## INFLUENCE OF POROSITY ON CHARGING SPEED OF POLYPYRROLE SUPERCAPACITORS

by

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## Abstract

In the field of energy storage, two main factors are essential for storage devices: the power density and energy density, both of which can be provided by supercapacitors. Supercapacitors offer a power to mass and cycle life greater than batteries and an energy density that is much greater than capacitors, making them appropriate for use in portable electronics, hybrid vehicles, and similar applications. Power to mass and discharge time are still not fast enough, however, for use in, for example flash cameras or cell phones or power quality applications. Charging time and power in these devices are often limited by the rate of ion transport into the electrodes. The hypothesis proposed in this thesis is that making electrodes porous increases their speed and hence power, but may reduce the capacitance at the same time. So in order to investigate the hypothesis various electrodes (e.g. pure polypyrrole (PPy) and its composites (carbon nanofiber (CNF) plus PPv) with varying porosities are made. Techniques used to investigate these samples are Cyclic Voltammetry (CV), Ionic Conductivity (IC) measurements, Electrochemical Impedance Spectroscopy (EIS) and Nuclear Magnetic Resonance (NMR) measurements. Through these techniques, it is found that the time constant reduces significantly (by  $\sim 1 \times 10^4$ times) for very porous electrodes as expected from hypothesis, and the capacitance reduces by a small factor (by  $\sim$  7 times) compared to that. Even for least porous samples a huge time constant reduction (by  $\sim 37$  times) compared to pure PPy is achieved with only  $\sim 2$  times reduction in volumetric capacitance. The plausibility of these improvements is checked by analyzing the ratelimiting factors in ion transport and it is found that ionic time constants at very high porosities are not representative of the speed of the full cell. The reason for this is due to solution resistance becoming a rate-limiting factor for porosities more than  $\sim 50$  %. In this case, any improvements in speed (power) can be achieved by reducing that resistance. Other methods for further improving the power densities are also suggested and they include reducing the separator and electrode thicknesses for instance.

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### **1** Introduction

With the extensive use of devices (e.g. smart phones, MP3 devices, digital cameras, cars, computers, etc.) that constantly require energy, energy storage is an issue of increasing importance. In the field of energy storage, two main factors are essential for storage devices: the power density and energy density. The energy density is the amount of energy that can be stored in a given weight or volume and the power density describes how quickly this energy can be delivered. The higher the power density, the less time is required to store or unload the required energy for a system [1], [2]. Until now, batteries have played a role in holding large amounts of energy but are generally charged very slowly. Capacitors have also helped to charge up quickly but store very little energy. Therefore, each device has a drawback that does not satisfy the needs for efficient energy storage.

There has been great interest in refining and developing more efficient energy storage devices. One such device, which has significantly improved over the last decade and has provided major advances in energy storage, is the supercapacitor. Supercapacitors or electrochemical capacitors (ECs), which are also called ultracapacitors, combine the high power density of capacitors with high energy density of batteries by using high surface area electrode materials (e.g. carbon electrodes). There are different types of supercapacitors but the current commercial ones are those consisting of two carbon electrodes, which provide capacitances (e.g. specific capacitors also provide higher energy densities ( $\sim 5 - 10$  Wh/kg) than batteries while maintaining the high power densities ( $\sim 1 - 2$  kW/kg) of conventional capacitors [1], [2], [3]. The different types of already-developed supercapacitors are outlined in section 1.1.1.

Among these supercapactiors, those having electrodes that combine materials such as conducting polymers and their composites (defined as hybrid materials; e.g. polypyrrole/ carbon nanofiber abbreviated as PPy/CNF as in this thesis) have the most potential to further improve the properties of supercapacitors. In this thesis, polypyrrole and carbon nanofiber (made by carbonizing the copolymer nanofibers that are made from electrospining of Copolymer precursor poly(acrylonitrile-co-acrylamide) (P(AN-AM))[4]) are synthesized (chapter 2) and their

combination is characterized (chapter 3) to investigate their effect on improving power while maintaining the same energy density. The CNF/PPy composites provide a specific capacitance of up to ~ 140 F/g, which is more than two times that of the commercial capacitors. The PPy provides the high capacitance but may have slow charging (hence low power density) due to slow ion transport in polymer. The rate of ion transport can be affected by various limiting factors (e.g. electrolyte resistance  $\rightarrow$  details in chapter 3) and is improved through making the electrodes porous so that the ions travel mostly in the liquid phase. This porosity is achieved through using a CNF (very porous material) as the matrix substrate for the PPy. The porosity (fraction of the volume of void space over the total volume) of these composites is tuned, in order to optimize the electronic and ionic conductivity (conductivity inside pores and PPy) to minimize the total resistance of the system and thereby enhance supercapacitors' performance in terms of charging time and capacitance. After obtaining porosity, the other factors that limit the ion transport should also be minimized to achieve capacitance and charging time improvements.

In order to indicate if the mentioned improvements are reached in our supercapacitor, a hypothesis is set for the thesis. This hypothesis specifies that increase in porosity enhances the ion and charge transfer and consequently the charge/discharge rate (power density) but on the other hand decreases the volumetric capacitance. A diagram showing our electrodes with pores is shown in Figure 1.1. This diagram shows that when you have pores, there is more open space for ions to travel through compared to when you have PPy where chains are leaving less space for ion transfer.



**Figure 1.1.** Structure of porous electrodes. Ions (blue circles) can go through pores much easier; they go from solution (on the right side of figure) into the electrode.  $R_i$  is the ionic resistance inside pores,  $C_{PPy}$  is the capacitance inside PPy and  $R_s$  is the resistance of solution outside the electrode, which is in series with the electrode.

A high volumetric capacitance (e.g. close to PPy) is desired to provide high energy-storage

capacity and therefore high energy density. The decrease in this capacitance is found to be not significant compared to the improvement achieved in charging time; hence a porosity level can be chosen, based on a designer's requirements, to minimize the trade offs. By performing various experiments and developing some circuit models that explain and verify some of those experiments, we are able to investigate the hypothesis. These methods are outlined in section 1.2; but first, in order to have an understanding of the operation of our hybrid supercapacitor, the concept of supercapacitors and the different kinds of them are described in section 1.1 and 1.1.1 respectively.

### **1.1 Supercapacitors**

Supercapacitors are electrochemical double layer capacitors that consist of two parallel plates similar to conventional capacitors but provide a higher energy density. The plates or electrodes in supercapacitors are made from porous activated carbon materials (giving them larger surface area for storing charge) that are separated with a liquid similar to batteries rather than a dielectric like capacitors. These electrodes can also be made from conducting polymers and metal oxides or a combination of all, to be described in section 1.1.1. Since supercapacitors combine features of both capacitors and batteries, all these devices are shown in Figure 1.2 and their comparisons are explained right after.



**Figure 1.2.** The structure and operation of batteries, capacitors and supercapacitors; a) the electrolyte is shown in orange, the positive electrode in blue and the negative electrode in red, b) the orange is the dielectric and the blue and red are metal electrodes, c) plates "create the double-layer by polarizing the electrolyte (yellow) in between them" [5].

As was mentioned before, batteries store high amounts of energy but cannot deliver it fast (slow charge/discharge rate) and capacitors store small amount of energy but can deliver it fast

(high power density; hence fast charge/discharge rate). Supercapacitors combine the high energy of batteries with high power of capacitors to provide both properties. Batteries can only go through several hundred cycles whereas supercapacitors can undergo hundreds of thousands to many millions of full charge/discharge cycles [6], [7]. The high number of cycles mainly corresponds to those types of supercapacitors consisting of two carbon electrodes (section 1.1.1), where there is no charge transfer between electrode and electrolyte and hence charge storage is highly reversible. This reversibility feature can result in high cycling stabilities, which in turn help supercapacitors to operate for many charge/discharge cycles. Knowing about the advantages of supercapacitors, it is now necessary to learn about the different types of them.

### **1.1.1 Supercapacitor Types**

Supercapacitors can be divided into three groups depending on the charge storage mechanism. The supercapacitor we study in this thesis combines groups one and two to form the third group, which is described as we proceed. The first group, which is called electric double layer capacitors (EDLCs), is the most commonly used supercapacitor in the market. EDLCs use activated carbon for both of their electrodes and form a double layer capacitance at the electrode/electrolyte interface through electrostatic charge accumulation (non-Faradaic) rather than electrochemical reactions at that interface. This, as mentioned before, allows for a highly reversible charge storage capability, which in turn can result in high cycling stabilities and long-life charge/discharge cycles. The carbon materials are highly porous and hence provide high capacitance (100 - 400 F/g) [8], [9]. Due to the porosity of carbon materials, the charge is also stored in the whole volume rather than just the surface (higher energy stored), which is the case for conventional capacitors [10], [6]. Also, having more porosity through activated carbon electrodes equals having more liquid phase for ions to easily and rapidly travel through and hence a faster charge/discharge rate, and a high power density.

The other group is pseudocapacitors, which operate based on Faradaic reactions, which involve charge transfer at the electrode/electrolyte interface through redox reactions, intercalation of ions and adsorption [8]. This group is based on conducting polymers (CPs such as PPy, polythiophene and polyaniline) and metal oxides (e.g. MnO<sub>2</sub>, RuO<sub>2</sub>). Conducting polymers can sometimes be considered as EDLCs as well since they may have electrostatic charge accumulation rather than electrochemical reactions at the electrode/solution interface [9].

Compared to EDLCs, pseudocapacitors have higher energy density and specific capacitance (e.g. 650 F/g) if made of metal oxides or porous CPs. The high specific capacitance of CPs is due to the ability to store charge not only on the surface but also in the whole volume of the polymer.

The last group is hybrid supercapacitors, which is a combination of the two previous groups and includes our supercapacitor (e.g. CNF/PPy composites). The supercapacitors' performances in terms of energy and power density are improved by combining these two groups. The hybrid supercapacitor that is made in this thesis is a CNF/PPy composite that provides high capacitance through the PPy layer and fast charging through CNF (a porous material that mainly acts as a conducting scaffold) as was explained before and will be explained in more detail in chapter 3 [6]. Details of the types and functions of different hybrid supercapacitors are not covered here but the work done by different groups is briefly outlined so that one can realize where our supercapacitor fits in compared to the rest.

### 1.1.2 Recent Developments in Supercapacitors

Among the groups working on hybrid supercapacitors, Marina Mastragostino and his group in Italy tested the use of conducting polymers in supercapacitors in 2002. They were able to use a conventional polymer, namely poly (3-methylthiophene) or pMeT, as the positive electrode and activated carbon as negative electrode in supercapacitors to form a hybrid system. Through their hybrid system, they claim to outperform the double-layer carbon supercapacitors presently on the market in terms of specific energy and power [11]. In later years, other groups also used combinations of different conducting polymers with other materials such as metal oxides, extended inorganic species and electroactive molecular clusters to form hybrid materials, which are claimed to have high cyclability, reversibility and specific capacitance. Some of these groups are Graeme M. et. al. in Manitoba, Canada, and Emmanuel F. C. et. al.; details of their work can be read in their papers [12], [7], [13].

Today, the supercapacitors with electrodes made from conducting polymers are not yet used in the market and the commercialized devices are mainly supercapacitors made from carbon electrodes, which have high surface area (1500–2400 m<sup>2</sup> g<sup>-1</sup>) [11]. The most recent supercapacitors developed are flexible carbon nanotube supercapacitors, which are made up of a gel electrolyte sandwiched between two carbon nanotube electrodes and are created by ink-jet printing methods [7]. Carbon-nanotubes have low capacitance compared to other carbon materials and also conducting polymers; hence conducting polymers, similar to the one used in this thesis, have been tested either to replace them or to be used with them to form composites with higher capacitance.

Having learned about the supercapacitor concepts, types and materials used, we can now have a better understanding of the operation of our supercapacitor and learn about the methods used to validate the hypothesis for these hybrid materials. The main chapters of the thesis covering these tests and models are outlined in the following section.

### **1.2** Outline of Methods Used for Electrode Characterization

Initially the different CNF/PPy composite materials were synthesized using varying mass densities of PPy electrochemically grown into CNFs. The PPy provided the high capacitance and the CNF was used as a conducting scaffold to provide pores for faster ion transport compared to pure PPy. The depositions created CNF/PPy composites with varying porosities. The porosity fraction was either calculated based on the void volume fraction of the electrodes or found using the scanning electron microscopy (SEM) technique. SEM provided images of the electrodes and showed the amount of PPy deposited and the void areas. Further, the percentage composition of the elements was found by a technique called energy-dispersive spectroscopy (EDS). The elemental ratios from EDS results were compared to Nuclear Magnetic Resonance (NMR) results to confirm the number of mobile ions contributing to ion transport. The synthesis procedure along with the morphologies of all the composites is outlined in chapter 2 of the thesis. The differences among these materials (e.g. density, capacitance, ionic and electronic conductivity) due to varying PPy amount using different deposition time were found and analyzed in a 0.1 M TBAP/PC electrolyte using techniques such as Cyclic Voltammetry (CV), Ionic Conductivity (IC) and Electrochemical Impedance Spectroscopy (EIS) measurements. All these methods and the corresponding experimental results are presented in chapter 3, called 'Electrochemical Characterization.' These techniques were used to test electrodes for their capacitance and charging rate to see if they support the hypothesis.

The CV experiments were performed in a three-electrode configuration setup at a scan rate of 1mV/s and an approximate voltage range of -0.6V to 0.6V (section 3.1). Through this method,

the total, volumetric and gravimetric capacitances of the samples were found and their charging times were also estimated. Following the hypothesis, the total and volumetric capacitances were found to be decreasing with decrease in PPy amount. The gravimetric capacitance was found to be more for porous samples resulting from the high surface capacitance due to pores.

Further, ionic conductivity measurements were conducted in a 4-electrode configuration, where impedance was found at various frequencies giving ion transport rates (directly measuring the displacement of ions and their transport rate) through the thickness of the composite films (section 3.2). The main purpose of this section was to find the diffusion coefficient of ions for electrodes of varying porosities. The results from this method suggested faster transport and higher diffusion coefficients, ionic conductivities and charging times for more porous samples. Changes in porosity, capacitance and thickness of materials were found to affect these properties [14]. To verify the experimental results, circuit models were developed in which each circuit element represents a physical phenomenon (3.2.3). These models were fitted against experiments to obtain parameter values in the circuits and to explain the transport behaviours at different frequencies used in ionic conductivity measurements.

Similar to CV experiments, a three-electrode configuration was used for EIS measurements to obtain impedance response at different frequencies under the application of a constant current or voltage at a fixed oxidation state (section 3.3). Results from EIS and ionic conductivity methods were used to analyze the charging and discharging rates and the corresponding rate-limiting factors (e.g. solution resistance ( $R_s$ ) or ionic resistance ( $R_i$ ; resistance inside pores or PPy) or electronic resistance (Re) or leakage resistance ( $R_i$ )) for electrodes with varying porosities. Since ion transport and charging rate can be affected by rate limiting factors (e.g. solution resistance for more porous electrodes), it was important to investigate those factors. Similar circuit models as ionic conductivity models were also developed here (section 3.3.3).

Other than ionic conductivity measurements, Pulse-Field Gradient NMR measurements were also used to find diffusion coefficients of electrodes as described in chapter 4. This method uses the electromagnetic properties of nuclei of the mobile ion  $(PF_6)$  to detect the rate at which ions move. The diffusion results can be used to verify the trend in the diffusion coefficients obtained from ionic conductivity measurements. The diffusion from NMR can also give a more

detailed picture of the diffusion, since it gives diffusion of ions both in the pores and inside the polypyrrole, whereas ionic conductivity probably only sees the ions in the pores. The ion counting results can also verify the number of mobile  $PF_6^-$  ions (participating in ion transport) also found from EDS.

Finally, in chapter 5, the results for all the methods and models used are compared and the trade offs in terms of volumetric capacitance, thickness and porosity are analyzed. Further, future works along with methods to improve experiments are also described. A literature review relating to each method used is outlined at the beginning of the corresponding chapter to make it easier for the reader to correlate each method with the related background work.

# 2 Growth and Structure of PPy and PPy/ CNF Composite Electrodes

In this chapter the process for synthesizing polypyrrole and polypyrrole/ CNF electrodes is explained and their properties, such as porosity fraction, electrical resistance and thickness are found. Further, the structure and elemental composition of these electrodes are analyzed by two morphological techniques, namely SEM and EDS. Initially, a description of conducting polymers and what they are made of is given for background.

Conducting polymers are conjugated (alternating single and double bonds) polymers with continuous overlapping  $\pi$  electron systems that create delocalized bonds along the backbone of the polymer. This feature produces materials with directional conductivity, strongest along the axis of the chain [15]. The band-like electronic structure of these polymers is generated from the splitting of interacting molecular orbitals of the monomer units so that their structure becomes similar to the band-structure of semi-conductors. They, therefore, act as electronic conductors. The polymer chain such as that in polypyrrole is shown in Figure 2.1.



**Figure 2.1.** Polypyrrole structure indicating the elements to be carbon, nitrogen and hydrogen for every pyrrole that is repeated 'n' times [16]

A polymer can be made highly conductive by doping (introducing holes or electrons into polymer chains) with either an electron donor or an electron acceptor. Polypyrrole is most commonly oxidized (P-doped) to achieve a higher conductivity; it may be reduced (n-doped) also, but this is done less frequently. The doping process is done electrochemically, generating

mobile charge carriers that enhance electrical conductivity. The electrical conductivity of conducting polymers relative to other materials is shown in Figure 2.2.



**Figure 2.2.** Electrical conductivity of conducting polymers compared to other materials. Conducting polymers are more conductive at the oxidized (Ox) state, hence going more towards conductors and less conductive at the reduced state (Re), therefore going towards insulators [17].

The polymer electronic states can be controlled through oxidation and reduction. This oxidation can affect some material properties, such as optical, structural and mechanical. Having these advantages, conducing polymers can be used in a variety of applications including supercapacitors, actuators and electrochromatic devices.

In this research, both PPy and CNF/PPy composites (polypyrrole is grown into CNF) were synthesized and characterized for potential application in supercapacitor electrodes. The carbon nanofibers used are cylindrical-shaped nanostructures that were synthesized or electrospun from copolymer precursor poly (acrylonitrile-co-acrylamide) (P (AN-AM)) by Nicole Lee from the materials department [18]. Electrospinning is a cost effective and simple method for the production of continuous nanofibers from different polymer solutions [4]. Electrospinning uses a high voltage source to generate a charged polymer jet from a polymer solution or melt. As the polymer jet travels through air, the solvent evaporates and the dried polymer jet reaches the conducting collector to form fibers [4]. CNF's can be made in a random arrangement of fibers or can be aligned; here the random structure is used.

Polypyrrole charge/discharge speed is improved (while maintaining the same energy density) when varied amounts are grown in CNF samples. Further, a compromise between specific surface area (to ensure high capacitance) and pore-size distribution (to provide easy access for ions of the electrolyte) is found. The polypyrrole is electrochemically doped with  $PF_6^-$  and becomes a p-doped conjugated polymer when oxidized.  $PF_6^-$  dopant ions balance charge inside the polymer. Details of the doping (deposition) will be outlined in the following section.

### 2.1 Electrodeposition

The synthesis of pure polypyrrole and its composites all follow the same procedure, except that for composite samples, varying amounts of PPy were deposited (by varying the deposition time). Polypyrrole can be grown either chemically or electrochemically. Electrochemical deposition is chosen here, since it generates more uniform films with higher conductivity and mechanical strength [19]. Polypyrrole polymerization happens through electrochemical oxidation of the pyrrole monomer. During the deposition, oligomers consisting of a number of covalently linked monomers precipitate onto the electrode (e.g. glassy carbon or CNF) onto which the polypyrrole is to be grown (Figure 2.3).



Figure 2.3. The electrochemical synthesis process of polypyrrole [20]

In the case of PPy/ CNF deposition, the electrode onto which the polypyrrole is deposited is CNF, as explained in section 2.1.2.

### 2.1.1 Apparatus and Chemicals

An SI 1287 Electrochemical Interface was used together with a three-electrode cell. For PPy growth either alone or on CNF, the following were required: distilled pyrrole, distilled water, a CNF sheet, tetraethylammonium hexafluorophosphate (TBAP) and propylene carbonate (PC) (reagents from Sigma-Aldrich).

### **2.1.2 Deposition Procedure**

PPy film (doped with  $PF_6$  ion) was grown electrochemically on a glassy carbon cylinder (working electrode), using a solution of 0.06 M distilled pyrrole (oligomers formed spontaneously in the presence of light and oxygen were removed by distillation), 0.05M tetrabutyl ammonium hexafluorophosphate (TBA  $\cdot$  PF<sub>6</sub>) and 1% volume distilled water in propylene carbonate. The solution was then bubbled with nitrogen to deoxygenate it. The solution was kept clean to prevent any side reactions in the deposition that may lead to defects in the PPy or PPy/ CNF films. To obtain clean and uniform pure polypyrrole films, a polished glassy carbon crucible was used as the working electrode. A copper sheet was used as the counter electrode and placed all around the cylindrical glassy carbon as shown in figure 2.4.



**Figure 2.4.** Pure polypyrrole deposition on glassy carbon cylinder, shown in grey color; Copper sheet shown in orange works as the counter electrode and encloses the glassy carbon.

A constant current with a density of  $0.125 \text{ mA/cm}^2$  was applied for 8 hours (for pure PPy) using the Galvanostatic mode of the Solartron at temperature of  $-35^\circ$  to  $-40^\circ$  C. The current applied was based on the area of the glassy carbon substrate (or area of any other substrate that

may be used in CNF/PPy deposition) exposed to the deposition solution. This deposition results in a film with a thickness of around 14  $\mu$ m. The thickness and the conductivity of the film vary by about 20% across the crucible surface [21]. The same procedure was applied for the CNF/PPy samples except that the deposition time for each was 8, 6, 4 and 3 hours creating multi-porous electrodes (these samples are classified based on their % porosity as follows: pure PPy = 0%, 8hour = 44 %; 6-hour = 54 %; 4-hour = 76 %; 3-hour = 81 % and pure CNF = 91 %; these porosity % values are calculated in section 2.2.1). The deposition time also changes the mass and thickness of the PPy deposited, hence the total thickness and mass of the CNF/PPy. The initial masses of CNF samples before deposition were measured with a digital balance as shown in table 2.1. Mass values after deposition were found using different methods as are explained in chapter 3 (Section 3.1).

Table 2.1. Initial CNF masses before PPy growth

Sample	0 %	44 %	54 %	76 %	81 %	91 %
Bare CNF	0.0	$7.5 \pm 0.4$	$3.7 \pm 0.3$	$5.0 \pm 0.1$	$3.5 \pm 0.2$	$4.5 \pm 0.6$
mass (mg)						

The experimental setup for CNF/PPy deposition was also different since the working electrode was the CNF and the counter was carbon paper, two of which were placed in the cell, one facing each side of the CNF. The setup is shown in Figure 2.5:



**Figure 2.5.** Deposition setup for PPy/ CNF; counters were connected to each other and then to the counter probe of Solartron. Working (CNF), was connected to the working probe.

During deposition,  $PF_6^-$  dopant ions are integrated inside the polymer to balance the backbone charge. The doping level of the oxidized state (as-grown state) is one dopant ion for

every three to four monomers [17], [22]. This ratio was further found both by the EDS experiments explained in this chapter and also by NMR experiments in chapter 5. After synthesizing the films, they were characterized in terms of electrical and electrochemical properties.

### 2.2 Physical and Electrical Characterization

After film deposition, properties, such as the electrical conductivity, and thickness were found. These characteristics are important since they affect other properties of the film such as the capacitance, ionic diffusion and strain. The following sections give information about the porosity %, electrical and dimensional properties of the electrodes.

#### 2.2.1 Porosity Estimation

After synthesis, the porosity fraction of different composites is estimated to find if samples with less PPy amount have indeed more porous structure. These porosity fractions are later used along with results from chapter 3 (e.g. charging rate, diffusion, etc.) to find the optimum point between volumetric capacitance and porosity to both improve power density while maintaining at least the same energy density (chapter 5). The electrodes' porosity fractions are found based on the void volume fraction in each sample as shown below:

$$\gamma = \frac{Vol_{total} - (Vol_{CNF} + Vol_{PPy})}{Vol_{total}}; \text{ if } \gamma = 0 \rightarrow \text{most dense; if } \gamma = 1 \rightarrow \text{most porous,}$$

where  $\gamma$  is the porosity fraction,  $Vol_{total}$  is the total volume of the sample (volume of CNF+PPy from measured dimensions),  $Vol_{CNF}$  is the CNF volume  $(Vol_{CNF} = \frac{measured\_mass_{CNF}}{\rho_{CNF}}; \rho_{CNF}=1.9 \times 10^6 \text{ g/m}^3;$  measured masses of CNFs are shown in table 2.1) and  $Vol_{PPy}$  is the PPy volume ( $Vol_{PPy}$ = charge-based-mass\_{PPy} /  $\rho_{PPy}; \rho_{PPy}=1.5 \times 10^6$ g/m<sup>3</sup>) [23], [24], [25]. The charge-based mass of PPy in this equation used for calculating PPy volume, is calculated in chapter 3, (table 3.1) and it is used instead of the measured mass, which may include some uncertainties due to including solution mass. The PPy density also is found either found from literature or by dividing the calculated mass of PPy by its volume [25]. From the porosity fraction equation, the porosities are found to be 0 % (pure PPy), 44 %, 54 %, 76 %, 81 % and 91 % (pure CNF) for samples depending on their PPy growth time (the increase in porosity % indicates decrease in PPy).

