carbon nanotubes with high capacitance manganese dioxide nanoplatelets. Here thicker electrodes have been prepared and liquid phase processing has also been employed for their production, again, by vacuum filtration of nanomaterial dispersions. This approach provides a compelling route to composite formation as the component dispersions can be combined in any ratio, enabling fine control over the electrode composition. The composites were prepared with a maximum

single-walled nanotubes to a maximum loading of 40 wt %.

Upon measuring the electrical properties of the composites, it was found that the increase in electrical conductivity spanned eight orders of magnitude over the composition range, following a percolation scaling law. A very low percolation threshold was obtained, (< 1 wt %) enabled by the high aspect ratio of the tubes. This is one of the most important advantages of using nanotubes compared with traditional conductive additives such as carbon black.

Electrochemical measurements demonstrated that the total capacitance of the composites was also enhanced by the addition of the nanotubes, though in a manner differing considerably from rule-of-mixtures type behaviour. Subsequent analysis found that the increased capacitance of the manganese dioxide material associated with the presence of the nanotubes also followed a percolation-like scaling law. Starting at a percolation threshold, dramatically improved capacitance occurred, requiring only small loadings of nanotubes. This behaviour was found to saturate at a nanotube loading of 6 vol%, indicating that the addition of nanotubes beyond this loading cannot further improve the utilisation of the MnO_2 . These insights were able to be elucidated due to the specific design of the experiment, whereby the manganese dioxide mass loading was kept constant for all composites, varying only the quantity of nanotubes added.

The fitting parameters for the increase in capacitance were found to vary with scan rate in a manner that is presently not understood. However, it is suspected that this is due to the influence of ionic diffusion limitations within the film, becoming dominant at high scan rates (above 1000 mV/s). Future experiments will benefit from taking into account these effects through characterisation of the electrode properties using electrochemical impedance spectroscopy.

It was also found that the presence of an interpenetrating nanotube network throughout the electrode substantially improved the mechanical properties of the films, to the point where a polymeric binder was not required. This highlights a considerable advantage of composite formation using nanotubes, as many binder materials provide no other functional benefits to the composite while occupying volume within the electrode structure.

As a result, thicker composites were able to be prepared ($\sim 10\text{ }\mu\text{m}$) with far greater capacitance compared with the thickest possible MnO_2 -only films, even with the assistance of a binder (1.7 microns).

These studies provided valuable insights into the properties of electrochemical capacitor electrodes produced by liquid phase processing of nanomaterials, for use within emerging printed electronics applications.

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