### 2.2.2 Electrical Conductivity Measurement (4-Point Probe)

The conductivity was found for the dried samples (air dried) through the configuration in Figure 2.6, which is called a four-point probe:



**Figure 2.6.** 4-probe setup for electrical conductivity measurement; in order to find the resistance of the whole sample, the resistance for section 'd' should be linearly scaled to account for the whole length.

Four thin gold wires were attached equally-spaced and in parallel on top of a glass slide. Current was passed through the two outer lines and a voltage was measured via a multimeter between the two inner lines. Each sample was placed along the length of these wires and the voltage and current lines were connected to a Hewlett-Packard 34401A multimeter in 4-pt resistance mode for resistance measurement. Having the resistance of the film, its conductivity can be found through the following formula:

$$R = \frac{d}{\sigma A} \to \sigma = \frac{d}{RA},\tag{2.1}$$

where A = width x thickness and 'd' is the distance between the two inner gold lines.

Conductivity is dependent upon various factors such as electrode preparation, temperature,

polymer morphology and deposition current density. The conductivity values of all samples are shown table 2.2.

Sample	0 %	44 %	54 %	76 %	81 %	91 %
Electrical conductivity (S/m) x 10 <sup>3</sup>	26.3 ± 1.9	2.3 ± 0.3	2.1 ± 0.3	$1.6 \pm 0.3$	$1.5 \pm 0.2$	2.0±0.1
$(S/m) \ge 10^{3}$						

Table 2.2. Electrical conductivity of all samples

As seen from the above table, electrical conductivity of samples is less for those having less amount of polypyrrole deposited on them, considering the uncertainties shown on the table.

### 2.2.3 Thickness Measurement

Other than electrical conductivity, another important film characteristic that needs to be measured is the thickness. CNF/PPy electrodes made here have different thickness values, which arise from different PPy amounts grown into CNF samples and also from the different initial thicknesses of CNFs. Difference in thickness has effects on the electrical resistance, capacitance, charging time and other electrochemical and electromechanical properties of the film. Hence, it is necessary to measure the thickness accurately before and after deposition in order to account for the changes in properties as the thickness is changed. Thickness also has effects on the diffusion of ions through the film. For the same material, the thicker the material, the longer it takes for ions to diffuse through the film. Film thickness is measured with a micrometer, which is accurate down to 1  $\mu$ m. Thickness of the samples before and after deposition is presented in table 2.3:

Sample	0 %	44 %	54 %	76 %	81 %	91 %
Thickness before (µm)	0	$50.0 \pm 0.9$	35.0 ± 1.3	65.0 ± 1.2	53.0 ± 1.0	38.0 ± 1.0
Thickness after (CNF + PPy) (µm)	14.0 ± 0.6	64.0 ± 1.4	47.0 ± 2.1	73.0 ± 2.1	64.0 ± 1.5	38.0 ± 1.5
Difference (µm)	$14.0 \pm 0.6$	$14.0 \pm 0.5$	$12.0 \pm 0.8$	8.0 ± 0.9	6.0 ± 0.5	0.0 ± 0.5

**Table 2.3.** Thickness of all samples before and after deposition of polypyrrole

### 2.3 Morphological and Compositional Characteristics

In order to have a better image of the structure of polypyrrole and polypyrrole/carbon nanofiber samples and to investigate the change in the diameter of each fiber after PPy is grown for each sample, a technique called SEM was performed. Another technique called EDS was also performed to learn about the percentage composition of these samples to figure out the number of mobile ions present and further use them as verification for ion counting results from NMR (chapter 4). Each method along with the information obtained from it is summarized below.

### 2.3.1 SEM

SEM produces a magnified image by using electrons instead of light to form an image. The sample used for SEM should be conductive so it doesn't build up charge. If it did, it would repel incoming electrons. The electron beam is rastered over the sample and a detector is used to collect electrons scattered from the sample. The scattered electrons produce signals that carry information (mostly images) about the surface topography, composition, electrical and sometimes chemical properties of the sample [26]. The SEM measurements were done with a Hitachi S-3000 Scanning Electron Microscopy device. The images obtained from the samples are displayed in Figures 2.7- 2.11.



Figure 2.7. SEM image of the pure PPy sample with scale indicated on the figure



Figure 2.8. SEM image of the 44 % sample with scale indicated on the figure



Figure 2.9. SEM image of the 54 % sample with scale indicated on the figure



Figure 2.10. SEM image of the 76 % sample



Figure 2.11. SEM image of the pure CNF sample

Looking at all these images, it is found that the thickness of each fiber strand is deceasing going from the sample with the most polypyrrole (44 %) to the one with the least or no

polypyrrole (81 % and CNF respectively). This may not be directly noticeable when just looking at the images, but calculating the diameter and surface area of each fiber for all samples, a decrease in this diameter and surface area is seen going toward more porous samples (Appendix A). It may not be possible to determine the porosity level of samples by comparing the SEM images, since the concentration of fibers may vary across the sample and a point chosen for imaging may not be a good representative of the whole sample. Hence, one can only realize the decrease in PPy by comparing the fiber diameters (Appendix A). In general, having less PPy leads to larger pores left open in the CNFs but decreases the volumetric capacitance. In the next chapters, the effect of change in porosity of samples and adding more or less PPy is investigated and the trade offs in achieving each are analyzed.

#### 2.3.2 EDS

Given the topography of the samples, the composition of each is also described. Sample elemental composition was found using EDS analysis. For this research, a 400-series Quantax from Bruker Company was used for EDS. EDS is a chemical microanalysis technique used for the chemical characterization and elemental analysis of a sample. It works by detecting the X-rays emitted from a sample that is hit by a beam of electrons as used in SEM. When these emitted X-rays hit the X-ray detector, they produce charge pulses that are proportional to the energy of X-rays. The charge pulse is converted to a voltage pulse, which is then sent to a multichannel analyzer to be sorted by voltage. The relative quantity of emitted X-rays versus their energy is used to determine the sample composition. In order to determine the presence of an element in the sample, the X-ray energy values from EDS are compared with known X-ray energy values. Using the EDS software, via each energy line in the energy spectrum, an element from the periodic table, is selected that corresponds to the element in the sample. The electrons penetrate a couple of microns into the sample to analyze the contents and features as small as 1µm or less.

There are two main reasons for finding the composition of samples. The first is to detect the impurities of the samples and analyze their effect on the conductivity, capacitance and performance of the materials. The other reason is to verify the  $PF_6^-$  content found from NMR (chapter 4 and Appendix C) to estimate the number of  $PF_6^-$  ions available for transport within the electrode.

In this research, only some samples (pure PPy and the 44 % sample) were tested for their composition, since the purpose of EDS was mainly to determine the  $PF_6$  content in each sample. The analysis for each sample is slightly different when scanning different parts of the same sample; this is due to non-uniform deposition and synthesis as well as presence of external materials (e.g. dust) due to lack of cleanness and purity. Only one or two results are presented for each sample as an example and the rest are in Appendix A. It should be noted that the peak heights in the energy spectrum-result from EDS are not direct measurements of abundance. Some elements are much better at scattering X-rays than others. Also, the "element quantification" software used for this EDS was not updated due to facility budget constraints and hence the results may contain uncertainties up to 25% due to not considering some factors in the measurements.

#### a) Pure Polypyrrole (0 %)

For pure polypyrrole three sections were scanned and results from all are presented in Figure 2.12.



**Figure 2.12.** Zoomed-in image of the energy spectrum of all sections of the pure PPy; each symbol used for each peak shows the element present in the sample.

The peaks shown represent the number of emitted X-rays (required to balance the energy difference created when an electron from a higher state fills up the electron vacancy at a lower state) versus the corresponding energy (keV) of the elements in the sample. The peaks, therefore,

suggest elemental mass fractions of the sample, which are listed in table 2.5. Based on the peaks, all elements from spot one have the largest amplitudes, but results from spot two seem to be closer to the expected elemental ratios, hence selected to be shown here as an example.

**Table 2.4.** Elemental composition of pure polypyrrole based on spot two of the corresponding energy spectrum; "nor. C" is the normalized weight % and Atom C is the normalized atomic percent, which is what is used here. Error is the total error on the measurement

	nor. C [wt.%]	Atom C [at.%]	Error [%]
Carbon	36.31	45.88	11.62
Nitrogen	9.69	10.50	3.70
Oxygen	15.07	14.29	5.17
Fluorine	32.66	26.10	10.69
Sodium	0.62	0.41	0.07
Phosphorus	4.23	2.07	0.19
Chlorine	0.24	0.10	0.04
Sulfur	0.34	0.16	0.04
Aluminium	0.85	0.48	0.07
	100.00	100.00	

Carbon, oxygen, nitrogen, phosphorous and fluorine were the most dominant elements found in pure PPy. Oxygen may have entered during deposition or electrochemical tests, but phosphorous and fluorine come from the  $PF_6^-$  in TBAP, which was used in the deposition solution and in the electrolyte for electrochemical tests. Carbon and nitrogen come from pyrrole and CNF. The other elements seen were from the impurities of CNF or test solution.

Comparing the atomic % ratios of the elements from spot two of the film to the expected values, it is found that the ratio of fluorine to phosphorus is  $12.6 \pm 5$ , which is nearly in agreement with the expected value of 6F: 1P. The error range is found based on the error of each element shown in table 2.5. The difference from the expected ratio may be due to either surface impurities or the above-mentioned calibration concerns with the instrument. The other important ratio to consider is N: P, which should be 3 or 4 at maximum doping. This indicates that during deposition, we should have 3 or 4 monomers for every dopant ion (PF<sub>6</sub>). This ratio from EDS for spot two is  $7.5 \pm 3$ , which is again very close to the expected value. The NMR results in chapter 5 suggest similar ratios.
Despite the fact that results from spot two are closer to the expectation, still the average of results for all sections should be considered. The average of F: P ratio is 8.38 and its standard deviation is 1.07. The average of N: P ratio is 2.58 and its standard deviation is 0.81. The number of fluorine, phosphorous and nitrogen all seem to be close within 40 % to both the expected values and the NMR results.

#### b) 44 %

Five different points of the 44 % sample were tested by EDS and almost all of them gave similar results. The graph for all spots except spot 1 is shown in Figure 2.13; spot 1 is very similar to spot 2.



**Figure 2.13.** Energy spectrum of all sections of the 44 % electrode; each symbol used for each peak shows the element present in the sample.

Similar to the polypyrrole sample, carbon, oxygen, nitrogen, fluorine and phosphorous were the most common elements in the sample. Although the aluminum peak appears to be larger than those of fluorine and phosphorous, its percentage composition is lower. The same analysis as used with pure PPy was performed for this sample in order to verify the quality and compositional characteristics of the sample. Among all the examined spots, spot 2 was chosen as an example to be analyzed in more detail. The F: P ratio of that spot was found to be  $12.6 \pm 6$ , 23

indicating a ratio just matching the expected value of 6 if the uncertainty is included. This spot, though, does not give a ratio of 3 or 4 for the N: P ratio, and it gives  $36.8 \pm 12$ , which is consistent with the NMR ion counting results in chapter 4 (ratio of ~23 to 24). These ratios are obtained and calculated from Table 2.6. I believe that some of these discrepancies in ratios, which are also seen in NMR results, are perhaps due to some impurities in the electrolyte that might have led to reduction of the films and escape of some PF<sub>6</sub><sup>-</sup> ions. Elemental composition of spot two of the 44 % electrode is shown as an example in Table 2.6.

**Table 2.5.** Elemental composition of 44 % electrode based on the energy spectrum obtained for spot two.

	nor. C [wt.%]	Atom C [at.%]	Error [%]
Carbon	29.38	36.04	9.39
Oxygen	34.30	31.58	10.99
Aluminium	2.66	1.45	0.15
Silicon	0.27	0.14	0.04
Sodium	1.09	0.70	0.10
Nitrogen	20.64	21.71	6.95
Fluorine	9.57	7.42	3.53
Phosphorus	1.23	0.59	0.07
Chlorine	0.73	0.30	0.05
Sulfur	0.13	0.06	0.03
	100.00	100.00	

As before, the average of the ratios from all spots of this sample is again calculated. The average of F: P ratio is 11.25 and its standard deviation is 7.36. The average of N: P ratio is 26.32 and its standard deviation is 1.57. These results suggest that the F:P ratio is consistently high, similar to other samples, but close to the expected 6:1 ratio if uncertainties considered. This high ratio can be due to instrument calibration issues as mentioned before. The N:P ratio is far from expectation but almost the same as the one found from NMR results (chapter 4).

Having discussed the synthesis method of our materials and their structure, measurments testing their capacitance, ionic conductivity, diffusion and charging time will be described. As mentioned in chapter 1, there are several methods that can be used to obtain these parameters and those are explained in the chapters 3 and 4.

# **3 Electrochemical Characterization and Circuit Modeling**

In order to characterize the electrodes described in chapter 2, in terms of capacitance and charging time, some electrochemical tests, namely Cyclic Voltammetry (CV), Ionic Conductivity (IC) and Electrochemical Impedance Spectroscopy (EIS) measurements were performed. These methods as also mentioned in chapter 1, can be used to determine capacitance, ionic conductivity and rate-limiting factors in ion transport respectively. These properties are found for electrodes of varying porosities, in order to investigate the effect of porosity on these properties and consequently on ion transport and charging rate. The differences in properties of different electrodes can be found by analyzing the electrochemical behaviour of the electrodes at various frequencies, scan rates, oxidation states (note: in this thesis, a fixed oxidation of 0.23 V is chosen) and currents. The combination of these techniques helps to understand the dynamics of the electrode and verifies some results of one technique with the others. The results of these experimental methods can be explained further via circuit models. Through all these investigations, the validity of the hypothesis, which states that increase in porosity enhances the charging rate but reduces the capacitance, can be checked. In order to understand the mechanism and concepts of charge and ion transfer in all the mentioned electrochemical methods and to develop corresponding circuit models, it is necessary to learn briefly about the charge storage mechanism in the types of composites we have.

Since the composites made here combine the 1<sup>st</sup> and 2<sup>nd</sup> group of supercapacitors (chapter 1), they have properties of both electric double layer capacitors (EDLCs) and pseudocapacitors in terms of charge storage mechanism. As was explained in chapter 1, EDLCs operate based on non-Faradaic reactions (electrostatic charge accumulation at the electrode/electrolyte interface and no charge transfer between the electrode and electrolyte) and pseudocapacitors based on Faradaic reactions (charge transfer between electrode and electrolyte through redox reactions, intercalation of ions and adsorption [27], [28]). A brief description of EDLCs and pseudocapacitors charge storage mechanisms is outlined here. In EDLCs, usually a positive charge is on the working electrode (on the backbone of the polymer), which gets attracted to the negative charge in the solution (PF<sub>6</sub><sup>-</sup> ion from solution), and forms a capacitive double layer at the interface, as mentioned. This phenomenon is shown in Figure 3.1. A circuit model,

representing the charge and ions behavior at the electrode/ electrolyte interface and inside the electrode is presented in section 3.2.2 to investigate the nature and origin of these behaviours.



**Figure 3.1.** Charge and ion transport is presented at the solution/electrode interface for an electrode that is negatively charged. The electrodes in this thesis are all positively charged, but they follow the same concept [29].

In pseudocapacitors, the ions represented in Figure 3.1, penetrate also through the volume of the electrode and exchange of charge happens between electrode and electrolyte. The rate of ions' penetration and diffusion through the electrode determines the charging time (response time) of the electrode, details of this transport are explained in sections 3.2 and 3.3. More details of the capacitance, charge storage and ion transfer, which are key components in determining the energy density and charge/discharge rate of our electrodes are presented in the following sections (3.1, 3.2 and 3.3).

# 3.1 Cyclic Voltammetry (CV)

Cyclic Voltammetry or CV is an electrochemical technique used to study electrode mechanisms in terms of adsorption, redox processes or charge transfer reactions. In the experiments presented, the voltage applied to the working electrode (WE) (with respect to the reference electrode (RE)) is swept between two values (e.g. -0.6V to 0.6V) at a fixed scan rate (e.g.  $\alpha = 1$  mV/s) and a current vs. potential curve is obtained. Initially, the current ramps up to the set potential and afterwards it reverses its direction down to the lowest potential [30], [31]. Current-potential characteristics of an electrode are affected by the ions' mass transport, and kinetics of charge transfer or Faradaic reactions at the surface of the electrode [32]. The main purpose of

using CV experiments in this research has been finding the raw capacitance, the specific capacitance and the volumetric capacitance of the different samples and investigating the amount by which these capacitance values (as well as charge/discharge rate) change as the sample porosity (or PPy mass) is varied (details in sections 3.2 and 3.3). The experimental methods used for CV measurements are explained in the following section. Further, the parameters extracted and calculated from the results of these experiments are presented.

## 3.1.1 Experimental Setup

For cyclic voltammogram measurements, a three-electrode cell having a reference, a working and a counter electrode is used. The working electrode current is measured in the following setup as an asymmetric configuration (metal electrode/film electrode/electrolyte) shown in **Figure 3.2**.



Figure 3.2. Set up for the cyclic voltammogram measurement

The electrodes are connected to the corresponding probes of a potentiostat (impedance analyzer and Solatron 1287A Potentiostat/Galvanostat) and a voltage is applied and swept at a specific scan rate. In this thesis, carbon fiber paper was used as the counter electrode and an RE-4 Ag/AgCl Reference electrode from BASi Labs was used as the reference. The working

electrode, to which the voltage was applied, was either a pure PPy or CNF/PPy composites. All these electrodes are placed in a 0.1 M TBAP/PC as shown in **Figure 3.2**. Since it has been seen that usually the first couple of cycles for a fresh new film look different from other cycles, the samples were cycled a couple of times before starting the actual test. These first few cycles allow the film to adapt to the surrounding environment (e.g. the electrolyte).

After the cycles, the film was brought to an oxidization state of ~ 0.24 V vs. Ag/AgCl reference electrode by applying a constant potential. Further, CVs were performed at scan rates of 1, 5, 10, 20, and 50 mV/s for couple of samples, but finally the slowest scan rate of 1 mV/s was used for all samples to determine their capacitance. Slower scan rates give enough time to electrodes to get fully charged or discharged (enough time for ions to penetrate fully into the electrode); hence they can show their full capacitive behaviour. The results for CV tests for different samples are presented in the following section.

#### 3.1.2 Results

CV tests were performed for all electrodes, which, according to chapter 2, are all represented based on their porosity percentage: pure polypyrrole (0 % porosity), PPy/CNF electrodes (8 hour (44 %), 6 hour (54 %), 4 hour (76 %), and 3 hour (81 %)) and pure CNF (91 % porosity). All the CV results are presented on the same graph (Figure 3.4) except for the pure PPy CV, which is shown separately in **Figure 3.3**. As mentioned before, these graphs are used to find the total, volumetric and specific capacitance of all electrodes and compare those for the various porosities.



Figure 3.3. CV graph for pure PPy from -0.6 V to 0.6 V vs. Ag/AgCl reference with a scan rate of 1 mV/s



Figure 3.4. CV graphs for all the CNF/PPy samples (1 mV/s scan rate) vs. Ag/AgCl reference

Looking at the plots, it is seen that all samples show a deviation from ideal rectangularshaped capacitance curve due to the presence of resistance and parasitic reactions. The expectation for having a rectangular-shaped curve arises from the capacitance of an ideal capacitor. For an ideal capacitor the stored charge at a given voltage is  $Q = C_{raw(total)}V$  and the corresponding current is  $I = dQ/dt = C_{raw(total)} dV/dt$ . In our CV experiments, dV/dt is the scan rate  $\alpha$  and hence the current is  $I = C\alpha$  and the resulting capacitance is  $C_{raw(total)} = I/dV/dt$  (I at the steady state or flat region is used). Using **Figure 3.4** and this capacitance equation, it is found that the electrode with the most PPy (44 %) has the highest capacitance and this capacitance decreases as the PPy content is reduced. The raw capacitance values found can be calculated per volume and per gram of the sample to give the volumetric ( $C_{\nu}$ ; F/m<sup>3</sup>) and specific capacitances (F/g) respectively, details of calculations are presented in Appendix F. It should be noted that for the specific capacitance calculations, the measured mass values might not give an accurate result due to the presence of some electrolyte from the electrochemical tests. Hence, the mass estimated from the amount of charge transferred during PPy deposition (deposition current) is used as an alternative to calculate the specific capacitance of each sample with respect to PPy mass (**Table 3.1** and **Figure 3.7** and Appendix F).

	Sample	0 %	44 %	54 %	76 %	81%	91%
	Length (m) x 10 <sup>-2</sup>	$2.50 \pm 0.08$	2.50 ± 0.35	2.20 ± 0.14	$2.60 \pm 0.04$	2.70 ± 0.13	2.40 ± 0.07
Dim <sup>1</sup> .	Width (m) x $10^{-2}$	$2.00 \pm 0.22$	$1.60 \pm 0.07$	1.90 ± 0.16	$1.50 \pm 0.05$	1.90 ± 0.15	$1.20 \pm 0.03$
	Thick. (µm)	$14.0 \pm 0.5$	$64.0 \pm 1.4$	$47.0 \pm 1.3$	$73.0 \pm 2.1$	59.0 ± 1.7	38.0 ± 1.5
Vol. Ca PPy): C 10 <sup>7</sup>	ap. (CNF+ $C_V$ (F/ m <sup>3</sup> ) x	18.60 ± 1.90	7.81 ± 0.61	5.59 ± 0.30	2.63 ± 0.21	2.31±0.12	$0.27 \pm 0.02$
Specifi (calcula includin mass): /mass p	c Cap. ated mass ng PF <sub>6</sub> <sup>-</sup> C <sub>PPy+CNF</sub> <sub>Py-added</sub> (F/g)	80.0 ± 9.6	127.4± 15.3	101.7 ± 12.3	116.2 ± 12.4	118.9± 14.9	6.7 ± 0.8
Cap. (P from C	$_{Py+CNF}$ ) (F) $\rightarrow$ V graph	$1.30 \pm 0.20$	$2.00 \pm 0.24$	$1.10 \pm 0.14$	$0.75 \pm 0.10$	$0.70 \pm 0.08$	$0.030 \pm 0.004$
Deposi (mA)	tion Current	1.30	1.20	1.10	0.98	1.20	N/A

Table 3.1. Basic characteristics of the samples

To summarize the results from Figure 3.3 – Figure 3.4 and Table 3.1, Figures 3.5 - 3.7 are presented as follows and further details are shown in Appendix F.





capacitance of pure PPy ( $\frac{mass \ of \ PPy \ in \ each \ sample \times C_{v_{-}PPy}}{calculated \ mass \ of \ Pure \ PPy}$ ). The higher the PPy mass, the

higher the capacitance. The dotted lines are the top and bottom error lines for the capacitance.



**Figure 3.6.** The volumetric capacitance is plotted against the percent porosity of each electrode. The expected volumetric capacitance  $(C_{v_ppy}(1-\gamma))$  based on bulk volumetric capacitance of pure PPy is also plotted. The higher the porosity %, the lower the volumetric capacitance.





Looking at both **Table 3.1** and Figures 3.5 - 3.7, it is seen that the volumetric and raw capacitance of electrodes increase as the amount of PPy grown into CNF is increased (porosity % decreases). Volumetric and total capacitances are used in obtaining the rate of charging, diffusion coefficient and ionic conductivity, which are all important in investigating the hypothesis (more details are explained in sections 3.2 and 3.3). The specific capacitance of polypyrrole is an intrinsic property that is expected to be the same across all the samples. Considering the errors in the above graphs, the specific capacitance for all porous electrodes is around the same order but higher compared to that of pure PPy. The reason for having higher specific capacitance (hence higher energy density) values for porous samples is due to having more pores ( $C_{dl} \alpha$  Area), which leads to more surface area. It should be noted that the volumetric and specific capacitance of PPy almost agrees with the expected value found in literature (90 - 120 F/g for specific capacitance and  $1 \times 10^8$  F/m<sup>3</sup> for volumetric capacitance [33], [34]). Having obtained the capacitance, the ion transport rates and rate-limiting factors that play a role in determining the charging rate of electrodes are also found via the electrochemical techniques in sections 3.2 and 3.3.

# **3.2** Ionic Conductivity (IC)

Ionic conductivity is conduction through ion transport within and at the phase boundaries of the film or polymer composites. Ionic conductivity measurements are used to measure frequency and impedance response of various ion transport processes through porous electrodes exposed to electrolyte solution on both sides. The interpretation of the impedance spectra requires understanding all the processes that occur in an electrochemical system [35]. These processes include ion transport (e.g. due to diffusion) between polymer layers and electrolyte solution and lead to reduction (discharging) and oxidation (charging) of the film to maintain electroneutrality [36], [37].

The main purpose of this section is to find ionic conductivity and hence diffusion coefficient values of electrodes of varying porosities and to investigate the effect of porosity on ion transport rate, and charging time. For this purpose, ionic conductivity measurements are performed for various electrodes in a 4-electrode configuration setup filled with a 0.1 M (TBAP)

in propylene carbonate (PC). These measured ionic conductivity ( $\kappa$ ) values (conductivity inside the pores and PPy) along with the measured capacitance ( $C_v$ ) values of section 3.1.2 are used to find the diffusion coefficient values ( $D = \frac{\kappa}{C_v}$ ) of electrodes (derivations in section 3.2.2 and Appendix D). From the diffusion coefficients, the time constant values are also found to estimate the charge/discharge time of electrodes ( $\tau = \frac{L^2}{D}$ ) and to investigate any improvement in them as the porosity is increased. The diffusion coefficients are further verified with values found from NMR measurement and Einstein relation calculations (Chapter 4). In order to further explain the phenomena seen in the ionic conductivity experiments, circuit models are also developed (section 3.2.2 and Appendix D).

There have been some groups working on ionic conductivity measurements for other purposes, but using similar methods to those used in this thesis. It is important to know about the methods that other groups have used for ionic conductivity measurements in order to understand how our method is different and how it can be improved. One of the groups that has used a very similar ionic conductivity measurement method to the one used here is a group in Spain (Otero and Ariza) [38]. The purpose of their measurement, though, is quite different from the one here. They investigate the ion transport through pure polypyrrole films to create an ion exchange membrane and control ion penetration by varying the oxidation and electrolyte concentration. Investigation of ion transport requires measurement of diffusion coefficient of ions across the film, which is found by a similar set up to the one used in this thesis [38]. The variation of oxidation state and electrolyte concentration could also be tried for the electrodes used here to investigate any potential improvements in charging time.

Other groups doing similar work include C. Ehrenbeck, B. J. Feldman and P. Burgmyer, who have also designed a 4-electrode setup, but with a different configuration and for a different purpose similar to Otero's [14], [39]. Burgmyer and Feldman have done measurements on freestanding membranes (e.g. polypyrrole) to test similar permeability properties. Their results and methods were useful in terms of giving us an idea of what approaches can be used for finding polypyrrole's ionic conductivity and what diffusion or ionic conductivity values may be obtained for polypyrrole [39]. Ionic conductivity measurements of Ehrenbeck for PPy at oxidized states were also useful in finding the same ideas as above and learning that PPy ionic

conductivity can be improved in oxidized states [14]. Knowing this fact, one can use the PPy at its oxidized state to get the best performance in terms of ionic conductivity and charging time. Other ionic conductivity measurement methods were also investigated, details of which can be found in the relevant references [40], [41], [42].

As mentioned before, the purpose here is to investigate the effect of porosity on ion transport rather than creating a permselective membrane similar to other groups. Initially the procedure for setting up the ionic conductivity experiment is outlined below.

## 3.2.1 Experimental Setup

For ionic conductivity measurements, an apparatus capable of 4-probe conductivity measurement is used. The film ionic diffusion behaviour was measured in a symmetrical configuration (electrolyte/film membrane/electrolyte) as shown in **Figure 3.8**.



Figure 3.8. Symmetrical configuration set up for the ionic conductivity measurement

The current ( $i_T$ ) flows through the two counter electrodes in the left and right beakers and the references are placed in the 2 middle slots, over which the potential difference ( $\Delta V$  or  $\Delta \Phi_t$ ) is measured. The film is located where the two beakers are connected and in between the two reference electrodes as shown in **Figure 3.8**. The reference electrodes are very close to the film through the sharp-tipped nozzles, which help reduce the solution resistance. The electrolyte (0.1 M TBAP/PC) is placed in the two beakers. The film is initially brought to an oxidized state of ~ 0.24 V in 3-electrode configuration similar to CV experiments and then impedance measurements are made using the impedance analyzer that was used in section 3.1. The experiment involves applying a small sinusoidal current and measuring the resulting voltage along with the phase angle or vice versa. The currents used for all the samples were 0.005 mA, 0.01 mA, 0.150 mA, 0.1 mA and 0.2 mA, among which 0.005 mA and 0.1 mA were found to give the best results with the greatest signal to noise ratio. These currents made sure that the voltage across electrodes is not too high (e.g. no more than 0.22 V) which would force the impedance response to be non-linear. For example, two currents of 0.005 mA and 0.1 mA were tested for the pure PPy and the higher current gave a noisy result due to perhaps getting into the non-linear region. The frequency range used for the samples was from  $1 \times 10^{-4}$ ,  $6 \times 10^{-4}$  or  $8 \times 10^{-4}$  to  $1 \times 10^{5}$  Hz. Two sets of graphs were obtained from the ionic conductivity measurements, namely the Nyquist plot and Bode plot. The following section presents the results obtained for all the electrodes.

## 3.2.2 Results and Modeling

The Nyquist (imaginary impedance vs. real impedance) and Bode plots (magnitude and phase vs. frequency) for pure PPy (0 %) and CNF/PPy composites with porosity percentages of 44 %, 54 % and 76 % are presented here. The same graphs were also obtained for the 81 % sample, but since the resistance measured for the film was very close to the solution resistance and it could not be distinguished from the solution resistance, the results were not reliable and hence are not presented. Among the experimental parameters obtained here, two appear to be relevant to ion transport: (1) the Warburg impedance (section 3.2.3 and Appendix D) of the electroactive ion from which the ions' diffusion coefficient can be found ( $Z_W = A_W.j\omega^{-0.5}$ , where  $Z_W$  is the Warburg impedance,  $A_W$  is the Warburg coefficient, j is the imaginary unit and  $\omega$  is the angular frequency), and (2) the high-frequency resistance of the film which determines the rate of permeability of all mobile ions in the film. The low frequency resistance of the film, which corresponds to the ionic resistance inside the polymer layers and pores, is also examined. These parameters (ionic conductivity, diffusion and time constant) are calculated from the impedance data obtained at high, intermediate and low frequencies as shown in Figure 3.9 - Figure 3.11. Their values are affected by thickness and the level of porosity and homogeneity of the electrodes, which can be understood and correlated by related circuit models that are developed in section 3.2.3.

The results from the pure polypyrrole sample are presented separately (**Figure 3.9**) since they cannot be fit to the same scale on the same graph. The plots from the other electrodes are all shown on the same graphs (**Figure 3.10** and **Figure 3.11**). Nyquist and Bode plots are shown on the same graph for pure PPy but separately for other electrodes.



**Figure 3.9.** Nyquist (negative imaginary (-Z'') vs. real impedance (Z)) and Bode plots (phase  $(\varphi)$  and log of impedance magnitude vs. log of frequency) for pure PPy (0.23 V oxidation) at an applied current of 0.005 mA over the frequency range of  $1 \times 10^5$  to 0.0001 Hz [43].



**Figure 3.10.** Nyquist plots for 44 %, 54 % and 76 % samples at an applied current of 0.1 mA over the frequency range of  $1*10^5$  to 0.0001 Hz. Film oxidation is at 0.23V [43].



**Figure 3.11.** Bode plot: phase ( $\varphi$ ) and log of impedance magnitude (log|Z|) vs. log of frequency

11.

In order to understand these experimental results, first a circuit model, as explained below, is developed. Its circuit elements represent the physical phenomena seen in the experiments. Further in section 3.2.3, the behaviours in different frequency regions of the Nyquist and Bode plots are explained in relation to the circuit model. The circuit model used to explain the results from the ionic conductivity measurement is shown in **Figure 3.12**.



Figure 3.12. Basic circuit used for ionic conductivity measurement results

In the figure, Rs is the solution resistance and Wm (called the "modified Warburg impedance") functions similar to original Warburg impedance (details in Appendix D) but it is not shown as a single Warburg element. This modified Warburg impedance is shown as a transmission line to represent a complex structure with more complicated electrochemical reactions. The transmission line (ladder-like circuit) is composed of a series of parallel capacitors CL corresponding to the double-layer or electrode capacitance and resistors R1, R2 and R1 corresponding to ionic, electronic and leakage resistances as shown in **Figure 3.13**.



**Figure 3.13.** Equivalent transmission line circuit of a PPy film in an electrolyte; L is the polymer film thickness (m);  $\varphi 1 \& \varphi 2$  are potentials (V) at the top and bottom lines at each intersection respectively, R1 and R2 are ionic and electronic resistances per unit length ( $\Omega/m$ ), i1 is the current in the top line (ionic current) and i2 is the current in the bottom line (electronic current), CL is the capacitance per unit length (F/m) and R1 represents leakage resistance (unit of  $\Omega$ m). Leakage resistance becomes dominant at low frequencies. In the derivation of the impedance for this circuit, R1 and R2 values are shown as  $\chi_1$  and  $\chi_2$  and the parallel combination of CL and R1 is shown with  $\zeta(\Omega)$  [44].

There have been similar models of ionic conductivity developed for polymers. A similar IC model to the model used here is developed for proton exchange membrane fuel cells by Gomadam P. and that mainly is used to conclude that continuum mechanics-based approach better accounts for the details of motion of ions within a porous electrode [43]. Hence, obtaining the diffusion coefficient or ionic conductivity is not of concern there, contrary to this thesis. As explained in section 3.2.1, there is also another model by Vorotyntsev and Deslouis that focuses on mixed electron-ion exchange in polymer films [45],[46]. For this research, since electronic conductivity is much higher than ionic conductivity across thickness, the effect of electron transport is very negligible and ionic charging will be the rate limiting mechanism.

The circuit in **Figure 3.13** is solved for the case that diffusion is from both sides (left and right) of the film. Solving this circuit requires finding and solving a differential equation initially considering the boundary conditions for the circuit. The boundary conditions for  $i_2$  are shown in **Figure 3.13**. The boundary conditions used in impedance calculations are  $i_1(0) = i_T$  and  $i_1(L) = i_T$ , and are shown as  $i_1(0) = \frac{1}{\chi_1} \frac{\partial \eta}{\partial x} = i_1(L)$ . From here the following relation

is found:  $\frac{1}{\chi_1} \frac{\partial \eta}{\partial x} |_0 = \frac{1}{\chi_1} \frac{\partial \eta}{\partial x} |_L$ . These boundaries physically represent that current is flowing from one side of the cell and coming out from the other side through the counter electrodes in each cell. The details of the derivations are covered in Appendix D and only the final equation is (3.1): presented as follows (equation 3.1):

$$Z = \frac{L}{(\sigma + \kappa)\pi r^{2}} \left[1 - 2 \times \left(\frac{\sigma}{\kappa} \left(\frac{1 - \cosh(L \times \sqrt{\frac{(1 + R_{l}jwC_{v}A)}{\sigma\kappa AR_{l}}}(\sigma + \kappa)}\right) - \frac{1 - \cosh(L \times \sqrt{\frac{(1 + R_{l}jwC_{v}A)}{\sigma\kappa AR_{l}}}(\sigma + \kappa)})\right)\right]$$

This equation is then added to the solution resistance in series to give the total impedance of the circuit. This impedance is simulated in Matlab to get the Nyquist and Bode plots (**Figure B.10** and **Figure B.11** as shown in Appendix B) similar to **Figure 3.9** - **Figure 3.11**. The model is fitted to the experiment by having all parameters fixed, except three main elements in the circuit, namely ionic conductivity ( $\kappa$ , which determines  $R_i$ , an initial value for which can be found from ionic conductivity measurement), leakage resistance ( $R_i$ ) and film volumetric capacitance ( $C_v$ , which determines  $C_L$ , an initial value for which is found from CV experiments). These modeling parameters have been optimized to best fit the experimental data. These parameters provide the diffusion coefficients and time constants, which are essential in determining the ion transport rate and charging time in order to verify the hypothesis. Assuming ion diffusion into the polymer thickness in the x direction, an effective diffusion equation (similar to differential equations shown in Appendix D for derivation of the impedance model) consisting of the mentioned parameters can be found that gives the diffusion coefficient values. This equation is as follows:  $\frac{\partial V(x,t)}{\partial t} = D \cdot \frac{\partial^2 V(x,t)}{\partial x^2} \rightarrow D = \frac{1}{RC_t}$ , where *D*, which is the effective

diffusion coefficient, can also be represented as ionic conductivity divided by volumetric capacitance  $(D = \frac{\kappa}{C_v} \rightarrow \kappa = \frac{L}{R_1 \times Area})$ , where  $\kappa$  is the ionic conductivity in the pores and in PPy, obtained from ionic conductivity measurement and  $C_v$  is the volumetric capacitance; note

that  $R_1$  is negligible). The time constant values for the experiment are found from  $\tau_{i-measured} = R_1 C_{Total}$  ( $R_1 = \frac{L}{\kappa \times width \times length}$ , width and length are for the film electrode and  $C_{Total}$ 

is found in section 3.1) and those for the model are found from  $\tau_{\text{mod}\,el} = \frac{L^2 C_v}{\kappa}$  ( $C_v$  and  $\kappa$  are found from model fitting;  $\tau_{\text{mod}\,el}$  is the time delay associated with ion diffusion into the polymer thickness). These time constant values are compared with the solution time constant in section 3.3.5 to determine which is the rate-limiting factor in charging rate.

The values obtained for the above parameters are similar for both the model and experiment and are presented in Table 3.2 (note that the 81% and 91% electrodes' models are not presented) in 3.2.3. Having the role of circuit components in mind and looking at the modeling graphs along with the experimental graphs, we can now explain the behaviours seen in both. Most of the modeling results (for the 0 % to 76 % samples) capture the main features of their corresponding experiments similar to what is shown in **Figure 3.14** for the 44 % electrode as a sample.



Figure 3.14. Model and fit for the Nyquist and Bode plots of the 44 % electrode

Discussion of the experimental graphs with respect to model and modeling results are presented in section 3.2.3.

#### 3.2.3 Discussion of Results in Relation to Modeling

As seen from the experimental graphs (Figure 3.9 - Figure 3.11) and the experiment-model-fit graphs, a semi-circled shape curve is obtained for the Nyquist plots, which can be represented as parallel capacitors and resistors in the modified Warburg impedance model. This semi-circle is theoretically supposed to cross the real axis at low and high frequencies, but do not do so in the experiment. The results from solving the impedance equation (equation 3.1) at high and low frequencies explain the origin of these intercepts (at high frequencies capacitors are shorted and parallel of R<sub>1</sub> and R<sub>2</sub> plus solution resistance are dominating, while at low frequencies, where capacitors are open, the leakage resistance is also included). The reason for the lack of this intercept at high frequencies is explained in Appendix B. Despite the lack of an actual intercept, the lines at each frequency end are extended manually until they hit the x-axis and from there the intercepts are estimated within 1 - 4 % error. The resistance at high frequencies corresponds to the solution and contact resistances (contact is negligible. e.g. ~ 1-2  $\Omega$ ) and it ranges from ~ 345-460  $\Omega$  including all electrodes.

The measured ionic impedance values at the lowest frequency are used to find the ionic conductivity of electrodes ( $\kappa = \frac{L}{R_i \times Area}$ , where L is the thickness of the film through which the ions transport, R is the film real resistance measured minus the solution resistance and Area is  $2\pi r$ ; r is the radius of the circular section of ionic conductivity setup, where the film electrode is placed (it is ~ 5 mm here; Figure 3.18)). From the ionic conductivity, as mentioned in section 3.2.2, the diffusion coefficient of electrodes can be found. Finally, from the calculated diffusion, the charging time or time constant of the electrode can also be found as mentioned before. The measured and modeling values for these parameters are shown in Table 3.2. All electrodes were tested at an oxidation state of ~ 0.23 V as was mentioned also in section 3.2.

Samples	Tests	Ionic Conductivity (κ, S/m)	R <sub>Faradaic</sub> (Leakage ) (Ω)	Diffusion Coefficient (m <sup>2</sup> /s)	$\tau$ (s) (diffusion time across thickness) = $L^2/D = R_i C_{total}$	Vol <sup>2</sup> . Cap <sup>3</sup> . $\rightarrow C_{\nu}$ (F/m <sup>3</sup> ) x10 <sup>7</sup>
Pure PPv (0	Model	1.0 x10 <sup>-6</sup>	2400	1.25 x 10 <sup>-14</sup>	1.57 x 10 <sup>4</sup>	8.00
%)	Exper <sup>1</sup> .	$(6.26 \pm 0.23)$ x10 <sup>-6</sup>	N/A	$(3.37 \pm 0.35)$ x10 <sup>-14</sup>	$(5.81 \pm 1.03)$ x10 <sup>3</sup>	18.60 ± 1.90
	Model	12.8 x10 <sup>-3</sup>	550	2.21 x10 <sup>-10</sup>	18.56	5.80
44 %	Exper.	$(2.05 \pm 0.04)$ x10 <sup>-3</sup>	N/A	$(2.63 \pm 0.18)$ x 10 <sup>-11</sup>	156 ± 22	7.81 ± 0.61
	Model	$1.90 \text{ x} 10^{-2}$	1000	$4.75 \text{ x}10^{-10}$	4.65	4.30
54 %	Exper.	$(1.10 \pm 0.03) \\ x10^{-2}$	N/A	$(1.97 \pm 0.17)$ x10 <sup>-10</sup>	$11.22 \pm 1.60$	5.59 ± 0.30
	Model	8.00 x10 <sup>-2</sup>	2000	7.39 x10 <sup>-9</sup>	1.33	2.00
76 %	Exper.	$(1.64 \pm 0.05)$ x10 <sup>-1</sup>	N/A	$(6.23 \pm 0.45)$ x10 <sup>-9</sup>	0.86 ± 0.12	2.63 ± 0.21
81 %	Exper.	$(1.73 \pm 0.23)$ x10 <sup>-1</sup>	N/A	$(7.48 \pm 0.57)$ x10 <sup>-9</sup>	$0.47 \pm 0.06$	2.31 ± 0.12
Pure CNF (91 %)	Exper.	$(1.78 \pm 0.07)$ x10 <sup>-1</sup>	N/A	$(6.49 \pm 0.04)$ x10 <sup>-8</sup>	$0.020 \pm 0.001$	0.27 ± 0.02

Table 3.2. All parameters found from IC experiment and model fit for all samples

 $Exper^{1} = experimental, Vol^{2} = volumetric, Cap^{3} = capacitance$ 

Looking at experimental and modeling graphs and according to Table 3.2, the following conclusions are drawn that verify the hypothesis. The ionic conductivity is increasing going down to electrodes with more porosity %, resulting in less series resistance along the electrode thickness. The lower series resistance results in faster ion transport (smaller time constant) and higher ionic diffusion. It should be noted that for pure PPy, the time constant may need to be divided by 4 (hence,  $1.45 \times 10^3$ ), since a two-sided diffusion case may need to be considered as will be more explained in section 3.5.5. The diffusion coefficients for 76 % to 91 % samples are almost the same as the pure solution diffusion coefficient (( $6.49 \pm 0.04$ )  $\times 10^{-8}$ ; note that the pure

CNF and solution diffusion coefficients are basically the same, since the CNF porosity is so high that the ions have the tendency to travel only through the pores where there is only solution). The diffusion coefficient for pure solution is also found from NMR in chapter 4 ((5.63  $\pm$  0.05) x10<sup>-10</sup>  $\frac{m^2}{s}$ ), but since NMR uses a different measurement approach, the diffusion coefficients found from this method cannot be directly compared to ionic conductivity measurement method (chapter 4 and 5). Also, the diffusion coefficient values from ionic conductivity measurements are solution resistance limited for very porous electrodes, similar to what will be explained in section 3.3.5. The diffusion coefficient values found from NMR are lower than those found from ionic conductivity measurements and this applies for the pure solution too as it is seen above. The high diffusion coefficient of solution obtained from ionic conductivity measurements, seem unphysical as a thermally driven diffusion (e.g. NMR). In other words, it cannot describe a thermally driven diffusion. Going back to the fact that the diffusion coefficient of very porous samples is the same as that for pure solution, we explain that samples with higher porosity have an ion transport through the thickness that is almost as fast as transport through a solution. Faster transport results in faster charging and smaller time constant. Shorter charging time means higher power, which is one of the features required. Although, there is a trade off in getting a faster charging and that is losing the capacitance as was shown in section 3.1. Therefore, a point, where both a relatively high charging and a high capacitance are achieved is desired. More details of this are discussed in chapter 5. Fortunately however, the amount of loss in capacitance, based on chapter 5 and  $C_{\nu}$  values in Table 3.2, required to achieve a large increase in speed is seen to be negligible compared to the improvements in diffusion and reduction in charging time constant.

The faster ion transport for more porous samples is also verified with the Bode plots in **Figure 3.11**. Assuming the starting phase of all electrodes to be the same (e.g.  $0^{\circ}$ ), the capacitive-resistive transition point occurs at a higher frequency (in a shorter time) for electrodes with less porosity %. This, similar to results from the Nyquist plots, confirms the hypothesis, suggesting faster charge/discharge rate for higher porosity % electrodes.

The increase in ionic conductivity due to increase in porosity fraction can also be verified theoretically with equation 3.2. Assuming the resistance of the electrolyte

 $(R_{electrolyte} = \frac{L}{\gamma \kappa_{electrolyte} Wd}$ , where W is the width and d is the length) to be parallel (hence, interconnected pores) to the resistance of PPy  $(R_{PPy} = \frac{L}{(1-\gamma)\kappa_{PPy}Wd})$ , the effective ionic

conductivity can be found as in equation 3.2.

$$\kappa' = \kappa_{PPy} (1 - \gamma) + \kappa_{electrolyte} \gamma, \tag{3.2}$$

where  $\kappa'$  is the effective ionic conductivity,  $\kappa_{PPy}$  is polypyrrole ionic conductivity,  $\gamma$  is porosity fraction and  $\kappa_{electrolyte}$  is the solution ionic conductivity inside the electrode pores. Although it is shown from both the experimental values and equation 3.2 that increase in ionic conductivity is due to increase in porosity, still the amount of increase may be different for the actual experiments compared to the expected (effective) values. The expected values for high porosity electrodes are found based on the assumption that the ionic resistance inside the pores is much lower than the one in the PPy; hence most ions are traveling through the pores. This assumption, which is embedded in equation  $\kappa_{electrolyte}\gamma$ , holds for high porosity samples as it is also shown from the experimental values. At lower porosities (e.g. 44 % and 54 % porosities), the  $\kappa_{electrolyte}\gamma$ model does not hold since there are other factors that are affecting or slowing down the transport (e.g. some ions may have become immobile or slowed-down due to having smaller pores in the electrodes). These factors could be the non-uniformities or tortuosities of the electrodes, about which more details are given in section 5.1. The expected and experimental ionic conductivities versus porosity % are shown in **Figure 3.15**.



**Figure 3.15.** Ionic conductivity values from expectation (equation 3.2) and experiment are shown in a log scale plot versus porosity %.

From Figure 3.15, it is seen that the ionic conductivity values from expectation and experiment are both increased with increasing porosity % as was mentioned and expected before. The values from 0 % and 76 % - 91 % electrodes are in agreement, confirming the assumption that all ions are actually traveling through the pores. This is also shown from NMR results in chapter 4, where the diffusion coefficient of ions in very porous electrodes is found to be very similar to that of the bulk solution. The ionic conductivity values for the 44 % and 54 % are higher for the expected values compared to experimental ones. The reason the experimental values are lower for these two samples is perhaps because the transfer of some ions is not as fast as expected due to non-uniformities of the electrode (due to non-uniform deposition) or their tortuosity, which may also result in the immobility of some of the ions. These phenomena are also verified from NMR results of chapter 4 for the 44 % and 54 % electrodes. As mentioned at the beginning of chapter 3, in addition to the ionic conductivity measurements, another experiment, EIS, is used to characterize ion transport of electrodes, and is explained in section 3.3.

# **3.3** Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy is an electrochemical technique that is used to study and measure charge transfer and other transport properties (i.e. ionic conductivity, diffusion or migration) of porous electrodes including conducting polymer films (e.g. PPy) and its composites (e.g. PPy/CNF). This method allows the analysis of these properties at different frequencies and with the application of small stimulus voltages. Other transient techniques, such as potential sweeps or steps and current interrupts require a high initial voltage (reported by Jaouen et al., 2003; Saab et al., 2002; Li and Pickup, 2003 [47]) but the electrodes used here cannot bear voltages higher than 2 or 3 volts.

Our aim in this section, similar to section 3.2, is to investigate the effect of porosity on ion transport rate, diffusion rate and charging time for composites of varying porosities. The ion transport rate is affected by the ionic conductivity of the electrode, which can be measured in a fashion similar to that used in section 3.2. As repeatedly mentioned in section 3.2, the ionic conductivity along with the capacitance measured from CV experiments determines the diffusion coefficient of ions in the electrode  $(D = \frac{\kappa}{C_y})$ . These parameters determine the charging rate of electrodes. Another element that affects the charging time, especially at low frequencies, is the leakage resistance as explained in Figure 3.13 of section 3.2.2. There are different rate-limiting factors (e.g. solution resistance vs. ionic resistance and leakage resistance; electrical resistance is found to be negligible and hence non-limiting) in ion transport, which are investigated based on ionic conductivity and EIS results. These factors are important since they affect the charging rate. Among these, the dominant factor determining the time constant should be found and further minimized for faster ion transport and charging rate. As the porosity % is increased, starting from pure PPy, the rate-limiting factors and hence the time constants (Table 3.4 and Figure 3.26) may also be different in each electrode. To investigate these phenomena, impedance responses of electrodes with varying porosities are obtained and further analyzed by circuit models (similar to the ones in section 3.2) that are developed to explain the physical phenomena seen in the experiments [48]. These circuits and their impedance equations are presented in section 3.3.2 and 3.3.4 and details of the derivations are in Appendix D.

Before proceeding to our own experiments, background work in similar approaches used in performing and modeling EIS experiments is briefly described. Details of these works can be found in the corresponding references. Among the groups working in this area, Viatcheslav Freger and Sarit Bason in Israel have used EIS to characterize ion transport in thin electrodes and have proposed a circuit model similar to the one used here [49]. Another group is Juan Bisquert et al. in Spain who has developed different impedance models (for homogenous and heterogeneous media) again similar to the ones used here to investigate various diffusion mechanisms in electrodes such as polypyrrole [50]. The main model used in this thesis is based upon a homogenous medium, but a model for the heterogeneous case is also described. Other groups studying similar phenomena include Meyers et al. who have developed a circuit similar to the circuit developed here, but have concentrated on a different aspect of transport [51]. After learning about the background work, we can now explain the procedures used for the EIS experiments of this thesis (section 3.3.1).

#### **3.3.1** Experimental Setup

For EIS measurements, an apparatus capable of 3-electrode impedance measurements is used similar to the CV setup that was shown in Figure 3.2 (section 3.1). Similar to CV experiments, a potentiostat (impedance analyzer and Solatron 1287A Potentiostat /Galvanostat) is used for measurements. A similar setup is shown in **Figure 3.16**:



**Figure 3.16.** Setup for EIS measurement; each of working (the part where there is electrical contact is outside the solution), counter and reference electrodes are labeled as B, A and C respectively.

The three electrodes, namely, A (counter electrode), B (porous film composite) and C (reference electrode) are immersed in 0.1M TBAP/PC electrolyte similar to CV tests. The current (i<sub>T</sub>) flows through points A and B and the reference, which monitors the voltage near the working electrode, is located at point C. The potential difference ( $\Delta \Phi t$ ) is measured between point C and point B. 'L' represents the thickness of the working electrode. Before each experiment, the film is brought to an oxidized state of  $\sim 0.24$  V in the EIS configuration. A small AC voltage (e.g. 30 mV or 40 mV, 0 DC voltage) is applied and the resulting current (magnitude and phase) is measured at varying frequencies (e.g. from  $1 \times 10^5$  Hz to  $1 \times 10^{-4}$  Hz or 6x10<sup>-4</sup> Hz or 8x10<sup>-4</sup> Hz) (Table B.1 in Appendix B). Smaller voltages, such as 5,10 and 20 mV were also tested and they were found to give similar outcome but resulted in 'overload current' for the Potentiostat (e.g. greater fraction of the desired current was parasitic current). Hence, a higher voltage (40 mV, a value that yet does not damage the polymer film) that give higher signal to noise ratio was chosen. Repeated EIS tests were done on the same samples to ensure the reproducibility of the experiments. Any discrepancies in the experiments were believed to be due to differences in electrolyte impurities, electrical contact resistances and level of uniformity of the deposition. The experimental results and related models to explain them are presented in section 3.3.2 for all electrodes.

## 3.3.2 Results and Modeling

The impedance data obtained from EIS measurements for pure PPy (0 %) and CNF/PPy composites (properties in **Table 3.3**) with porosity percentages of 44 %, 54 %, 76 % and 81 % are plotted in two different spectra: Nyquist plot and Bode plot (Figures 3.9 - 3.10) [43]. Various parameters characterizing the electrical and chemical properties of the electrodes can be obtained from the experimental results. For example, as also explained near the beginning of section 3.3, from the film impedance and frequency spectra, the diffusion coefficient, the ionic conductivity, the charging time and the leakage resistance can be obtained that all together give information about energy storage and charge/discharge rate of the electrodes. The Nyquist (linear scale) and Bode plots (logarithmic scale) for all electrodes are presented in **Figure 3.17** and **Figure 3.18**. **Figure 3.17** shows one of the zoomed in Nyquist plots; additional Nyquist plots showing greater frequency ranges are displayed in Appendix B (Figures B.1 and B.2).



**Figure 3.17.** Experimental data for 0 %, 44 %, 54 %, 76 %, and 81 % samples at an applied voltage of 40 mV over the frequency range of  $1 \times 10^5$  to 0.0001 Hz. Film oxidation is at 0.23 V. Nyquist plot: negative imaginary (-Z'') vs. positive real impedance (Z).



Figure 3.18. Bode plot: phase ( $\theta$ ) and log of impedance magnitude (log|Z|) vs. log of frequency

In order to better understand the general behaviours seen in the experimental plots, a circuit model, similar to the one developed in section 3.2, is developed in this section (other improved circuit models are explained in section 3.3.4). Further, in section 3.3.3, an example EIS response (**Figure 3.22**), representative of the behaviours seen in our experiments, is associated with this circuit to explain our experimental results via this circuit. Learning first about the circuit model makes it easier to understand the physical concepts governing the behaviours seen in experiments. Various groups as was explained before have developed different circuit models. The model used here is similar to some of those models and is similar to the model developed in section 3.2 but with different boundary conditions for the circuit. The model here uses a finite transmission line in place of the Warburg element to account for all the resistances and capacitances along the film electrode [52].

In the case of this research, two main models and their variations are developed, but interpretation of results is mainly based on the first model. The first model, which is similar to the model in section 3.2 and to one that was first developed for conducting polymers by Albery et al., is shown in Figure 3.19 [53]. The elements used in this model are associated with Nyquist plots in section 3.3.3. Both Models include capacitors (C corresponding to the double-layer or electrode capacitance), resistors (R corresponding to leakage, charge transfer, electrode or electrolyte resistance), and transmission lines (ladder-like circuits composed of a series of parallel capacitors and resistors (Figure 3.20), referred to as modified Warburg  $(W_m)$ ), which all can be arranged in different combinations depending on a material's behaviour [48], [54]. Another component that the first model does not have, but the second model has is the equivalent of a constant phase element (CPE) that can be used in place of capacitors. CPE, which does not have a physical meaning, accounts for the inhomogeneities (ionic charge adsorption, non-uniform thickness and charge trapping) of the film that affects the charge carrier flow and leads to capacitance and time constant distribution [44], [55], [56], [57]. The second model (Figure 3.23), which is similar to the model in Figure 3.20, uses a series of capacitors and resistors added to the parallel branch of the transmission line that perform the same function as CPE (Figure 3.23 of section 3.3.4). The first model is presented and explained (Figure 3.19) in this section. This model is used as the main basis for all the fittings performed for the EIS experiments and the second model is described briefly (section 3.3.4) as an improvement to the first model.



Figure 3.19. A circuit describing the impedance response of the PPy and PPy/CNF samples

In the circuit of Figure 3.19,  $W_m$  is the modified Warburg impedance,  $C_{dl}$  is the double layer capacitance,  $R_{ct}$  is the charge transfer resistance and  $R_s$  is the solution resistance. The  $C_{dl}$  and  $R_{ct}$  form a parallel RC circuit that represents the semi-circled area that is shown in Nyquist plots at high frequencies as later explained in section 3.3.3. In place of the Warburg circuit ( $W_m$ ), the following transmission line circuit is used (**Figure 3.20**).



**Figure 3.20.** Equivalent transmission line circuit of a PPy or PPy/CNF in an electrolyte;  $\varphi 1 \& \varphi 2$  are potentials (V) at the top and bottom lines at each intersection respectively, R<sub>1</sub> and R<sub>2</sub> are ionic and electronic resistances per unit length ( $\Omega/m$ ), i<sub>1</sub> is the current in the bottom line and i<sub>2</sub> is the current in the top line, C<sub>L</sub> is the capacitance per unit length (F/m) R<sub>s</sub> is the solution resistance ( $\Omega$ ), L is the polymer film thickness (m) and R<sub>l</sub> represents leakage resistance (unit of  $\Omega m$ ). Leakage resistance becomes dominant at low frequencies [44].

In the derivation of the impedance equation in Appendix D, R<sub>1</sub> and R<sub>2</sub> values are shown as  $\chi_1$  and  $\chi_2$  and the parallel combination of C<sub>L</sub> and R<sub>l</sub> is shown with  $\zeta(\Omega)$  (circuit diagram is also

presented in Figure D.1). The reason R<sub>1</sub>, R<sub>2</sub>, C<sub>L</sub> and R<sub>l</sub> are used initially instead of  $\chi_1$  and  $\chi_2$  is to have a better physical meaning of these circuit elements.

The total impedance of the circuit in **Figure 3.20** is found by solving a differential equation similar to section 3.2.2, considering different boundary conditions for the circuit. The boundary conditions are  $i_1(0) = 0$  and  $i_2(L) = 0$  and  $i_1(0) = -\frac{1}{\chi_1} \frac{\partial \eta}{\partial x} |_0; i_2(L) = \frac{1}{\chi_2} \frac{\partial \eta}{\partial x} |_L$ . The ionic current  $(i_1)$  is zero where we have electrical contact to the film electrode and the electronic current  $(i_2)$  is zero when the end of the electrode is reached and the solution phase is started. Other details and derivations are covered in Appendix D and only the final equation is presented here (equation 3.3).

$$Z = \frac{L}{A \times (\sigma + \kappa)} \left[1 + \frac{2 + (\frac{\sigma}{\kappa} + \frac{\kappa}{\sigma}) \cosh(L \times \sqrt{\frac{(1 + R_l j w C_v A)}{\sigma \kappa A R_l}} (\sigma + \kappa))}{(L \times \sqrt{\frac{(1 + R_l j w C_v A)}{\sigma \kappa A R_l}} (\sigma + \kappa)}) \sinh(L \times \sqrt{\frac{(1 + R_l j w C_v A)}{\sigma \kappa A R_l}} (\sigma + \kappa)})\right]$$
(3.3)

This equation does not include the solution resistance, the charge transfer resistance and the double layer capacitance and after those are added the final impedance is as follows (equation 3.4):

$$Z_{\text{total}} = (Z_{\text{dl}} \times Z_{\text{s}})/(Z_{\text{dl}} + Z_{\text{s}})$$

$$Z_{\text{final}} = Z_{\text{total}} + R_{\text{s}}$$
(3.4)

Where  $Z_s$  is the impedance in equation 3.3 in series with the charge transfer resistance, and  $Z_{dl}$  is the impedance for the double layer capacitance.

The impedance in equation 3.4 is simulated in Matlab to get the Nyquist and Bode plots to be fitted with the corresponding experimental plots. Similar to model-fitting of section 3.2.2, the fitting parameters that have been used here are ionic conductivity ( $\kappa$ ), leakage resistance ( $R_l$ ), film volumetric capacitance ( $C_v$ ), charge transfer resistance ( $R_{cl}$ ) and double layer capacitance ( $C_{dl}$ ), which all are used as variable parameters in the simulations (note that the initial values for  $C_v$  and  $\kappa$  are the measured values in sections 3.1 and 3.2). These parameters are found through fitting the impedance equation to the experimental results until the best fit is achieved. Using these fitted parameters, the values for model diffusion coefficient ( $D = \frac{\kappa}{C_v}$ ) and model time

constant  $(\tau_{\text{mod}\,el} = \frac{L^2}{D})$  are calculated similar to section 3.2.2 and compared against the corresponding experimental ones  $(\tau_{i-measured} = R_i C_{Total} = \frac{L^2}{D})$ . As was mentioned in section 3.2,  $R_i$  is found from ionic conductivity measurements and  $C_{Total}$  from CV measurements. Similar to section 3.2, the diffusion values determine the ion transport rate, which consequently can determine the charging time (time constant) of electrodes. A comparison between experimental and modeling values is presented in **Table 3.3**, in section 3.3.3.

It was found through simulations that the electronic conductivity is so high compared to the ionic conductivity (inside electrode pores and PPy) that it can be ignored (electronic conductivity was found from the measured electronic resistance in chapter 2 and the ionic conductivity was measured in section 3.2). If this is the case, the modified Warburg impedance equation reduces down to the following as  $\sigma \rightarrow \infty$ :

$$Z1 = \sqrt{\frac{R_l}{\kappa A.(1 + R_l j w C_v A)}} \cdot \operatorname{coth}(L \times \sqrt{\frac{(1 + R_l j w C_v A)}{\kappa A R_l}})$$
(3.5)

The  $Z_s$  equation in equation 3.4 would then be the charge transfer resistance in series with equation 3.5.

After getting the simulation results, the potential for having simpler circuit models for more porous electrodes is investigated. It is found that for very porous electrodes (e.g. 76 and 81 %), a simple  $R_l C_{PPy}$  circuit plus solution resistance in series is enough and no Warburg element is needed. Despite this, still the more complicated model including the modified Warburg is used for all electrodes to give a better coverage of the impedance behaviour.

Equations 3.3 - 3.5 are for the case when diffusion of ions is from one side of the electrode. It is also possible to have 2-sided diffusion, which is modeled by having two transmission lines the same as the one in equation 3.3 in parallel and considering half of the length for each transmission line (details of this circuit are in Appendix D). The 2-sided diffusion transmission line and the one in equation 3.4 are used to plot Nyquist and Bode plots as shown in Appendix B. The modeling results in Appendix B (Figures B.3 – B.6) capture the main features of their corresponding experiments (**Figure 3.17** and **Figure 3.18**) similar to what is shown in **Figure**  3.21 for the 44 % electrode experiment and its fit.



**Figure 3.21.** Nyquist and Bode plots for 44 % compared to the fit from the 2-sided diffusion model in Appendix D

Now, having both the model and experiment, we can explain both of them in relation to each other. Discussion of the experimental graphs with respect to model and modeling results are presented in section 3.3.3.

#### 3.3.3 Discussion of Results in Relation to Modeling

Looking at the modeling graphs along with the experimental graphs and using the circuit model (**Figure 3.20**) developed in section 3.3.2, we can now better explain the behaviours seen in experimental graphs. To better associate the circuit model to these behaviours and use it to explain these behaviours in different frequency regions of the Nyquist plots, an example EIS Nyquist plot along with this circuit is presented in **Figure 3.22**. The behaviours that are

11.

important in determining the charging time of electrodes happen mainly in three different frequency regions that are marked as "a", "b", "c" above the Nyquist graph of **Figure 3.22**. Since determining the time constant is of concern for investigating the hypothesis, the behaviours seen in these regions should be understood and hence are explained in the following paragraphs (more details in Appendix B).



**Figure 3.22.** Impedance plot for Randles equivalent circuit, representing the kinetic (region 'a' in figure) controlled region, the mass transport (diffusion) controlled region (region b) and the capacitive region (region c). Note that this is just an example graph and the values do not correspond to any results used here. A circuit representing this behaviour is also presented, where each element represents the behavior of each EIS region as shown and W corresponds to the Warburg region on the EIS graph [58].

In explaining the behaviours seen in the 3 main mentioned frequency regions of Nyquist plots, there are some important concepts that should be considered for each region. These concepts are the solution resistance of each electrode, and the impedance slope in the Warburg region and in the low frequency sections, which all are essential in determining the time constant of the electrode. The time constant is also affected by the rate-limiting factors in ion transport, which are investigated, in section 3.3.5, using the results obtained from EIS responses in the mentioned frequency regions. One of the main elements that is later (section 3.3.5) found to be rate-limiting in ion transport and hence determinant of electrodes' time constant is the solution resistance.

Solving the impedance equation (Figure 3.19) of section 3.3.2 at high and high-intermediate frequencies (from  $\sim 1 \times 10^5$  Hz to  $\sim 0.1$  Hz or higher), the impedance of the circuit is found to be composed of solution, contact, charge transfer, ionic and electronic resistances. The electronic and contact resistances are negligible and only the other resistances are considered in series. Hence the important factors to consider at these frequencies are the semi-circled shape curve and the solution resistance [59]. The semi-circle (for some electrodes, we have a quarter of a circle and the semi-circle shape is not that apparent) is modeled with a parallel RC circuit (Rct and Cdl  $\rightarrow$  values of these are found in this section and shown in Table 3.3), which was explained in section 3.3.2. The RC circuit shows the rate at which ions are inserted into the electrode from the solution. At very high frequencies where the double layer capacitor is shorted, all the resistances, except the solution resistance, are also negligible since all the current travels through the shorted path (Figure 3.19). Hence, the intersection point on the real x-axis (impedance) at very high frequencies is the solution resistance. In our measurements (Figure 3.17 and Figure 3.21), the solution resistance (e.g. here,  $R_s$  ranges from ~ 27 - 130  $\Omega$  including all electrodes), contrary to the expectation does not intersect the real axis (details in Appendix B). Despite the lack of this intercept, the R<sub>s</sub> values are still estimated from the plots similar to what was explained in section 3.2.3 (1 - 4 % uncertainty).

The importance of the solution resistance is in determining the time constant when considered as a rate-limiting factor. The solution resistance value depends on the distance between working and counter electrodes and hence depends on the cell geometry in a real device. In order to find if the solution resistance is the rate-limiting factor in ion transport, this distance should be minimized to provide a low solution resistance that is not suppressing the effect of other rate-limiting factors. If the solution resistance is much higher than the ionic or other resistance values, regardless of the role of these resistances, only the solution resistance would limit the ion transport. Hence, to prevent this issue, we have tried to minimize the solution resistance, so other rate-limiting factors in ion transport can also be realized if they exist. The time constant from solution resistance is compared against the ionic time constant ( $\tau_{i-measured} = R_i C_{Total}$ ) of electrodes to determine the rate-limiting factor in ion transport. As it will be later explained in section 3.3.5, the solution resistance, when compared to other resistances (e.g. ionic resistance), is found to be a rate-limiting factor in more porous electrodes (e.g. more than 50 %); hence, it is important in determining the time constant or charge/discharge rate for
those electrodes. It should be noted that although the  $R_s$  values are different for different electrodes due to different distance between the counter and working electrodes, they are still representative of the working electrodes time constant for more porous electrodes. This is because if even the same  $R_s$  value is assumed for all electrodes, the solution time constant is still slower than the ionic time constant for more porous electrodes. Details of these phenomena are described in section 3.3.5.

Moving on from the high frequency section of the Nyquist plots to the intermediate frequency region, the Warburg behavior (indicating that ions have not reached the end of the electrode), also called infinite response, is seen. This Warburg impedance forms a straight line inclined at 45° in the complex impedance plane. This impedance describes the slow ionic transport within the films that can be represented by a ladder transmission line consisting of parallel resistors and capacitors as was shown in Figure 3.20. The 45° slope observed in this region in Figure 3.22 is due to diffusive behaviour in an effectively infinite layer and implies a charge transfer response. After this region, a transition to the capacitive region is seen (Bode plot in Figure 3.18), which the phase angle at which it occurs depends on the solution resistance (usually, this phase angle is between  $45^{\circ}$  and  $90^{\circ}$ ). This phase angle can be used to estimate the ionic RC time constant of the electrodes. Samples reaching this phase transition point at shorter times (e.g. more porous electrodes) have faster charging rate, higher ionic conductivity and faster diffusion. These phenomena can also be seen from the phase plots (Bode plot) in Figure 3.18. Further information can be found in Appendix B. Some electrodes, here, do not reach a phase between 45° and 90° due to leakage or other parasitic effects, and their time constant at -45° phase may need to be considered instead (Bode plot in Figure 3.18).

At very low frequencies, based on the impedance equation (equation 3.4) in section 3.3.2, the leakage, the ionic and electronic resistances play a role in determining the total impedance (since the electronic resistance is negligible compared to ionic, it can be ignored). The main point to consider at this frequency is the slope of impedance plots in the Nyquist graphs, which is significantly affected by the leakage resistance (solving equation 3.4 in section 3.3.2 proves that). If this slope is -90°, then an ideal capacitive behaviour is shown, otherwise the response deviates from a straight line (parallel to the imaginary impedance axis) at low frequencies. This deviation, which partially is assumed to be due to leakage of electrodes, can also be affected by

capacitance distribution across the electrodes. This capacitance variation is estimated to be due to the non-uniformities of the sample, the pore sizes, and the pore distribution within electrodes. These factors are modeled by either having a leakage resistance ( $R_l$ ) in the transmission line (**Figure 3.20** in section 3.3.2) or by using a constant phase element (**Figure 3.23**, section 3.3.4) in place of the capacitors used in transmission line circuit of **Figure 3.20** in section 3.3.2.

Now that the modeling and experimental graphs are explained, the parameter values obtained from both are obtained and summarized in **Table 3.3**.

Samples	Tests	R <sub>l</sub> (Leakag e) (Ω)	Diffusion Coefficient (m <sup>2</sup> /s)	τ (s) along thickness (diffusion time)	C <sub>dl</sub> (F)	R <sub>ct</sub> (Ω)
	Model	6800	$2.25 \text{ x}10^{-14}$	8.71 x10 <sup>3</sup>	1.1 x10 <sup>-5</sup>	115.0
0 %	Exper <sup>1</sup> .	N/A	$(3.18 \pm 0.35) \times 10^{-14}$	$(5.81 \pm 1.03) \times 10^3$	N/A	N/A
	Model	1220	$2.11 \text{ x} 10^{-11}$	184.61	$2.6 \text{ x} 10^{-3}$	7.2
44 %	Exper.	N/A	$(2.63 \pm 0.18) \times 10^{-11}$	$156 \pm 22$	N/A	N/A
	Model	1380	$1.23 \text{ x} 10^{-10}$	17.92	18.0 x10 <sup>-3</sup>	11.5
54 %	Exper.	N/A	$(1.97 \pm 0.17) \times 10^{-10}$	$11.22 \pm 1.60$	N/A	N/A
	Model	1950	5.17 x10 <sup>-9</sup>	1.03	1.0 x10 <sup>-1</sup>	7.0
76 %	Exper.	N/A	$(6.23 \pm 0.45) \times 10^{-9}$	$0.86 \pm 0.12$	N/A	N/A
	Model	5700	6.41x10 <sup>-9</sup>	0.54	1.0 x10 <sup>-5</sup>	11.0
81 %	Exper.	N/A	$(7.48 \pm 0.57) \text{ x}10^{-9}$	$0.47 \pm 0.06$	N/A	N/A

**Table 3.3**. All parameters found from experiment and model-fit for all samples

 $Exper^{1} = Experimental$ 

The  $C_v$  values are found from CV experiments and  $R_l$ ,  $C_{dl}$ , and  $R_{ct}$  are found from the fit. The experimental diffusion values are calculated from  $\kappa$  values obtained from ionic conductivity measurements, from which the diffusion time constants are also calculated (section 3.3.2). It should be noted that the experimental  $\kappa$  assumed for EIS is the same as the one used for ionic conductivity measurements, and that is because there is no direct method of measuring the ionic conductivity using EIS experiments. When the  $\kappa$  values used from ionic conductivity measurements are compared against the  $\kappa$  values from the EIS model, it is concluded that the fit values are close to the  $\kappa$  values measured from ionic conductivity experiments. Hence, if we were able to measure the actual  $\kappa$  values for EIS, it would have turned out to be close to the ones we used from ionic conductivity measurements. The diffusion and time constant values from the EIS model are also very similar to the derived  $\kappa$  values from ionic conductivity measurements. It should be noted that the time constant value for the pure PPy sample may need to be divided by 4 (hence,  $1.45 \times 10^3$  s) if a two-sided ionic diffusion is considered, as to be explained in section 3.5.5. Comparing the experimental and modeling results from Table 3.3, a decreasing trend in time constant and increasing trends in diffusion and ionic conductivity are seen when going from 0 % to 81 % porosity. Since the experimental values found from EIS and ionic conductivity measurements are very similar for capacitance, ionic conductivity and diffusion, only the values from ionic conductivity measurements are chosen for investigating the enhancements achieved in charging time (reduction in time constant) as the porosity is increased (chapter 5). Also, along with that the trade offs in losing the capacitance in exchange of gaining high charging rate are also shown in chapter 5. It should also be noted that this charging time constant improvement might not be reliable if the solution time constant is limiting; hence the time constant values from diffusion and solution are compared in section 3.3.5. Before this however, the potential for improving the fits, specifically for pure PPy was investigated and it is explained in the following section (3.3.4).

#### 3.3.4 Improved Model

The first approach to improve the model in 3.3.2 (1-D model) is to add series resistances along the length to account also for the resistances charges may face along the length of the electrode (2-D model shown in Appendix D), rather than just the thickness. These extra resistances along the length may add to the limiting factors in ion transport and play a role in determining the time constant. It is found that this extended model does not improve the fit results; indicating these resistances to have only a minor effect on charge and ion transport. This minor effect is also seen x10<sup>-5</sup> calculating length (4.3)by the time constant along the s)

$$\Rightarrow \tau_{length} = \frac{R_2 \times Length \times C_{total} \times \sqrt{\frac{D}{\omega}}}{Length}, \text{ where } R_2 = \frac{Length}{\sigma \times L \times width}, \text{ D is the diffusion and } \omega = 2\pi \text{ x}$$

frequency), which is found to be much lower than the one along the thickness (~  $1.18 \times 10^4$  s).

The time constant along the thickness is therefore concluded to be the rate-limiting time constant. Hence, a fit from the 1D model suffices and provides a reasonable fit to the experimental results. The derivations of the time constant along length are in Appendix E.

The second model used to improve the fits, especially at low frequencies, includes a simple model of CPE in the form of a series of parallel resistor-capacitor branches added to the transmission line that was shown in **Figure 3.20**. These resistor-capacitor branches play the role of the CPE by accounting for inhomogeneity of the electrodes and the capacitance distribution (**Figure 3.23**). To solve the circuit, in place of  $\zeta$  (parallel resistor-capacitor branches used in **Figure 3.20**, we can include these added elements.



**Figure 3.23.** A more complicated circuit of **Figure 3.20**.  $C_{L1}$ ,  $C_{L2}$ , and  $C_{L3}$  are three different capacitors representing the inhomogeneity of the films and the paths ions should go through.  $R_{l1}$ ,  $R_{l2}$ ,  $R_{l3}$  represent the different leakage resistors corresponding to the resistance in the different chains along the thickness that lead to discharging of capacitors.

A sample fit for the pure polypyrrole with this new model is shown in **Figure 3.25** and the fit from the original model is also shown in **Figure 3.24**.



Figure 3.24. PPy fit based on equation 3.4 – 3.5 in section 3.3.2



Figure 3.25. Improved fit for pure PPy sample using model in Figure 3.23

Looking at both fits at low frequencies, the better fit from the improved model is apparent. The fit can even get better by adding more and more of these elements, but since reasonable results are obtained from the original fit from model in **Figure 3.20**, there is no need to make the circuit more complicated. Also, the physical interpretation of the fit numbers may be problematic if we are adding many of these resistors and capacitors. One way to justify the presence of these elements can be the varying resistances and capacitances across the thickness, which may be due

to the varying pore sizes, the non-homogeneity and varying thicknesses across PPy and the random distribution of fibers. One of the main factors to consider for the results and fits obtained is the rate-limiting factors that affect the time constant. As it was mentioned near the end of section 3.3.3, in order to verify the reductions in time constant, these rate-limiting factors should be investigated; the details are covered in the following section.

#### **3.3.5** Rate Limiting Factors in Ion Transport

The most important factors to discuss from sections 3.3.1 - 3.3.3 are the rate-limiting components in ion transport that are essential in determining the ionic conductivity of the electrodes and following that the charging time constant, and the diffusion coefficient. These rate-limiting components, which can be any of solution, ionic, electronic, charge transfer and contact resistances as well as thickness of the electrodes or separator or resistance due to parasitic reactions should be found and minimized. The main focus is on the rate-limiting resistances and a description is also given for the thickness effect at the end of this section (more details of thickness effect is in section 5.3 of chapter 5). Since it may not be apparent which resistance is the limiting one, all resistance values along with their time constants are found and compared. After finding all the resistance values, it is determined that the contact, the electronic and charge transfer resistances are all negligible and it is only necessary to compare solution and ionic resistance values to determine the rate-limiting element in charging. Hence, the values found for only these two are shown. The solution resistance value depends on the distance between the working and counter electrodes. Hence, it should be noted that if this distance is very large (e.g. more than couple of millimeters considering the cell and electrode sizes used here), the solution resistance may become much larger than the ionic or other resistances and the effect of these resistances or other factors in determining the electrodes ion transport behaviour cannot be detected anymore (their effect may be suppressed). For this reason, the aim in this thesis has been to minimize the distance between electrodes as much as possible (yet more reduction is required if any further time constant improvement is necessary as will be explained farther down this section) in order to prevent the suppression of other factors that may limit the ion transport rate. Since the solution resistance values found for different electrodes are different due to slight variations in the distance between working and reference electrodes, a series of other tests with a fixed reference and working electrode distance are performed to give a better approximation of the solution resistance. These tests are performed in EIS configuration using

the same setup and electrodes as before, except for the working electrode that is now stainless steel. Through these experiments (explained in Appendix H), a fixed solution resistance value of  $\sim 28 - 30 \ \Omega$  is found that is similar to the solution resistances estimated before for the cells having a distance of 2-3 mm between their reference and working electrodes. These solution resistance values are used to estimate the solution time constants for all electrodes. A comparison between the charging time constants found from ionic and solution resistances for all electrodes is shown in **Table 3.4** and **Figure 3.26**. Comparing these values, the dominant time constant for each electrode can be detected.

In order to check the validity of the solution and ionic time constants and to investigate the potential for the existence of other rate-limiting factors, actual time constant values from CV experiments are also determined. Based on these results, it is found that in some cases, other factors such as depletion of ions in the pores or resistance due to parasitic or Faradaic reactions or non-uniform geometry of electrodes may be limiting, but in terms of rate-limiting resistances, solution resistance is the most rate-limiting one for higher porosity electrodes. Values from CV experiments are also presented in **Table 3.4** and **Figure 3.26**.

Sample	0 %	44 %	54 %	76 %	81 %	91 %
$R_i(\Omega)$	$\frac{4.47 \text{ x} 10^3 \pm}{536.73}$	78.00 ± 11.54	10.22 ± 1.16	1.14 ± 0.05	0.66 ± 0.06	N/A
τ <sub>i_measured</sub> (s)	$(5.81 \pm 1.13) \times 10^3$	$156.00 \pm 34.03$	11.22 ± 2.21	0.86 ± 0.12	0.47 ± 0.06	$0.02 \pm 0.02$
$ au_{i\_model}$ (s)	8.71 x10 <sup>3</sup>	184.61	17.92	1.03	0.54	0.18
$\tau_s(s)$	$169.57 \pm 32.21$	54.35 ± 10.79	85.81 ± 18.15	$\begin{array}{r} 36.58 \pm \\ 6.80 \end{array}$	25.96 ± 3.75	$1.42 \pm 0.22$
$ au_{CV_1}$ (s)	$\begin{array}{r} 486.0 \pm \\ 78.8 \end{array}$	187.5 ± 31.0	92.5 ± 15.6	46.0 ± 7.1	32.3 ± 6.2	N/A
$\tau_{CV_2}(s) = \tau_{CV_1} \mathbf{x} \ 4$	1944.0± 315.2	$\begin{array}{c} 750.0 \pm \\ 124.0 \end{array}$	370.0 ± 62.4	$184.0 \pm 28.3$	129.2 ± 24.8	N/A

Table 3.4. Ionic and solution resistance and corresponding time constant values

$$\tau_i - measured = R_i C_{Total} = \frac{L^2 \times C_v}{\kappa} = \frac{L^2}{D} \rightarrow R_i = \frac{film \ thickness}{\kappa \times width \times length}$$
, where  $\kappa$  is measured from

ionic conductivity measurements (section 3.2) and D is the diffusion coefficient.  $R_s = \frac{d}{\sigma A} \rightarrow \tau_s = R_s C_{Total}$ , where d is the distance between reference and working and is measured each time for each test and  $\sigma_s$  is the measured solution conductivity (0.184 S/m) from ionic conductivity measurement and finally A is the area of the electrode exposed to solution. The time constants from CV experiments are found at 63 % of the total (peak to peak) current amplitude by dividing the delta voltage (voltage at 63 % of the total current amplitude - voltage at current of  $-\alpha C$  at steady state  $-\alpha C$  is the scan rate  $(\frac{dV}{dt})$  times capacitance, which corresponds to the initial current at time zero) by the scan rate. Two different  $\tau_{CV}$  values are shown in **Table 3.4** and  $\tau_{CV_2}$  is 4 times  $\tau_{CV_1}$  ( $\tau_{CV_1} = \frac{\Delta V}{\alpha}$ , where  $\alpha = \frac{dV}{dt}$ ). For CV measurements, it is sometimes assumed that diffusion of ions into the electrode is from both sides and only up to half of the thickness from each side. Depending on the uniformity of the structure of the electrodes, their pore distribution and pore sizes, and solution resistance on each side of the electrode, transport of ions might be through the whole thickness, up to half of the thickness or a mixture of both. Hence, we may not be certain about how far the ions have traveled through the thickness. Considering these assumptions, the time constant values obtained from CV measurements can be considered either as actual time constants when a 1-sided diffusion case is assumed (ions traveling all the way through the thickness) or as <sup>1</sup>/<sub>4</sub> of the actual time constants when a 2-sided diffusion case (ions are traveling up to half of the electrode thickness) is realized. If ion transport in CV experiments is considered 1-sided, then  $\tau_{CV I}$  values can be compared to the ionic and solution time constant values for which a 1-sided diffusion is also considered. If, on the other hand, the time constants from CV measurements are considered to be for a 2-sided diffusion case, then  $\tau_{CV}$  2 values, which are 4 times the  $\tau_{CV}$  1 values, should be used (Table 3.4).

In order to estimate which case may be more dominant in the experiments performed in this thesis, we found the solution resistance on each side of the working electrode in order to check the likelihood of a 1-sided or a 2-sided diffusion (experimental details in Appendix H). The results from the solution resistance experiments show that the solution resistance on the backside

(side facing against the reference and counter electrodes) of the working electrode is almost 10 times the solution resistance on the front side of the working electrode, suggesting that the one-sided diffusion dominates for these samples. Having a 1-sided diffusion, the time constant values obtained from CV measurements can be directly used as actual time constants without the need to be multiplied by 4. They can hence be directly compared to ionic and solution time constants. For the pure PPy case, since the ionic time constant is always higher than all the other time constants, the possibility of 2-sided diffusion may exist; hence, in that case, the  $\tau_{CV_{-1}}$  value may need to be multiplied by 4, as also shown in **Figure 3.26**. The values for all these charging time constants are plotted versus porosity % on a logarithmic scale as shown in **Figure 3.26**.



**Figure 3.26.** Log plot of time constant measured from CV experiments and calculated from both of ionic and solution resistance, all plotted vs. porosity %.

From both **Table 3.4** and **Figure 3.26**, it is seen that the ionic time constant is higher than the solution time constant for the 0 % and 44 % electrodes; hence, their corresponding ionic resistances are controlling the charging rate. The solution resistance dominates at higher porosity % electrodes (e.g. 81 %); hence ionic resistance no longer determines the time constants for those electrodes. Therefore, after a point, only solution resistance limits transport and hence the time constants cannot be improved any farther (given the same total capacitance and thickness) unless the solution resistance is reduced. To confirm these results, actual time constants from CV measurements are also shown in Table 3.4 and Figure 3.26. For the 0 % and 44 % electrodes, the CV time constants are shown to be higher than the solution time constants, similar to the ionic time constants obtained from ionic conductivity measurements. Two different CV time constants are shown for 0 % electrode; one corresponding to the actual value measured from CV measurements and the other to 4 times that measured value. The factor of 4, as mentioned, is due to the 2-sided diffusion of pure PPy. If the actual time constant for the pure PPy is to be compared with other measured CV time constants, it should be multiplied by 4. The CV time constant value obtained for the 0 % electrode may be an underestimation of the actual time constant since its CV graph has not reached a plateau. The CV scan rate (1 mV/s) used for the 0 % electrode is perhaps not slow enough to give enough time for the electrode to fully charge; hence, the current amplitude and the CV time constant based on that, would be lower than the case that the scan rate is slower. The fact that the ionic time constant of pure PPy is much higher than the actual time constant also implies the possibility of this underestimation. For porous samples (e.g. more than 50 % porosity), the CV time constants are approximately similar to solution time constants and higher than ionic time constants, again verifying that solution resistances are the dominant rate-limiting factor in these samples. At these porosities, the ions' transport is via the solution in the pores (solution resistance) rather than the solution in PPy layers (ionic resistance). Hence, solution resistance rather than ionic resistance limits the transport of ions. Up to the 44 % electrode, the decrease in ionic time constant suggests increase in charge/discharge rate as the porosity is increased. Beyond that point, since the solution resistance is rate determining, the decrease in ionic time constant may not be a sign for increase in charging rate.

For the case that the time constant cannot be improved further due to solution resistance limiting, the solution resistance ( $R_s$ ) should be decreased if any charging rate improvements are to be obtained. A factor required for reducing  $R_s$  values is assumed to be the distance between the reference and working electrode and in commercial supercapacitors the distance between the counter and working electrodes that should be minimized. The aim is to minimize the solution resistance  $R_s$  in order to make sure that it is not the rate-limiting element. Another method to decrease the solution resistance is to change the concentration of the electrolyte, reduce the electrolyte viscosity and to use a high conductivity solution [3]. In order to get an estimate of the reduction in  $R_s$ , solution resistance is assumed to be equal or smaller than the ionic resistance values used for more porous electrodes. The relationship between the two resistances is shown in equation 3.6.

$$R_{s} \ll R_{i}$$

$$\frac{l_{s}}{\sigma_{s}A} = \frac{l_{i}}{\sigma_{i}A} \rightarrow \sigma_{s} = \frac{l_{s}\sigma_{i}}{l_{i}},$$
(3.6)

where  $R_s$  is the solution resistance,  $R_i$  is the ionic resistance,  $l_s$  is the distance between working and reference electrodes,  $\sigma_s$  is the solution conductivity, A is the area of the electrode,  $l_i$  is the electrode thickness and  $\sigma_i$  is the ionic conductivity of solution in the pores and electrode layers. Based on this equation, the solution ionic conductivity and hence the solution resistance for all electrodes can be estimated. This estimate states that the solution resistance should be reduced down to less than or equal to ~ 0.7  $\Omega$  if an improvement in time constant is required for porosities more than 50 %. This reduction also enhances the power density of electrodes; details are in sections 5.2 and 5.3.

In two-electrode cells, where there is no reference electrode, reducing the separator thickness is perhaps a good way of increasing the power to mass ratio. This also helps to reduce the solution resistance and increase the ionic resistance compared to that. In that case, if still a further charging rate improvement is required, the electrode thicknesses should be reduced. These thicknesses should be minimized to help enhancing the time constant. The electrode thickness can be estimated based on ionic conductivity of electrodes and a known separator thickness and ionic conductivity, which are all related through equation 3.7 as follows:

$$\frac{l_{electrode}}{l_{separator}} = \frac{\sigma_{electrode}A}{\sigma_{separator}A} \rightarrow l_{electrode} = \frac{\sigma_{electrode}l_{separator}}{\sigma_{separator}}$$
(3.7)

where  $l_{electrode}$  is the electrode thickness,  $l_{separator}$  is the separator thickness (e.g. 12 µm),  $\sigma_{separator}$  is the ionic conductivity of the separator (e.g. 1.64 x10<sup>-2</sup> S/m),  $\sigma_{electrode}$  is the ionic conductivity of the electrode (values given in section 3.2) and A is the area of the electrode and separator. Based on this equation and the values mentioned for the separator, assuming the same area for the electrode and the separator, the maximum thickness that is required to provide the lowest charging time constant (0.026 s) for porous electrodes is 1.5 µm [60]. Further details of the separator and electrode thickness along with the effects they have on power and energy density are explained in sections 5.2 and 5.3.

Generally, in chapter 3, all the rate-limiting factors in ion transport were analyzed and experimental results were explained using proposed circuit models. It is found from all the investigations and experimental and modeling results that porosity enhances ion transport and charging rate up to a point after which the solution resistance starts limiting the rate of transport. In order understand the details of ion transport within our electrodes, nuclear magnetic resonance (NMR) measurements are also performed and described in the following chapter (chapter 4). It should be noted that in this chapter, it was also found that increase in porosity results in decrease in capacitance, which is not desirable. Hence, the trade offs should be considered and a balanced point covering both properties should be found, which are described in detail in chapter 5.

# **4** Nuclear Magnetic Resonance (NMR)

One of the methods to measure the rate of transport and diffusion of ions (e.g. hexafluorophosphate,  $PF_6$ ) and to learn about their behaviour within polymer or CNF chains is a technique called NMR spectroscopy, which is explained briefly in the following sections [61], [62]. NMR finds applications in several areas of science, such as chemistry, agriculture, food science and similar [61]. This technique is useful for detecting the number of ions that are mobile within an electrode and indicating if the expected mobile ion is in fact mobile. Lastly, NMR can give information about the varying diffusion coefficients an electrode may have, detected from diffusion experiments that are explained in section 4.3.2. The purpose in this research is to use a variety of NMR experimental methods (e.g. Diffusion, relaxation time and ion counting measurements) to study the ion environment and transport within electrodes with varying porosities. This information is compared with the ion transport results of chapter 3.

#### 4.1 **Principles**

NMR is a powerful spectroscopic technique used to study molecular structure along with physical, chemical, and biological properties of matter subjected to a magnetic field. This information is found through analyzing the interactions between the magnetic moments of the sample nuclei and the applied magnetic field [62]. NMR principles are based on the magnetic properties of nuclei, which possess intrinsic magnetic moments (Figure 4.1). These magnetic moments (arising from intrinsic nuclear spin) allow the observation of NMR absorption spectra caused by transitions between nuclear spin levels [63]. While fundamentally, NMR is a quantum phenomenon, the NMR experiments here may be understood from a purely classical explanation. The magnetic moments can be shown as vectors with two orthogonal components: a transverse component (in the X-Y plane) and a longitudinal or Z component perpendicular to that plane.



**Figure 4.1.** Magnetic moment represented as a vector with 2 components, one in the X-Y plane (transverse component) and the other perpendicular to that plane (longitudinal or Z component). The red line represents the vector that rotates about the Z-axis with a frequency close to resonance (Larmor frequency), when placed in a magnetic field  $B_0$ .

In a magnetic field, the nuclear spins tend to align preferentially along the direction of the magnetic field. This phenomenon is shown in **Figure 4.2**:



**Figure 4.2.** Left: nuclei of atoms that are randomly oriented with no field applied. Right: an external field is applied and the low energy states line up with the magnetic field applied and the high-energy ones line up opposite to the magnetic field [64].

Nuclear spins are found to obey the Bloch equations:

$$\frac{d\mu}{dt} = \gamma \vec{\mu} \times \vec{B},\tag{4.1}$$

in which  $\vec{\mu}$  represents the spin angular momentum of a nucleus,  $\gamma$  is the gyromagnetic ratio and *B* is the magnetic field experienced by the nuclei.

Net magnetization aligned along the static field stays there, but this equation shows that a component of magnetization perpendicular to the applied field will press around it, much like a gyroscope. The application of a pulse of oscillating magnetic field can be used to tilt an equilibrium magnetization from the field axis into the perpendicular plane if the oscillation frequency is close to the precession frequency ( $\gamma B_0$ ). A pulse that flips magnetization from the field axis into the plane perpendicular is known as a 90<sup>o</sup> pulse. A pulse that flips the

magnetization from along the field axis to opposite the field axis, is known as a  $180^{\circ}$  pulse.

A variety of other interactions can affect the behavior of nuclear spins, including chemical shielding, J-coupling, dipole-dipole couplings and nuclear electric quadrupole couplings. Of these, only the chemical shift plays an important role in the experiments performed here. Chemical shifts arise from the electronic structure of a molecule partially shielding the nuclear spins and result in slightly different resonance frequencies for nuclei in different chemical environments.

# 4.2 Experimental Setup

NMR measurements were made using a home-built NMR spectrometer based upon an 8.4 T superconducting magnet. Samples consist of 3 or 4, 4x8mm pieces of PPy or PPy/CNF films equilibrated at potential of 0.24V. Measurements were made on samples after either a short (10s) rinse or an overnight soak in neat PC. Spin counting experiments use either a small piece of Teflon, an NaBF<sub>4</sub>/ H<sub>2</sub>O solution or an Na<sub>2</sub>HPO<sub>4</sub>/H<sub>2</sub>O solution as a reference. Pulse widths of 90<sup>0</sup> were typically 7  $\mu$ s for <sup>19</sup>F and 4.5  $\mu$ s for <sup>31</sup>P<sub>0</sub>. The setup for the experiment consists of tuning capacitors, a probe station, a magnet and a computer workstation as shown in **Figure 4.3**:



**Figure 4.3.** General image of an NMR setup with the different components is shown [66]. The sample is placed in the tube that is also placed in the radio frequency coil. After that, proper connections were made depending on whether we want Fluorine or phosphorous measurements.

## 4.3 NMR Measurements

After preparing the samples, different measurements such as T1, T2, diffusion and ion counting are performed on the samples as explained in the following sections.

#### 4.3.1 T1, T2 Relaxation Times

Following an rf excitation pulse, the relaxation of nuclear spins towards thermal equilibrium is generally described by two separate relaxation phenomena, longitudinal (spin-lattice  $\rightarrow$ T1) relaxation and transverse (spin-spin  $\rightarrow$ T2) relaxation [63]. The time it takes for this relaxation is important for NMR, since it gives information about the dynamics and motion of spins. T1, which characterizes the longitudinal relaxation process, describes the rate at which the nuclear spin magnetization relaxes back along the z-axis to thermal equilibrium. In this relaxation, energy is transferred to the lattice and is released as heat or thermal vibration. This type of relaxation is mostly due to fluctuations in the local magnetic fields. It should be noted that the rates of T1 relaxation are dependent on the NMR frequency and so change with magnetic field strength, B0 [61]. The pulse sequence used for T1 measurements is presented in **Figure 4.4** 



Figure 4.4. Pulse sequence for T1 relaxation

This pulse sequence is called inversion recovery, in which initially a 180° pulse is applied that flips the equilibrium magnetization to the -Z axis. Then during the time constant  $\tau$ , the magnetization relaxes back towards equilibrium via spin-lattice relaxation. After time  $\tau$ , the magnetization is flipped into the X-Y plane by a 90° pulse and starts precessing around the Zaxis [69]. The equation describing the observed NMR signal as a function of time  $\tau$  is shown in equation 4.2.

$$y(\tau) = y_0 - 2y_1 \exp(-\tau / T1),$$
 (4.2)

where  $y(\tau)$  is the observed signal,  $y_0$  and  $y_1$  in principle represent the signal that would be observed following a single 90° pulse from a sample in equilibrium (ideally  $y_0 = y_1$ , but because  $\pi$  pulses usually fail to perfectly invert the magnetization,  $y_1$  is often slightly less), and T1 is the relaxation time.

T2, which characterizes the transverse relaxation process, is a decay constant describing the rate at which the nuclear spin magnetization comes out of phase (decoherence) in the transverse (x-y) plane. The initial phase coherence of nuclear spins is lost due to the varying precession frequencies of different spins, which is due to random fluctuations of the local magnetic field. It should be noted that T2 is always less than or equal to T1 [69]. T2 relaxation can be caused by the same mechanisms that cause T1 relaxation, but also by spin-spin exchanges, which do not require energy transfer to the lattice. The pulse sequence for T2 is shown in **Figure 4.5** 



**Figure 4.5.** Pulse sequence for T2 relaxation;  $\tau$  is the echo time.

This method of T2 measurement is called Hahn Spin-Echo, in which a 90° pulse is initially applied to flip the magnetization into the x-y plane. Then during the  $\tau$  delay, the magnetization evolves under chemical shifts, T2 relaxation and inhomogeneity in the static field. After time  $\tau$ , a 180° pulse inverts the magnetization so that at time  $2\tau$  the effects of chemical shifts and inhomogeneity are undone (spin magnetization is rephased).

The equation describing the T2 relaxation behaviour as a function of time 
$$\tau$$
 is:  
 $y(\tau) = y_0 \exp(-2 \tau / T2),$  (4.3)

where  $y(\tau)$  is the observed magnetization with echo time  $\tau$ ,  $y_0$  is the amplitude of the equilibrium magnetization, and T2 is the relaxation time.

Knowing the relaxation times provide information on the ion environment and on how fast spins "forget" the direction in which they are oriented. The T1, T2 values from the experiment

are obtained through fitting the experimental graph with the exponential equations 4.2 and 4.3. As an example, one sample fitting is shown for the 44 % sample:



**Figure 4.6.** T1 measurement for the 44 % sample by fitting the experimental data to equation 4.2; T1 is found to be  $1140 \pm 50$  ms.



**Figure 4.7.** T2 measurement for the 44 % sample by fitting the experimental data to equation 4.3; T2 is found to be  $2014 \pm 75$  us.

T1 and T2 values of all electrodes are found using the same method and they are all listed in

the following Table for all samples:

Sample	Pure	44 %	54 %	76 %	Pure CNF
	polypyrrole				
T1 (ms)	$822 \pm 36$	$1142 \pm 55$	$1050\pm48$	$272 \pm 18$	$2104 \pm 66$
T2 (ms)	$0.50\pm0.02$	$2.0\pm0.8$	$2.1 \pm 0.1$	$1.2 \pm 0.1$	$12.9 \pm 1.4$

 Table 4.1. Relaxation times for various samples

The T2 values are expected to be shorter (faster relaxation) for the ions in PPy or PPy/CNF than in bare solution, since the free rotation of molecules is hindered in the composites (slower motion of ions in pure PPy or PPy/CNF). This brings the fluctuation rate of the inter and intramolecular couplings that contribute to relaxation, closer to the resonance frequency where they are more effective at relaxing the spins. The relaxation, hence, occurs faster, resulting in a shorter T2. Based on this theory, T2 should be longer for more porous samples (slower relaxation), since the ions there are almost as free as they are in bare solution; therefore, here the T2 should increase as we go from pure PPy to pure CNF. This trend is seen in Table 4.1 for all the samples soaked in PC overnight. The 76 % sample that was soaked for 20 seconds, though, does not follow this trend. T2 should be smaller or equal to T1 as mentioned before and this is seen from Table 4.1 for the pure polypyrrole.

#### 4.3.2 Diffusion

Another phenomenon that is measured using NMR is the diffusion of  $PF_6^-$  ions within the sample. Similar to section 3.3, the diffusion coefficients are found for different porous samples to investigate the effect of porosity on ion transport and hence the charging rate. A brief description of the mechanisms of the diffusion measurement is initially given and further results are presented and analyzed to learn about the ion transport nature. A simple pulse program sometimes used for diffusion measurements is shown in Figure 4.8a. After the magnetization of the spins is flipped into the transverse plane by the first 90° pulse, a short and strong gradient G is applied along the Z–axis that makes the field become B (Z) = B<sub>0</sub> + GZ. The total applied field is then dependent on 'Z' and hence the precession frequency also varies along 'Z'. When the gradient is removed some phase variations exist between different spins along the Z-axis. Next, time  $\tau_{diff}$  is allowed for the ions to diffuse and then an opposite and equal gradient –G is applied.

If during the diffusion time, the atoms do not change their positions, the phase differences are reversed and the magnetization would be fully restored (relaxations neglected). If the positions of atoms are changed, the negative gradient finds them at different locations compared to the original and the phase differences will be reversed incorrectly. Therefore, a phase dispersion and loss of signal occurs in the sample at the end of the second gradient pulse.

Dispersion results in smaller signals. Faster diffusion leads to greater displacement during the diffusion time, resulting in greater signal loss. Measurements are made as a function of gradient strength and a detailed calculation shows that signal strength is expected to obey the following equation:

$$A(x) = A_0 \exp((\gamma \delta G)^2 (\Delta - \delta/3) D), \qquad (4.4)$$

where  $A_0$  is the signal amplitude, G is the gradient strength,  $\gamma$  is the gyromagnetic ratio,  $\delta$  is the finite width of the gradient pulse,  $\Delta$  is the diffusion time ( $\tau_{diff}$ ) in Figures 4.8a and 4.8b and D is the diffusion coefficient. The values for these parameters are shown in **Figure 4.10** and **Figure 4.11**.

The diffusion method explained is a simpler form of the diffusion used for this research. Because the T2 times of ions in our samples are shorter than the time required for diffusion to move the ions appreciable distances, two extra 90° pulses are applied in between the gradients to store the magnetization along the Z-axis for the diffusion delay and then to restore it to the x-y plane afterwards (Figure 4.8b). Two additional 90° pulses are applied at the conclusion of the sequence to again store the magnetization along z during the gradient ring-down. The two forms of pulse sequences are shown in 4.8a and 4.8b.



**Figure 4.8.** a) Simple diffusion measured with only one  $\pi/2$  pulse; b) Pulse sequence for NMR diffusion with extra  $\pi/2$  pulses;  $\tau_{T2}$  represents times during which the magnetization decays according to T2 and  $\tau_{diff}$  shows the time that it does not decay according to T2. During the  $\tau_{diff}$  time, magnetization is stored along the Z-axis and decays according to T1. Every time there is dephase and rephase, a gradient is also applied.

For diffusion measurements, the sample was again brought to a potential of  $\sim 0.24$  V and soaked in PC overnight; further, it was placed in the sample NMR tube and put in the NMR system. The experiment was then repeated as a function of the gradient strength as shown in **Figure 4.8**. The resulting spectrum for the 54 % sample, as an example, is shown in Figure 4.9.



**Figure 4.9.** Signal obtained from the diffusion experiment for the 54 % sample. The data from integrating this signal were saved in a text file, which could be later used with the diffusion equation to be explained to find the diffusion coefficient

The integral of the experimental spectrum is found and equation 4.4 shown before and 4.5 to be shown below are fitted to this integrated result. The diffusion coefficient in those equations is found through this fit. All the parameters in equation 4.4 except  $A_0$ , and D are fixed when fitting.

From the fittings, it is found that in most samples examined here, two diffusion coefficients seem to exist, which is not surprising for these porous samples. One diffusion coefficient corresponds to the diffusion of ions embedded in the PPy (slower diffusion) and the other to the ions in the solution in the pores (faster diffusion). Hence, knowing these, one can learn about the nature of ion transport across the thickness and how the time constant is distributed as a result. The diffusion in the PPy layers may also be different due to inhomogeneities of the samples and non-uniform structure. The effect of this inhomogeneity was also investigated in chapter 3, where a better fit of the model to the experiment requires considering the distributed capacitance (distributed time constant) and diffusion across the thickness of the sample that is created likely due to this inhomogeneity. In order to take the two diffusion coefficients into account, equation 4.4 is modified to incorporate two diffusion coefficient terms as shown in equation 4.5.

$$y = y1 \exp((\gamma \delta G)^2 . (\Delta - \delta/3) . D1) + y2 \exp((\gamma \delta G)^2 . (\Delta - \delta/3) . D2$$
 (4.5)

Fitting the experimental data with equation 4.5 (2-diffusion case of equation 4.4), the diffusion coefficient and signal amplitude of all the samples can be found. Diffusion experiments were

performed for all samples and as an example, diffusion fitting of the 0.05M NaPF<sub>6</sub><sup>-</sup> in PC and the 44 % sample soaked overnight in pure PC are shown in **Figure 4.10** and **Figure 4.11** respectively. The 0.05M NaPF<sub>6</sub><sup>-</sup> in PC fits the Gaussian function very nicely. The 44 % sample along with the other ones do not show a good fit as well as the 0.05M NaPF<sub>6</sub><sup>-</sup> in PC, since the short T2's of these samples have a very serious impact on the sensitivity, making the measurements very challenging.



**Figure 4.10.** Diffusion coefficient fitting of 0.05M NaPF<sub>6</sub><sup>-</sup> in PC using equation 4.4 along with the experimental data; single component fitting. D is in units if cm<sup>2</sup>/s. In place of G from equation 4.5, we have  $G = g_{max}$ . Voltage ( $g_{max} = 84.57$  and Voltage is a changing variable).



**Figure 4.11.** Diffusion coefficient fitting of 44 % sample, using equation 4.5 along with the experimental data; There are two diffusion coefficients used.

The two diffusion coefficients found using the fit from equation 4.5 are displayed as shown for each sample (all units are converted to  $m^2/s$ ) in Table 4.2:

Sample	Diffusion 1 (m <sup>2</sup> / s)	Diffusion 2 (m <sup>2</sup> / s)
0 %	$(3.31 \pm 3.10) \times 10^{-13}$	N/A
44 %	$(6.75 \pm 2.50) \times 10^{-11}$	$(5.08 \pm 3.80) \times 10^{-12}$
54 %	$(1.07 \pm 0.30) \times 10^{-10}$	$(7.81 \pm 4.40) \times 10^{-12}$
76 %	$(1.01 \pm 0.50) \times 10^{-10}$	$(5.33 \pm 13.70) \times 10^{-12}$
91 %	$(1.10 \pm 0.05) \times 10^{-10}$	$(7.92 \pm 0.80) \times 10^{-13}$

Table 4.2. Two different diffusion coefficients obtained for each electrode

As mentioned before, the lower diffusion coefficients are believed to correspond to the diffusion of ions embedded in the PPy and the higher to the diffusion of ions in the solution in the pores (as it was shown in Figure 4.10, the diffusion coefficient of bare solution with NMR

measurements is ~  $5.63 \times 10^{-10} \text{ m}^2/\text{ s}$ ). The non-uniformities in the sample structure, which can affect the ions accumulation and transport through different sample sections, can explain the two diffusion coefficients obtained. It might be surprising that our measurements observe two distinct diffusion coefficients for most samples but only a single T2 relaxation time. This is likely due to the fact that the pulse sequences used for the different experiments weight components with different relaxation times very differently. Specifically, the gradient encoding and decoding times in the diffusion pulse sequence dramatically suppress components having short T2 times. If there are lots of short T2 components, they may completely dominate the T2 measurement so that the long T2 component may contributes insignificantly. In the diffusion experiment, however, the long T2 component may contribute significantly.

The diffusion coefficient values from NMR and ionic conductivity measurements (section 3.2) are found in two different approaches; hence, in order to relate and compare them, a method linking the two should be used. This method is used to estimate the diffusion based on the drift velocity of the charged particles and the applied field and it includes using the Einstein relationship for calculating the diffusion coefficient. The Einstein relation for calculating diffusion coefficient is used as follows (equation 4.6) and it is derived in detail in Appendix C.

$$D = \frac{\mu_q k_B T}{q},\tag{4.6}$$

where  $\mu_q$  is the electrical mobility (charged particles move due to an electric field),  $k_B$  is the Boltzmann's constant, *T* is the temperature (e.g. 300 K) and *q* is the unit charge.

The mobility equation (4.7) may be written in terms of electrical conductivity and charge.

$$\mu = \frac{v_d(m/s)}{E(V/m)} \Rightarrow (m^2/Vs)$$

$$\sigma_i = qN\mu$$

$$\Rightarrow \mu = \frac{\sigma_i}{qN}$$
(4.7)

where  $v_d$  is the electron drift velocity, *E* is the electric field,  $\sigma_i$  is ionic conductivity, N is the number density of electrons and  $\mu$  is the electron mobility. A sample calculation showing how the values for these parameters are found is in Appendix C.

Combining this with the Einstein relation yields equation 4.8:

$$D = \frac{\sigma_i K_B T}{Nq^2} \tag{4.8}$$

Now, using equation 4.8, the diffusion values for the pure solution (0.1M TBAP/PC), the 81 %, 76 % and 54 % samples are presented in Table 4.3 for both the NMR (all samples soaked in pure PC overnight) and the Einstein relation results. A sample diffusion calculation for the 44 % electrode is shown in Appendix C and others follow the same procedure except that the volume fraction of polypyrrole is changed and consequently, the number of ions per volume and the mobility of ions is changed.

Sample	0 %	44 %	54 %	76 %	91 %	Pure Solution
Diffusion coeff. (NMR→ m <sup>2</sup> /s)	$(3.31 \pm 3.10)$ x10 <sup>-13</sup>	$(3.63 \pm 1.88)$ $x10^{-11}$	$(5.73 \pm 2.5) \times 10^{-11}$	$(1.01 \pm 0.50) \times 10^{-10}$	$(1.10 \pm 0.05)$ $x10^{-10}$	$(5.63 \pm 0.05) \times 10^{-10}$
Diffusion coeff. (Einstein Relation→m <sup>2</sup> /s)	2.95 x10 <sup>-14</sup>	2.35 x10 <sup>-11</sup>	3.73 x10 <sup>-11</sup>	4.70 x10 <sup>-10</sup>	4.89 x10 <sup>-10</sup>	4.94 x10 <sup>-10</sup>

Table 4.3. Diffusion coefficients of all samples obtained from NMR and Einstein Relation

As seen from the Table, the diffusion coefficients are increasing going from the pure polypyrrole to pure CNF indicating faster ion transport, as the material is more porous. The values used for NMR diffusion coefficients in Table 4.3 are obtained from Table 4.2. For more porous samples, as explained in section 3.2.3, since the diffusion is assumed to be mostly through the pores (details also in section 5.1), the diffusion values close to pure electrolyte diffusion (~  $5.63 \times 10^{-10} \text{ m}^2$ / s as found from NMR) are chosen as diffusion coefficients for those electrodes (ionic conductivity results for those porosities also show the same range of numbers as in Appendix G (Table G.1)). For less porous samples (e.g. 44 % and 54 %) that may have mix diffusion through both PPy and pores (details in section 5.1), the average of the diffusion coefficients in Table 4.2 are considered. For pure PPy, since the diffusion is more strongly weighted by the PPy rather than pores, only one diffusion coefficient is obtained from NMR as indicated in both Tables 4.2 and 4.3. These chosen NMR diffusion coefficient values are compared later in Appendix G (Table G.1) with those obtained from the ionic conductivity method. While the agreement between these techniques is not quantitative, they show similar

trends. The increasing trend in diffusion coefficient obtained from NMR going from 0 % to 91 % electrode is also seen in these electrochemical experiments, verifying the increase in charging rate for more porous samples. This level of agreement seems quite good given that the NMR measurements in most cases separate ions in solvent filled pores from those within the polymer, while the ionic conductivity results do not. The electrochemical experiments give a better approximation for the pure PPy diffusion coefficient (closer to value found in literature  $\rightarrow$  3.97 x10<sup>-13</sup> – 1 x10<sup>-14</sup> m<sup>2</sup>/s) compared to NMR [70], [17], [37]. It is not expected to get the right diffusion coefficient value from Einstein calculations for pure PPy, since the Einstein relation holds for solutions rather than a medium where there are lots of interactions between particles, such as pure PPy. Despite this fact, a reasonable value close to results from ionic conductivity measurements is obtained for the pure PPy as it is later shown in Appendix C and G.

#### 4.3.3 Phosphorous and Fluorine Ion Counting

The last measurement that was performed with NMR was an ion-counting experiment. The ions that are expected to be moving in and out of the samples during electrochemical characterization are  $PF_6^-$  ions. Chien-Hsin Tso, a Master's student at UBC Physics Department has previously confirmed this expectation in her paper called: "An NMR Study of  $PF_6^-$  ions in polypyrrole [17]." The purpose of this section is to identify the number of  $PF_6^-$  ions existing between the polypyrrole chains and in the pores to verify the expected abundance. Any loss or immobility of ions suggests that some charge flow may correspond to parasitic reactions rather than ion migration. One method to find if all the ions are present in the electrode and all are moving or not, is to compare the number of  $PF_6^-$  ions is expected to be the same for all the samples; hence, any difference indicates a loss or gain in ions. Based on knowledge from literature, one dopant ion (PF<sub>6</sub><sup>-</sup>) is transferred for every 3 or 4 pyrroles or monomers during deposition of the PPy sample [17], [71].

For the ion counting experiment a different NMR probe was used. This probe does not contain Teflon parts since a small piece of Teflon (0.0046 g) is used as a reference in the tube where the sample is and having another Teflon in the background affects the results. The purpose of having a reference Teflon piece is to find the number of Fluorines in the sample with respect

to the known number of Fluorines in Teflon. The experimental setup for ion counting is similar to other experiments and the Hahn Echo pulse program (**Figure 4.5**) is used as before.

Before any tests, samples are soaked in pure propylene carbonate either for 10 seconds or overnight. Both cases are tested to see if there would be any difference in the results. Due to some inconsistencies in the results (e.g. loss of  $PF_6^-$  ions), various tests were repeated several times, before and after soaking and electrochemical tests, to identify where ions might be escaping. Properties of these electrodes are in Table C.1 of Appendix C.

Two types of ion counting measurements were performed, one with varying echo delay as in the T2 measurements described earlier and the other with one single echo delay. For both the single and arrayed echo delays, two signals are obtained through the experiment, one corresponding to the Teflon (broader peak) and the other to the sample (narrower peak) as shown in **Figure 4.12** for the 54 % sample as an example.



**Figure 4.12.** Signals obtained from ion counting test for the 54 % sample. The broader peak is for Teflon and the narrower, shorter peak for PPy/CNF sample.

The goal is to find the number of  $PF_6^-$  ions inside the electrode from this spectrum. For this purpose, each peak is integrated using the NMR software (Xnmr). In the case of arrayed echo delay, an array of points is obtained, whereas in the single echo delay, only one point is obtained through integration. For the arrayed case, the points are fitted to the equation used for T2

measurement, except that the T2 equation has to be modified to incorporate two amplitude coefficients and two T2 values as in equation 4.9.

$$y(\tau) = y_1 \exp(-2\tau/T21) + y_2 \exp(-2\tau/T22)$$
(4.9)

Either each peak can be fitted to this equation separately and the resulting amplitudes can be used together, or one fitting can be used for both peaks. A sample fit to the integrated graph is presented here in Figure 4.13 for the 54 % sample; one fitting is used for both integrated peaks:



**Figure 4.13.** Ion counting fit for the 54 % sample using equation 4.9; T22 is the relaxation time for Teflon which was fixed to the value found for Teflon alone; the other parameters were varied until the best fit was obtained. T21 shows the relaxation time for CNF/PPy and y1 shows its signal intensity.

For fitting, all the parameters are varied except for the T2 of Teflon, which is fixed at 50.03 ms and is determined from a T2 measurement on the Teflon sample alone. The signal intensities of CNF/PPy and of Teflon are used to calculate the number of Fluorines in the sample (a sample calculation for the 54 % sample is shown in Appendix C and the results for other samples are shown in Table C.3 or C.4).

In order to make sure that the number of Fluorines in the TBAP/PC solution within the pores and layers of the samples is reliable when compared to the number of Fluorines in Teflon, Teflon was separately tested against a TBAP/PC solution of known (0.1 M) concentration. This calibration of the Teflon standard was performed by replacing the PPy sample with a known mass of 0.1M TBAP in PC. The number of Fluorines in the Teflon found this way was a factor of 2.14 less than would be expected from the Teflon mass alone. The reason for this is believed to be that Teflon is a semi-crystalline polymer and signals with different relaxation times arise from the crystalline and amorphous regions. In our experiments, signals from the crystalline regions are not observed due to the range of echo delays selected. Therefore, the Teflon peak was underestimated by a factor of 2.14 and has to be multiplied by this factor as shown in equation 4.10.

Not all results are presented here, but in Appendix C those results for overnight soaking are compared with 10 second soaking and some sample results for other cases are shown for comparison. Looking at Tables C.3 and C.4 in Appendix C, it is found that for pure PPy, the ratio of pyrroles to  $PF_6^-$  ions is close to literature value of 0.25 and in the same range, no matter how much soaking is done and how long electrochemistry tests are performed [17], [71]. For other samples that contain CNF, the ratios are expected to be similar to the pure PPy but they are much higher indicating some  $PF_6^-$  ions are lost from the samples. The ratios seem to be higher for those samples that are soaked overnight compared to those that are only soaked for 10 seconds. It is believed that this is due to the porous nature of the samples and their high surface area, which allows even small quantities of impurities to undergo redox reactions that consequently allow ions to escape. This phenomenon may also be due to the insertion of some ions from pure PC that may have replaced the  $PF_6^-$  ions.

Investigating samples before and after electrochemical tests, the number of  $PF_6$  ions seems to be decreasing after the first time an electrode goes through these tests. Although, this is only consistent 80 % of the time and may change depending on the soaking time and the length and number of electrochemical tests performed on the electrode. Also, any change in voltage or current applied during all the tests affect the number of ions that remain in the sample at the end. These factors may result in inconsistent behaviour of even the electrodes with the same porosity % (e.g. sample 1 of the 44 % gives a ratio close to 3, but sample 2 gives a ratio that is almost 50 times; more electrochemical tests were performed on sample 2; details in Table C.3 of Appendix C).

Other calibration standards were also used in place of Teflon. For example, NaBF<sub>4</sub> was used in place of Teflon to verify the results obtained using Teflon. In addition to tests with the NaBF<sub>4</sub> standard, other experiments (e.g. phosphorous measurement with Na<sub>2</sub>HPO<sub>4</sub> standard) were also performed to assure the validity of Fluorine measurements through comparing its ratio with the phosphorous ratios obtained by phosphorous measurement. Some sample results will be presented for both NaBF<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> tests (Appendix C). The number of  $PF_6^-$  ions and the pyrroles and the ratio between the two along with the corresponding explanations and calculations are also in Appendix C.

The NMR experiments described would be much less sensitive to ions in a "solid-state," which were unable to tumble. The possibility that some ions were so immobilized that they were not detected was considered and to investigate this possibility, we performed phosphorous NMR experiments with Fluorine decoupling. Immobilized ions would lead to very broad <sup>31</sup>P spectra due to dipolar couplings with the surrounding Fluorines. These couplings however may be removed by applying a strong continuous excitation to the Fluorines while observing the <sup>31</sup>P [72]. The decoupling test was used on the 54 % sample, since it showed the least number of Fluorines compared to other electrodes in the other ion counting tests. For the decoupling test, the 54 % sample was soaked overnight and was tested with and without 19F decoupling. The 19F decoupling did not appreciably change the number of ions found, suggesting that the more straightforward experiments did observe all of the ions present. But, the number of ions shown from these experiments with decoupling is still far less than expected, perhaps due to the reasons mentioned before.

In order to verify some of the ratios obtained for samples, EDS tests were done as was explained in chapter 2. Further comparison of NMR results with other EDS or electrochemical characterizations are presented in Appendix A and C.

## 4.4 Summary

Initially, T1 and T2 measurements were required to find the relaxation time needed for ions in both the ion counting and diffusion measurements before the signal is retrieved. Further, diffusion measurements were performed. The main purpose of the NMR measurements was to find the diffusion coefficient of samples. Some samples as was explained have two diffusion coefficients, the higher one corresponding to diffusion in solution in the pores and the smaller one to diffusion inside PPy. The non-uniform structure of electrodes and pores also affect the mobility of ions, which in turn affects the diffusion coefficient. This phenomenon was also seen in the EIS models in chapter 3.

The last measurement was ion counting, from which it was found that there is no consistency seen in the number of  $PF_6^-$  ions found for the different tests and different soaking periods. This was not true for the pure PPy, but rather true for the porous samples (PPy/CNF). This phenomenon for the PPy/ CNF may be due to their high surface area that makes them more susceptible to loss of ions, possibly due to some as-yet not understood parasitic reactions. Electrolyte condition, sample condition, oxidation state, number of electrochemical tests (cycles), and the amount of time that the porous sample is left in the solution after the tests all are seen to affect the number of of  $PF_6^-$  ions expected can be calculated from charge from current using similar calculations that were done for  $PF_6^-$  mass calculation in chapter 3, section 3.1.2. Those calculated numbers would not necessarily be the same as the numbers found from NMR, due to factors such as cycle time or soaking time of electrodes that were mentioned to affect the number of  $PF_6^-$  ions.

Having the diffusion coefficient of all samples from NMR, the results can be compared to the diffusion coefficients obtained from the electrochemical characterization, namely EIS and ionic conductivity (IC), which this is done in Appendix G.

# **5** Discussion and Conclusions

The purpose of this section is to bring together results from all characterization methods and circuit models (chapters 3 and 4) to perform an overall final analysis of the effect of porosity on each parameter (e.g. capacitance, ionic conductivity, diffusion and time constant) and the effects of each parameter on the other. Also, the aim is to make conclusions about rate limiting factors, how they can be minimized and how that affects the power to mass ratio. Further, suggestions are made regarding future work for power enhancements while maintaining at least the same energy density. Finally, the usefulness of the porosity approach along with its significance for supercapacitor applications are summarized. Through the analysis of the effect of porosity on each parameter and considering the trade offs resulting from changes in each parameter, the validity of the hypothesis can again be checked both theoretically and experimentally. The hypothesis as mentioned in chapter 1, stated that increase in porosity results in enhancements in ion transport and reduction in charging time, but decreases the volumetric capacitance in exchange. For this chapter, initially, a theoretical relationship between parameters is given and further results from all experimental methods are compared to verify these relations and to be checked with the hypothesis.

### 5.1 Charging Rate Improvements and The Trade Offs

In this section, having in mind the hypothesis, the theoretical relationships between factors affecting the electrode film energy and power densities are explained and further compared with the experimental results. There are two main factors to consider, namely capacitance (both volumetric capacitance and specific capacitance) and time constant (which is related to charge/discharge rate and hence, power density). In this thesis the focus has been on reducing the time constant related to mass transport within electrodes by increasing the porosity. Time constant is both related to the resistance inside pores and in PPy and to the volumetric capacitance and thickness of the electrodes. All these parameters are dependent on the resistance inside pores and the effects that porosity has on them and consequently on the charging time constant should be investigated. In previous chapters, these effects were experimentally figured by ionic conductivity and NMR experiments (chapter 3 and 4). They are now to be checked also

theoretically.

Initially, the charging time constant is estimated by considering the resistances inside pores and in PPy (which affect the rate of transport of ions and charging) and assuming a fixed capacitance and thickness. The total capacitance is also considered along with the resistance to constant as  $\tau_{i-\exp ected-combined} = R_{i-\exp ected-combined}C = \frac{l^2 C_v}{\kappa'}$ , where obtain the ionic time  $au_{i-expected-combined}$  is the expected ionic time constant in pores and PPy,  $R_{i-expected-combined}$  is the expected ionic resistance inside pores and PPy, C is the total capacitance, l is the thickness of the electrode,  $C_{\nu}$  is the volumetric capacitance and  $\kappa'$  is the effective ionic conductivity. The effective ionic conductivity is estimated based on ionic conductivity in pores ( $\kappa_{electrolyte}\gamma$ ) and in PPy ( $\kappa_{PPy}(1-\gamma)$ ), with  $\kappa_{electrolyte}$  being the conductivity of electrolyte in the pores (these ionic conductivity concepts were explained in section 3.2.3) and  $\kappa_{PPy}$  to be the ionic conductivity in PPy. The ionic conductivity that we measure by ionic conductivity measurement (section 3.2) includes both of these ionic conductivities. The expression for this new ionic conductivity ( $\kappa'$ ) is  $\kappa' = \kappa_{PP_v}(1 - \gamma) + \kappa_{electrolyte}\gamma$ . For this thesis, the conductivity of ions in the pores is assumed to be the same as the bulk electrolyte conductivity (e.g. 0.184 S/m), very much greater than the ionic conductivity in PPy ( $\kappa_{PPy}(1-\gamma) \ll \kappa_{electrolyte}\gamma$ ), meaning most ions are traveling through the pores rather than through PPy (Figure 1.1; continuous and relatively uniform pores are assumed). The expected resistance of ions in the pores and the resulting time constant is shown in the model of equation 5.1:

$$R_{i\_expected} = \frac{l}{\kappa_{electrolyte}\gamma A} \rightarrow \tau_{i\_expected} = \frac{l^2 C_{\nu}}{\kappa_{electrolyte}\gamma},$$
(5.1)

where  $R_{i\_expected}$  is the expected ionic resistance inside pores, *l* is the thickness of electrodes,  $\kappa_{electrolyte}$  is the ionic conductivity inside pores, A is the area of electrodes and  $\tau_{i\_expected}$  is the charging time constant inside pores.

In order to check if the assumptions in equation 5.1 hold for all electrodes, the expected ionic resistances inside pores for all electrodes are compared to the measured ionic resistances (including resistances in both pores and PPy; section 3.2). Based on this comparison (Appendix B, **Table B.3** and **Figure 3.15**), it is found that the measured and predicted resistance values at

very high porosities (e.g. 76 % and 81 %) are very similar, suggesting the ions are mostly traveling through the pores as predicted and their transport is now mainly limited by the resistance in pores. For porosities less than about 50 %, the ionic resistances measured are shown to be much higher ( $\sim$  10 to 40 times from **Table B.3**) than the expected ionic resistances, indicating that some ions are traveling also through PPy. Even though the ionic resistance is higher than expected at these porosities, it is still nearly three orders of magnitude lower than that of pure PPy films. However, the charging times of these electrodes cannot be quantitatively explained with the model in equation 5.1. The reason for the mismatch of the resistance and time constant values may be a result of the violation of some of the assumptions made for ionic transport within our electrodes.

These assumptions are also considered when deriving time constant models similar to equation 5.1 that account for capacitance and thickness changes in the electrodes as well. Equation 5.1 predicts that as porosity increases, the time constant decreases, both because the volume fraction of electrolyte with its high conductivity increases, but also because Cv (which depends upon porosity) decreases (**Figure 3.6**). To address our hypothesis however, equation 5.1 will be restated to allow prediction of time constant as a function of porosity for electrodes of either fixed total capacitance or fixed thickness. Increasing porosity results in a decrease in the volumetric capacitance (small decrease compared to pure PPy as mentioned in **Figure 3.6**), which is not desired due to a resulting decrease in energy storage capacity per volume. Also, if a fixed capacitance is assumed, changes in thickness and the resulting changes in time constant should also be considered. Before deriving time constant models that include these factors, the assumptions that were referred to above and are used in the derivations are outlined as follows:

- Our electrodes are assumed to contain pores that extend through the sample and relatively homogeneously distributed; hence, any dead-end pores or various pore sizes or pore distributions or tortuosity are not accounted for in the models to be presented (pore size effect can be explained in very porous samples).
- 2) The time constant assumed for charging through the thickness of PPy on carbon nanofibres is short compared to charging through the entire electrode.

- 3) Tortuosity effects are not accounted for in the models presented. This relates back to the structure of the electrodes. Pores do not extend straight through the electrode. This affects the rate of transport, especially for less porous samples, where ions are more likely to follow tortuous paths. Even for more porous samples, there may be rough and non-uniform paths through which ions have to pass.
- 4) Ion transport is by migration rather than diffusion. At charged states, usually PPy may pull some ions inside, leading to depletion of ions outside. This leads to a higher concentration of ions within PPy, which results in concentration gradients that may cause diffusion.

As was mentioned before, two cases of the model in equation 5.1 should be considered to account for thickness or capacitance changes. The first model for the charging time constant accounts for capacitance changes at a fixed thickness. The model accounts for changes in volumetric capacitance with respect to porosity; hence using  $C_{v_{-effect}} = C_{v_{-}ppy}(1-\gamma)$ , where  $C_{v_{-}effect}$  is the effective volumetric capacitance including the porosity fraction  $\gamma$ , and  $\gamma$  is the porosity fraction ( $\gamma$ =0 for a dense electrode with no pores). Considering all these, the resulting time constant is as follows:

$$\tau = \frac{l^2 C_{\nu_p py} (1 - \gamma)}{\kappa_{p Py} (1 - \gamma) + \kappa_{electrolyte} \gamma}$$
(5.2)

Similar to equation 5.1, the model in equation 5.2 again holds for very porous electrodes and it also indicates that for a fixed thickness, the time constant decreases as porosity increases. On top of that, the model in equation 5.2 also shows the decrease in capacitance for a fixed thickness, as the porosity is increased. The trade offs in capacitance and time constant with porosity, assuming a fixed thickness, are also shown in **Figure 5.1**. The experimental values obtained for each of these parameters at different porosities also show the same values and trends as the expected values in **Figure 5.1**.






Figure 5.1. a). Logarithmic plot of equation 5.2 and  $C_{v_{-effect}}$ , showing expected trade offs for the capacitance and time constant as porosity increases; b) linear scale plot of this logarithmic plot.

a)

**Figure 5.1**. amounts to the theoretical prediction of our hypothesis, which states that the capacitance and the time constant are decreasing as the porosity is increasing. Figure 5.1 shows that even a small amount of porosity (with uniform pores that penetrate straight through the material) makes a huge reduction in  $\tau$  with a minor penalty in capacitance. Comparing these data to the experimental data (similar values and trade offs are seen in the experimental results as in **Figure 5.2**), they seem to fit relatively well at high porosity, but not so well at low porosity, most likely due to the fact that at low porosity, the pores do not penetrate completely through the film. Other reasons for the mismatch at lower porosities could be due to the 4 assumptions mentioned before. For very porous electrodes, the expression  $\kappa_{PPy}(1-\gamma)$  can be omitted from the denominator of equation 5.2; hence, accounting only for the transport of ions through pores.

The second model derived from equation 5.1 assumes a fixed total capacitance, achieved by changing the thickness to compensate for the reduced Cv with porosity-increase. As mentioned, experimentally, our capacitance values are decreasing with porosity-increase, but their decrease is insignificant compared to significant reductions in charging time constants (sections 3.2 and 5.2). In order for the capacitance  $(C = C_{v_{-}PPy}Al)$ ; where A is the electrode area and l is the electrode thickness) to be fixed and assuming  $C_{v_{-}PPy}$  is only dependent on the amount of PPy, and that Area is fixed, then the thickness l, needs to be increased as porosity is increased. This is with the assumption that  $l = \frac{l'}{1-\gamma}$ , which leads to the capacitance to be  $C = C_{v_{-}PPy}A\frac{l'}{(1-\gamma)}$ , where l' is the new thickness needed to compensate for the increase in porosity. The capacitance of a porous film can then be written as  $C_{v_{-}effect} = C_{v_{-}PPy}(1-\gamma)$ , as in equation 5.2 and its thickness as  $l = \frac{l'}{1-\gamma}$ . In each case,  $C_{v_{-}PPy}$  and l' is a constant. The time constant derived for this second model is shown in equation 5.3:

$$\tau = \frac{l'^2 C_{\nu_{-}ppy}(1-\gamma)}{(1-\gamma)^2 \kappa'}$$
(5.3)

Again, assuming  $\kappa_{PPy}(1-\gamma) \ll \kappa_{electrolyte}\gamma$ , the model of equation 5.4, can be re-written as follows with  $C_{v_{-}PPy}$ , l' and  $\kappa_{electrolyte}$  all being constant:

$$\tau = \frac{l'^2 C_{\nu_{-}ppy}(1-\gamma)}{(1-\gamma)^2 \kappa_{electrolyte} \gamma}$$
(5.4)

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Similar to what was found for ionic resistance values and time constants of equation 5.1, this model again holds for very porous electrodes. Considering equations 5.2, 5.3 and 5.4, an optimum porosity and thickness point should be found that makes charging faster without overly reducing capacitance. Based on these equations, the time constant reduces with reduction in volumetric capacitance, assuming a constant thickness and ionic or solution conductivity. Since reduction in volumetric capacitance is not desired, time constant reduction should be achieved through decreasing the thickness instead. Reduction in thickness is preferable to increase the power, which again is not desirable due to decreasing the energy density (equation 5.5. in section 5.2). Hence, perhaps the best method to maintain both a high volumetric capacitance (e.g. avoid using maximum porosity) and a low thickness is to stack layers of electrodes together to increase the active surface area. The thickness and porosity can be adjusted to give the designated optimum performance, with the tradeoffs determined (qualitatively at least). All the mentioned models can suggest how to design a fast capacitor in situations where the models hold.

As mentioned in assumption number 1, equations 5.1, 5.2 and 5.4 explain the effect of pore sizes at very porous electrodes. It is found that for very porous electrodes the effect of pore size is, perhaps, not too much significant and it is not affecting the rate of transport of ions. This is verified when the measured ionic resistances for those samples match the corresponding expected ionic resistances. For this reason, it was concluded that equations 5.1, 5.2 and 5.4 hold for those very porous samples. Ions for these electrodes are assumed to travel mostly through pores across the electrode thickness (choosing the least resistant path). If, on the contrary, these ions are transported through PPy due to, for example, facing a dead-end or a small pore or a path blockage, their transport may be slowed down and the model in equations 5.1, 5.2 and 5.4 would not hold anymore. This is true for less porous samples (e.g. 44 %), where their measured ionic resistances are higher than the expected ionic resistances. One potential reason can be that the pore sizes are so small that interacting with pore walls is slowing down the ion transport. The presence of this issue is investigated in very porous samples via NMR. NMR diffusion coefficient results for ions in the pores of very porous samples are compared to the diffusion coefficient of ions in the pure solution (Table 4.3). Through this investigation, the diffusion coefficients from both cases are found to be very similar for very porous samples, suggesting the behaviour of ions in pores to be very similar to their behaviour in bulk solution. This indicates that most ions in very porous samples are basically traveling through pores as it was also shown

with the measured and expected ionic resistances. This again explains why models in equations 5.1, 5.2 and 5.4 hold for very porous samples.

One other factor that is not accounted for in the models and should be considered when analyzing charging times for electrodes, is the existence of very large pores in our electrodes (violates assumption number one). There may be a case where there are lots of small size pores and one or two very large pores. All ions may go through the large pore, since it has the least ionic resistance. The pores in our electrodes are assumed to be in parallel and hence, the maximum resistance that they can have is always equal to the minimum value, which, here, is the ionic resistance value of the larger pore. This small ionic resistance provides a small ionic time constant compared to other pores, but that does not necessarily determines the charging time of the entire electrode. The electrode starts charging up from one side of the thickness and each subsequent section is charged later than the previous section. So, by the time the next section is charged, the previous section may have started discharging. For this reason, there is a time constant distribution across the electrode thickness, which may rather determine the actual charging time constant of the entire electrode compared to the ionic time constant from the larger pore.

Analyzing the ionic time constants found from corresponding expected or measured ionic resistances (section 3.3.5 and Appendix B, **Table B.3**) for very porous electrodes, they are found to be very small as predicted by the hypothesis, but are not representing the charging time for the entire cell. As was mentioned in section 3.3.5, after certain porosity (e.g.  $\sim 50$  %), the solution resistance limits the rate of transport of ions rather than ionic resistance in the electrodes (as shown from both measured solution and CV time constants (section 3.3.5, **Figure 3.26**)). Hence, the solution resistance mainly determines the time constants obtained for these porous electrodes in this cell geometry. For these electrodes, any further reduction in time constant is achieved by reducing the electrolyte resistance (to at least as small as the ionic resistance) or the separator thickness, which are described as future works in (section 5.3). Assuming that solution resistance and other sources of resistance can be reduced so that ion transport within the electrode is still a key rate-limiting factor, then there are implications for improvements in the design of devices.

Up to this point of this section, the theoretical relationships between various parameters affecting speed and energy capacity per volume are investigated. In order to see if all the proposed models hold for all the experimental results, all the experimental parameters are compared to investigate if the same changes predicted from models are seen in the results. For this purpose, the fractional changes in each parameter with porosity compared to pure PPy is shown in Table 5.1. Actual parameter values are presented in Table G.1.

<b>Table 5.1.</b> Ratios of volumetric capacitance, time constant for ionic transport within the
electrode, and effective diffusion coefficient resulting from ionic conductivity for all electrodes
compared to the pure polypyrrole (0 % porosity), based on the experimental results of chapter 3.

Sample	Ratio of C <sub>v</sub> (w.r.t. 0%)	Ratio of ionic conductivity (w.r.t. 0 %)	Ratio of ionic transport charging time (w.r.t. 0 %)	Ratio of Diff. Coeff. from ionic conductivity (w.r.t. 0 %)
0%	1	1	1	1
44%	0.42	$3.27 \text{ x} 10^2$	$2.68 \text{ x} 10^{-2}$	$7.79 \text{ x} 10^2$
54%	0.30	$1.76 \text{ x} 10^3$	1.93 x10 <sup>-3</sup>	$5.84 \text{ x}10^3$
76%	0.14	$2.62 \text{ x} 10^4$	1.48 x10 <sup>-4</sup>	1.85 x10 <sup>5</sup>
81%	0.12	$2.76 \text{ x} 10^4$	8.09 x10 <sup>-5</sup>	$2.22 \text{ x}10^5$
91%	0.015	$2.84  ext{ x10}^4$	3.44 x10 <sup>-6</sup>	$1.93 \text{ x} 10^6$

The ratios presented in Table 5.1 are also shown in a logarithmic graph (Figure 5.2) consisting of the ratio of each parameter with respect to pure PPy vs. electrode porosity %.



**Figure 5.2.** Logarithmic graph including fractional ratio of time constant (based on measured ionic resistance), ionic resistance based diffusion coefficient and NMR-based diffusion coefficient, ionic conductivity (from migration) and volumetric capacitance with respect to (w.r.t.) pure PPy (0% electrode). The thicknesses of the electrodes are not exactly the same; hence, the time constant values are not expected to necessarily behave in any particular pattern.

As seen from Table 5.1 and Figure 5.2, and as mentioned in each previous chapter, the volumetric capacitance and ionic transport charging time constants are decreasing going toward electrodes with higher porosity % and the ionic conductivity and diffusion coefficients (from ionic conductivity measurement method that works based on migration and from NMR) are increasing (faster ion transport and hence faster charging). The ionic charging time constant and diffusion coefficient values shown here are found based on ionic resistance (resistance inside pores and PPy) values for all electrodes. The ionic time constants and diffusion coefficients are decreased by ~ 37 times and increased by ~ 779 times respectively going from a non-porous sample (0 %) to the least porous sample (44 %). The improvement in charging time constant and effective diffusion for the most porous (81 %) electrode compared to the least porous (44 %) electrode is ~ 332 and ~ 87 times respectively. Finally, these parameters for 81 % electrode compared to 0 % have decreased by ~ 1.2 x10<sup>4</sup> times and increased by 2.2 x10<sup>5</sup> times

respectively. All these ratios indicate a massive improvement for both the time constant and diffusion coefficient produced by increasing porosity. The estimated improvements in both of these parameters indicate a huge enhancement in ion transport and as a result the charging rate. Another factor showing a decrease in ionic time constant is the increase in the ionic conductivity (increased by  $2.8 \times 10^4$  times for the 81 % electrode compared to 0 %), which grows with almost the same rate as diffusion. The reduction in time constant results in speed enhancements, which are desired for supercapacitor improvements. This could probably be improved on if the detailed pore structure could be controlled.

Despite all these improvements, it should be noted that based on what was explained in section 3.3.5 and at the beginning of this section, there are limiting factors in ion transport that affect the time constant of the entire cell. Although, the ionic resistances (and time constants) at very high porosities are shown to be very small; hence creating an easy and fast path for ions' transport, the transport of ions is limited by solution resistance at those porosities. Despite this fact, even if the time constant improvements at very low porosities are considered, still huge speed (and power) improvements are seen compared to pure PPy (with minimal size penalty) (**Figure 5.1**).

As explained based on theoretical models of equations 5.1 - 5.4, the experimental results (Table 5.1 and **Figure 5.2**) also show that the trade off in getting a lower time constant is the loss of volumetric capacitance, which is not desired. The amount, by which the capacitance decreases, though, is small compared to the amount of increase in time constant (Table 5.1 and **Figure 5.1**). For instance, the decrease in volumetric capacitance for the 44 % compared to 0 % electrode is almost 2.4 times, but the decrease in time constant is ~ 37 times, hence the amount of capacitance loss is small compared to reduction in charging time constant. This gives an optimum point where both fast ion transport is provided and high capacitance is maintained. The same trend is true for other porous electrodes as well. The porosity increase, also increases the ionic conductivity and effective diffusion coefficient, which are found to grow at much higher rates compared to the amount of loss in volumetric capacitance (Table 5.1). Considering the optimum point between time constant and capacitance, the optimum power and energy densities can be estimated as explained in the following section (section 5.2).

The diffusion coefficient ratios that are shown in Figure 5.2 are found based on both ionic conductivity measurements and NMR. The actual values of these diffusion coefficients are shown in Appendix G (Table G.1) to be compared with diffusion values found from NMR method. The diffusion from NMR cannot be directly compared to the values found from the ionic conductivity measurement method since each is using a different approach to find the diffusion coefficient. In NMR, we are measuring the actual diffusion of ions that is driven by heat, whereas in ionic conductivity, we are measuring the diffusion by applying an external field that forces the ions to move. Despite this fact, the diffusion values from both methods seem to be in good agreement in terms of increasing with porosity-increase, but for all the electrodes the diffusion values from ionic conductivity measurements are higher than NMR diffusion values (Table G.1). At low concentrations, the diffusion from ionic mobility can be related to the real thermal diffusion coefficient through Einstein relationship. As was shown in section 4.3.2, **Table** 4.3, the values found from Einstein relationship almost matched the NMR values. One last point to note about the differences in results from NMR and ionic conductivity measurements is that NMR measurements in most cases separate ions in solvent filled pores from those within the polymer, while the ionic conductivity results do not.

### 5.2 **Power and Energy Density Estimation**

Using an optimum point where time constant is low and volumetric capacitance is quite high, we can obtain electrodes with high speed (power to mass ratio) while maintaining at least the same energy storage capacity per volume (energy density) or energy per mass (specific energy), which were the original goals of this thesis to enhance supercapacitors. The absolute power and energy (as well as energy and power values with respect to mass and volume) for all electrodes are investigated by using values in Table 5.1 and expressions in equation 5.5 as follows:

$$C = C_{v}Al$$

$$E = \frac{1}{2}CV^{2} \rightarrow E = \frac{1}{2}C_{v}AlV^{2}$$

$$E_{vol} = \frac{1}{2}C_{v}V^{2} \text{ or } E_{mass} = \frac{1}{2m}C_{v}AlV^{2}$$

$$\tau = R_{i}C = \frac{l}{\kappa A} \cdot C_{v}Al = \frac{l^{2}C_{v}}{\kappa} , \qquad (5.5)$$

$$P = \frac{E}{\tau} \rightarrow P = \frac{A\kappa V^{2}}{2l}$$

$$P_{vol} = \frac{\kappa V^{2}}{2l^{2}} \text{ or } P_{mass} = \frac{A\kappa V^{2}}{2lm}$$

where *C* is the total capacitance,  $C_v$  is the volumetric capacitance, *A* is the electrode area, *l* is the electrode thickness, *E* is the energy of electrode, *V* is the delta voltage used in CV experiments,  $E_{vol}$  is the energy per volume,  $E_{mass}$  is the energy per unit mass of the cell, *m* is the mass of the electrode,  $\tau$  is the time constant,  $R_i$  is the ionic resistance within electrodes,  $\kappa$  is the ionic conductivity, *P* is the power of the electrode,  $P_{vol}$  is the power per volume of the cell and  $P_{mass}$  is the power per unit mass of the cell. If the power and energy densities calculated for our electrodes are going to be compared to those of commercialized supercapacitors, we should consider a symmetric supercapacitor that consists of two same electrodes (e.g. PPy for both electrodes), one being the negative electrode and the other the positive. Using this approach (rather than only considering a single electrode), we are doubling the mass. This way the total operating voltage of the cell is the same as the voltage that was used for a single electrode in our CV measurements. During discharge, each electrode starts from either extreme of the total voltage (e.g. 1.2 V) and comes to a voltage of zero (e.g. one electrode starts at -0.6 V and the other at 0.6 V and they come to meet at 0 volt). This is shown in **Figure 5.3** as follows:



Figure 5.3. Voltage diagram representing a full cell with two identical electrodes (e.g. PPy)

The energy that is calculated in this case would be as shown in equation 5.6:

$$electrode1: E_{1} = \frac{1}{2}C_{1}(\frac{V}{2})^{2}$$

$$electrode2: E_{2} = \frac{1}{2}C_{2}(\frac{V}{2})^{2}$$

$$E_{mass\_total} = \frac{1}{2}C_{1or2}\frac{2V^{2}}{4 \times 2 \times mass \ of \ 1 \ electrode} = \frac{C_{1or2}V^{2}}{8}, \ (5.6)$$

Where  $E_1$  is the energy density of electrode 1,  $E_2$  is the energy density of electrode 2,  $C_1$  and  $C_2$  are the specific capacitances of each respectively, V is the operating voltage of the full cell (for two electrodes together) and  $E_{mass total}$  is the total energy density of the full cell.

Based on equation 5.6, the energy calculated based on a single electrode, over-estimates the energy by a factor of 4, which this should be accounted for when comparing the energy or power densities to that of commercialized supercapacitors. The power and energy densities estimated for our electrodes are based on the configuration in Figure 5.3. Using the specific energy expression in equation 5.6, the specific energies of electrodes are found to be in the range of  $\sim 3$ - 6 Wh/kg. The energy we are obtaining is very similar to the range of most commercialized supercapacitors (1 - 10 Wh/kg) [73], [74], [75], but it is much smaller than the specific energies reported for literature-based supercapacitors such as graphene-based and graphene/polyaniline supercapacitors (~ 85 - 90 Wh/kg and up to ~ 160 Wh/kg respectively) [76], [77]. The power to mass ratios are also found from equation 5.5 but by assuming a decrease by a factor of 4 (equation 5.6.). The power densities are found based on charging times as was shown in equation 5.5. The charging time constants are based on ionic resistances up to  $\sim$  50 % porosity, but beyond that point, since the solution resistance dominates the ionic resistance, the solution resistance determines the time constant. Hence at this point, any improvements in power to mass ratio require reducing this time constant, which in turn require reducing the electrolyte resistance down to less than or equal to ionic resistance. Details of the amount of this reduction are explained in section 5.3.

Despite the dominance of solution resistance over ionic resistance after  $\sim 50$  % porosity, the power densities based on ionic time constants are, nevertheless, calculated for all electrodes. This is done in order to give an estimation of the total power density enhancements for the case that solution resistance is reduced down to at least the ionic resistance (e.g. it is not a rate-

limiting factor anymore). The maximum power density that is achieved by ionic based charging time constants (derived from ionic resistance) is ~  $4 \times 10^4$  W/kg, which is much higher than most of the values recorded in literature for other conducting polymer, carbon-based and carbon nanotube supercapacitors [78], [79], [73], [80], [29], [80], [81]. There is only one report that is claiming higher powers of up to 160 kW/kg [82], the maximum high power claimed after that is 20 kW/kg [83]. This power is calculated for the most porous electrode used and may be an over estimation of the power density, since as explained, for more porous electrodes, the solution resistance is actually determining the power. If only the ionic based power density of electrodes less than 50 % porosity (e.g. 44 %) is considered, it is still shown that a power density (~ 1.5x10<sup>2</sup> W/kg) comparable to some of the values recorded in literature for conducting polymer supercapacitors is achieved [78], [79], [73], [80], [29], but not to all, as mentioned above. For the 44 % electrode, the power based on actual time constant from CV experiments is also calculated and found to be ~  $1.2 \times 10^2 W/kg$ , which is similar to the power density found from ionic time constant. Among all the electrodes, the maximum power based on actual time constant from CV experiments (section 3.3.5, Figure 3.26) is also found to be ~ 5.8  $\times 10^2$  W/kg (energy storage device capable of storing ~ 5 Wh/kg and being recharged in less than a minute (31 s from CV experiments shown in Figure 3.26)), which is still comparable to some of power values reported in literature for other conducting polymer, carbon-based, and commercialized supercapacitors [78], [79], [73], [80], [29], but not to all (e.g. graphene based supercapacitors [76]).

In calculating the power and energy densities of our electrodes, the mass and voltage that are considered are only for the working electrode (mere sample) and do not consider the total mass of the assembled cell (mass of electrolyte and packaging) and the voltage that is divided across both electrodes. Hence, the power to mass ratios and the energy densities are just approximations and might not be directly compared to the values in literature or to those for other commercialized products. It should be noted that some of the mentioned polymer, carbon, carbon nanotube based or other commercialized supercapacitors provide a high energy but a low power or the opposite [77], [83], [80]. Our supercapacitor, on the other hand, tries to keep the balance between the two and it provides high power while maintaining the same specific energy. In recent years, there have been some conducting polymer-based supercapacitors that are claimed to provide both higher power and high energy and among them the best reported is a graphene-based supercapacitor, details of which can be found in the related reference [76].

In order to further enhance our power and energy, the parameters affecting them should be analyzed in expressions of equation 5.5 and the required changes in these parameters should be investigated. Also, the concepts assuming a symmetric cell as in Figure 5.3 should be considered. From the expressions in equation 5.5, it is found that energy density is dependent on thickness, area and volumetric capacitance and given a fixed voltage (e.g. 1 V), it can be maximized if all these three parameters are maximized. The power is also dependant on area, ionic conductivity and thickness and can be increased if thickness is decreased, but ionic conductivity and area are increased. Considering the power to mass ratio (specific power), assuming a fixed ionic conductivity and voltage, the effect of decrease in thickness on power is by a power of 2. It should be noted that thickness can be considered as both the electrode and separator thickness. As has been repeatedly mentioned before, the aim is to maximize the power densities (reducing the time constant) while maintaining the same specific energies. In order to achieve this goal, as it was also mentioned in section 5.1 and as it is shown from equation 5.5, the capacitance and the ionic conductivity should be increased and the thickness should be decreased (area and voltage are assumed to be constant). Reducing ESR (in the case of this thesis it is estimated to be the solution resistance for porosities higher than 50 %) can increase the ionic conductivity (details in section 5.3). Since decrease in thickness may decrease the energy density (equation 5.5), a balance between the thickness and capacitance should be maintained so to provide a high power with at least the same energy density if not higher. Some of these parameter adjustments that can provide high power while maintaining at least the same energy densities are described in 'Future Work' in section 5.3.

### 5.3 Future Work

In this section some future work is suggested that is aimed at further enhancing the performance of electrodes, especially those that are very porous, in terms of speed of charging and energy density. As was mentioned in section 5.2, the rate-limiting factors in ion transport that are important in determining the charging time constant and speed, are the solution resistance and the electrode and separator thickness. These factors should be minimized if a fast charging rate is required. Initially, some methods for reducing solution resistance are suggested and further, required thickness values for electrodes and separators are analyzed.

The methods to reduce electrolyte resistance were explained before in section 3.3.5 and can be again seen here via equation 5.6. The amount of reduction in solution resistance value is also estimated by the same equation (details in section 3.3.5) as follows. Given that the solution resistance should ideally be less than or equal to the ionic resistance, then

$$R_{s} \ll R_{i}$$

$$\frac{l_{s}}{\sigma_{s}A} = \frac{l_{i}}{\sigma_{i}A} \Rightarrow \sigma_{s} = \frac{l_{s}\sigma_{i}}{l_{i}} \Rightarrow R_{s} = \frac{l_{i}}{\sigma_{i}A}$$
(5.6)

As it is seen from the equation, the reduction in solution resistance depends on the geometry of the electrode. Hence, it cannot be directly compared to the range of values given in literature (e.g. 0.01  $\Omega$  - 0.3  $\Omega$ ) [84], [85] but may be compared to literature electrolyte conductivities (e.g. up to at least 1 – 3 S/m) [85], [86], [87]. Some other methods to minimize the electrolyte resistance are to change the concentration of the salt in the electrolyte and to reduce the viscosity. Also, in commercialized supercapacitors with two-electrode cells, the distance between electrodes should be minimized to reduce the solution resistance ( $R = \frac{l}{\sigma A}$ ). After the solution resistance is reduced at least to as small as ionic resistance value, the power densities can be improved and are no more limited by solution resistance after ~ 50 % porosity. Having a solution resistance that is less than or equal to ionic resistance, the power density found from this solution resistance might enhance to at least ~ 4 x10<sup>4</sup> W/kg, which is the value found from the lowest ionic based time constant (section 5.2).

In two-electrode cells, where there is no reference electrode, reducing the separator thickness is perhaps a good way of increasing the power to mass ratio. This also helps to reduce the solution resistance and increase the ionic resistance compared to that. In that case, if still a further charging rate improvement is required, the electrode thicknesses should be reduced. Reduction in separator thickness is basically reduction in the distance between the electrodes in a two-electrode cell, which decreases the time constant ( $\tau = R_s C$ ). As was explained in section 3.3.5, the electrode thickness can be estimated based on ionic conductivity of electrodes and a known hydrophobic separator (from Gore Company, formerly called Excellerator Developmental Gen3 (EDG3)) thickness and ionic conductivity, which are all related through equation 5.7 as follows:

$$\frac{l_{electrode}}{l_{separator}} = \frac{\sigma_{electrode}A}{\sigma_{separator}A} \rightarrow l_{electrode} = \frac{\sigma_{electrode}l_{separator}}{\sigma_{separator}},$$
(5.7)

where  $l_{electrode}$  is the electrode thickness,  $l_{separator}$  is the separator thickness (e.g. 12 µm),  $\sigma_{separator}$  is the ionic conductivity of the separator (e.g. 1.64 x10<sup>-2</sup> S/m) [60],  $\sigma_{electrode}$  is the ionic conductivity of the electrode (values given in section 3.2) and A is the area of the electrode and separator.

Based on this equation and the values mentioned for the separator, assuming the same area for the electrode and the separator, the maximum thickness that is required to provide the lowest charging time constant (0.026 s) for porous electrodes is 1.5 µm [60]. One potential method that can be used to reduce the thickness is to reduce the deposition time for, for example, polypyrrole in the case of this thesis or modify the fabrication method of CNF. If the time constant is required to be reduced further, a separator with less thickness or higher ionic conductivity may have to be used instead. Using power expression in equation 5.5, it is seen that if the thicknesses of the electrode or separator are, for example, reduced to  $\sim 1 \,\mu m$ , then the average power density for a two-electrode cell is estimated to be ~  $0.3 \times 10^6$  W/kg, assuming a constant area and ionic conductivity. The trade off in reducing the thickness is reduction in energy density (by  $\sim 0.3$  $x10^{6}$  times given a constant area and capacitance), which can be compensated for by increase in volumetric capacitance. The increase in volumetric capacitance can be achieved by reducing the porosity, which in turn reduces the time constant. Hence, a better solution is to stack multiple layers of electrodes together to increase the surface area and hence the total capacitance. In this thesis since the volumetric capacitance reduction is not significant compared to reduction in time constant (section 5.1 and Figure 5.1 and Figure 5.2), lower number of stacks may be required.

After the solution resistance and the thickness are reduced, a point comes where the resistance along the length may also start becoming significant as the thickness becomes very small compared to the length. In this case the resistance along the length should now be reduced if any further improvement in charging time constant and power to mass ratio is required.

Other than the mentioned methods required for power or energy density improvements, other factors should also be considered in our experimental strategies to further push these improvements. Some of the factors that should be considered in our future experiments are listed below:

- 1. Side and parasitic reactions
  - a) There are usually Faradaic reactions happening in an electrochemical cell, which affect the capacitance, charging and energy storage in the electrode. Parasitic reactions include corrosion or reaction between electrolyte and some material in the electrode, which can happen if the current or potential applied are high. To prevent any side chemical reactions inside the electrochemical cell, a low bias voltage should be selected.
- 2. Oxidation state of the electrode at the beginning of the test and its drift during the test
  - a) The potential of the electrode at the start of an experiment and its drift during the experiment affects its behaviour in oxidation and reduction. According to Otero and Ehrenbeck, the ionic conductivity of a film is higher at its oxidized state [38], [14]. Hence, the drift of potential should be prevented to avoid any significant change in ionic conductivity and impedance behaviour. Here, the potential of the electrode is not consistent from start to the end of the test and it has a slight drift, which can affect the results. The electrode potential should be monitored throughout.
- 3. Deposition conditions and resulting effects
  - a) Deposition conditions, such as temperature, current consistency, and accuracy in deposition solution concentration may all affect the thickness uniformity, capacitance, electrical resistance, electrode doping level ( $PF_6^-$  is the dopant ion in this case) and purity across the film electrode. Any change in the latter parameters can affect the charge and ion transport rate and hence charging time. These parameters, specifically, the homogeneity of the films, can also be affected by the amount of time by which the sample is left in the fridge before the start of deposition. Lack of homogeneity can result in thickness variation across the electrode, which may lead to capacitance distribution in the film and as mentioned, multiple charging time constants across the same electrode [88]. To some extent, the thickness also affects the rate of diffusion of ions through the film. For thicker films, diffusion becomes more important. The capacitance of the film electrode increases

with the thickness of the electrode, since that increases the surface area of the electrode. It is found by Skotheim *et al*, that when the capacitance is calculated from charging current in cyclic voltammetry, for up to a PPy thickness of 0.2  $\mu$ m, a linear relationship between capacitance and film thickness is recorded [89].

The mentioned factors can be used as a possible future work for enhancing the experiments and making the results improved and more reliable.

Overall, reducing the solution resistance and the electrode or separator thicknesses can provide significant improvements in power density. Improvements in volumetric capacitance can also compensate for the decrease in energy density when the thicknesses are reduced. Also, considering the factors required in improving our experiments and minimizing the defects, is helpful in further enhancing our power and energy density. Finally, by providing small-sized devices with high power and energy, we are satisfying the needs for enhancing some electronic devices (e.g. camera, wireless devices, medical devices, etc.) in today's technology.

### 5.4 Summary

Overall, it is concluded that an increase in porosity enhances ionic conductivity and hence migration based 'diffusion', and as a result leads to faster charging as was shown in Table 5.1 of section 5.2. Based on the derived models of section 5.1, which assumed continuous, uniformly distributed pores, the ionic resistances and hence ionic time constants for less porous electrodes (e.g. 44 % and 54 %) are higher than expected. More work is needed to determine the reasons, but one potential reason can be that the ions are violating the mentioned assumptions that were used in deriving those models. For very porous electrodes, the reduction in actual time constants of the entire cell is not represented by the ionic based time constants but rather by solution time constants (since the solution resistance is the rate-limiting factor at those porosities). Hence, in order to obtain actual charging time improvements (or power to mass ratio enhancements) for the entire cell, one method is to minimize the solution resistance as was mentioned in sections 5.3 and 3.3.5. The improvement of the charging rate and speed can also be achieved by reducing the electrode or separator thickness values as was shown in section 5.3. In exchange for the increase in charging rate, the increase in porosity lowers the volumetric capacitance, which is not desirable. As was mentioned in section 5.2, the decrease in volumetric capacitance is

insignificant compared to the increase in ionic time constants; hence a high power can be achieved while maintaining the same capacitance and energy if not higher. As mentioned in section 5.3, one method to increase the volumetric capacitance with increase in speed, is to use stacks of multiple layers of the very porous electrodes to increase active surface area. Using the equations given in different sections of this chapter, the device designer is able to consider all the parameters affecting speed and energy density and to manage the tradeoffs between them. Electrodes are made to either give high charge/discharge rate with low volumetric capacitance or the opposite, or a combination of both.

If considering the potential power density improvements and future work done for the electrodes of this thesis, these electrodes can be used in for quick charge applications such as cordless power tools and for pulse power systems such as cell phones, camera flash, satellites and lasers. For example, for flash of the camera that should have a fast response time, using a supercapacitor with very short charging time constant is necessary. A high power supercapacitor has an advantage over a capacitor since it has a much lower weight, has 10 times the capacitance and operates at a voltage half of that of a capacitor.

Today and in the future, the efforts that are likely to enable major advancements in supercapacitors and make them more useful for a wide range of applications, involve reducing equivalent series resistance (ESR), reducing impurities of the materials to prevent self-discharge (the thermodynamic pressure resulted from energy difference between a charged and discharged supercapacitor), improving fabrication and packaging methods, optimizing electrolytes and electrodes (understanding the relationship between pore size and ion accessibility) and finally exploring hybrid capacitors [90]. These factors were also shown in this thesis to be significant for supercapacitor energy storage and speed enhancements and methods including reducing ESR, optimizing electrolytes and reducing thickness values were suggested to improve them.

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# Appendices

## Appendix A Detailed Results of EDS

Some details of EDS results are given in this appendix.

### Fiber Radius and Surface Area Calculations:

The diameter of fibers is found based on the SEM images and the image scale. Further, these diameters are used to calculate the surface area added to each fiber in all samples. One sample calculation is shown for the pure CNF:

Fiber surface area =  $2 \times \pi \times r \times L = 2 \times \pi \times (\frac{(0.42 \pm 0.034) \times 10^{-6}}{2}) \times L$ =  $(1.32 \pm 0.11) \times 10^{-6} \times L$ ,

where L is the length of the fiber, which cannot be found.

Same calculation and diameter measurement is done for all other samples and the results are presented below:

Table A.1. Fiber diameter and surface area

Sample	44 %	54 %	76 %	91 %
Fiber	$1.41 \pm 0.05$	$1.36 \pm 0.11$	$0.63 \pm 0.03$	$0.42 \pm 0.03$
diameter				
(µm)				
Fiber	$4.43 \pm 0.16$	$4.27\pm0.35$	$1.98\pm0.09$	$1.32 \pm 0.11$
surface area				
$(\mu m)^2 x L$				

When comparing the surface area and diameter for all samples, the decrease in both is seen as we go from 0% to 91% sample.

Elemental composition for all spots of the different samples are shown as follows:

## **Pure CNF:**

Spot 1:



Figure A.1. Elemental spectrum of spot 1 of the pure CNF sample

**Table A.2.** Elemental % composition of spot 1 of pure CNF

Results table									
	AN	Series	Net	unn. C [wt.%]	nor. C [wt.%]	Atom C [at.%]	Compound	norm. stoich. C [wt.%]	Error [%]
Carbon	6	K series	173717	58.18	58.18	66.10		58.18	18.02
Oxygen	8	K series	7521	17.27	17.27	14.73		17.27	5.71
Fluorine	9	K series	4686	14.53	14.53	10.44		14.53	4.91
Nitrogen	7	K series	934	8.04	8.04	7.83		8.04	3.07
Phosphorus	15	K series	5987	1.07	1.07	0.47		1.07	0.07
Sulfur	16	K series	1452	0.28	0.28	0.12		0.28	0.04
Sodium	11	K series	736	0.19	0.19	0.11		0.19	0.04
Aluminium	13	K series	1053	0.18	0.18	0.09		0.18	0.04
Chlorine	17	K series	895	0.20	0.20	0.08		0.20	0.04
Magnesium	12	K series	156	0.03	0.03	0.02		0.03	0.00
Silicon	14	K series	156	0.03	0.03	0.01		0.03	0.00
			Total	100.00	100.00	100.00		100.00	



Figure A.2. Elemental spectrum of spot 5 of the pure CNF sample



Figure A.3. Elemental spectrum of spot 4 and 5 of the pure CNF sample

## **Pure Polypyrrole:**

Spot 1:

Results	Primary energy Tilt angle			15.0 keV 0.0°					
	AN	Series	Net	unn. C [wt.%]	nor. C [wt.%]	Atom C [at.%]	Compound	norm. stoich. C [wt.%]	Error [%]
Carbon	6	K series	40506	24.51	24.51	32.94		24.51	8.04
Nitrogen	7	K series	2175	11.36	11.36	13.09		11.36	4.20
Oxygen	8	K series	5949	10.53	10.53	10.63		10.53	3.74
Fluorine	9	K series	21550	46.78	46.79	39.75		46.79	14.98
Aluminium	13	K series	3674	0.85	0.85	0.51		0.85	0.07
Phosphorus	15	K series	23012	5.61	5.61	2.92		5.61	0.24
Chlorine	17	K series	1148	0.35	0.35	0.16		0.35	0.04
			Total	100.00	100.00	100.00		100.00	

 Table A.3. Elemental % composition of spot 1 of pure CNF

Spot 3:

**Table A.4.** Elemental % composition of spot 3 of pure CNF

	AN	Series	Net	unn. C [wt.%]	nor. C [wt.%]	Atom C [at.%]	Compound	norm. stoich. C [wt.%]	Error [%]
Carbon	6	K series	26901	37.69	37.70	46.94		37.70	12.27
Nitrogen	7	K series	553	10.25	10.25	10.95		10.25	4.20
Oxygen	8	K series	2791	16.10	16.10	15.05		16.10	5.69
Fluorine	9	K series	3853	31.67	31.67	24.93		31.67	10.78
Phosphorus	15	K series	4163	3.03	3.03	1.46		3.03	0.16
Sulfur	16	K series	308	0.25	0.25	0.12		0.25	0.04
Sodium	11	K series	216	0.22	0.22	0.15		0.22	0.05
Aluminium	13	K series	791	0.56	0.56	0.31		0.56	0.06
Chlorine	17	K series	232	0.22	0.22	0.09		0.22	0.04
			Total	100.00	100.00	100.00		100.00	

## PPy/ CNF (44 %):

Spot 1:

	AN	Series	Net	unn. C [wt.%]	nor. C [wt.%]	Atom C [at.%]	Compound	norm. stoich. C [wt.%]	Error [%]
Carbon	6	K series	26901	37.69	37.70	46.94		37.70	12.27
Nitrogen	7	K series	553	10.25	10.25	10.95		10.25	4.20
Oxygen	8	K series	2791	16.10	16.10	15.05		16.10	5.69
Fluorine	9	K series	3853	31.67	31.67	24.93		31.67	10.78
Phosphorus	15	K series	4163	3.03	3.03	1.46		3.03	0.16
Sulfur	16	K series	308	0.25	0.25	0.12		0.25	0.04
Sodium	11	K series	216	0.22	0.22	0.15		0.22	0.05
Aluminium	13	K series	791	0.56	0.56	0.31		0.56	0.06
Chlorine	17	K series	232	0.22	0.22	0.09		0.22	0.04
			Total	100.00	100.00	100.00		100.00	

 Table A.5. Elemental % composition of spot 1 of PPy/CNF

Spot 4:

 Table A.6. Elemental % composition of spot 4 of PPy/CNF

	AN	Series	Net	unn. C [wt.%]	nor. C [wt.%]	Atom C [at.%]	Compound	norm. stoich. C [wt.%]	Error [%]
Carbon	6	K series	73804	26.57	26.57	33.54		26.57	8.54
Nitrogen	7	K series	4919	16.34	16.34	17.69		16.34	5.63
Oxygen	8	K series	22856	30.92	30.92	29.31		30.92	9.95
Sodium	11	K series	2479	0.50	0.50	0.33		0.50	0.06
Silicon	14	K series	4465	0.53	0.53	0.29		0.53	0.05
Phosphorus	15	K series	6789	0.85	0.85	0.42		0.85	0.06
Chlorine	17	K series	8293	1.17	1.17	0.50		1.17	0.07
Sulfur	16	K series	1350	0.17	0.17	0.08		0.17	0.03
Aluminium	13	K series	15984	1.98	1.98	1.11		1.98	0.12
Fluorine	9	K series	6053	20.97	20.97	16.74		20.97	7.10
			Total	100.00	100.00	100.00		100.00	

## Appendix B EIS and IC Modeling and Rate Limiting Factors

Modeling data for both EIS and ionic conductivity measurements are given in this appendix.

### **B.1. EIS and IC Modeling and Experimental Data Analysis**

The voltage and frequency range for the EIS experiments are in Table B.1:

Table B.1. Sample dimensions and the voltage and frequency used in the experiments

Sample	0 %	44 %	54 %	76 %	81%	91%
Applied Voltage (mV)	40	30	40	40	40	
Frequency range (Hz)	$0.0001 \text{ to} \\ 1x10^5$	0.0008 to 1x10 <sup>5</sup>	$0.0006$ to $1x10^5$	$0.0001$ to $1x10^5$	$0.0001$ to $1 \times 10^5$	





Imaginary vs Real impedance-Experiment

Figure B.1. Zoomed-out version of Figure 3.17, with frequencies indicated



Figure B.2. The 2<sup>nd</sup> zoomed-in version of Figure 3.17, with frequencies indicated

### **Nyquist Plots:**

### High Frequency section:

As seen from Figures B.1 – B.2, at high frequencies (from ~  $1 \times 10^5$  Hz to ~ 0.1 Hz or higher) a semi-circled shape curve is seen that is due to film electrode/electrolyte interface effects (charge and ion transfer) [59]. These phenomena are modeled with a parallel RC electrical circuit (Z= Rct/ (j $\omega$ CdlRct +1), where R<sub>ct</sub> is the charge transfer resistance and C<sub>dl</sub> is a double layer or an adsorption-related capacitance) that intersects the real impedance axis at zero when  $\omega \rightarrow \infty$  and at Rct (charge transfer resistance; can be used to determine the rate of charge transfer at the electrode/electrolyte interface and is inversely proportional to the electron transfer rate) when  $\omega$  $\rightarrow 0$ . Charge accumulation in the polymer/solution interface creates the double layer capacitance. At high frequencies ( $\omega \rightarrow \infty$ ), the double-layer capacitance short circuits, which results in small charge transfer across the interface [59].

#### Low Frequency section:

EIS results from the electrodes do not show an ideal capacitive behaviour (Im[Z(w)] increases indefinitely as  $\omega \rightarrow 0$  (very long times), but Re[Z(w)] remains frequency independent), similar to what is shown in **Figure 3.22** (section 3.3.3) [47]. The electrodes, here, rather show a non-ideal 123 behaviour with a phase angle corresponding to their capacitance. Their non-ideal behaviour was modeled in section 3.3.2 with a capacitive-distributed system that plays the role of a CPE. The CPE can be difficult to relate to underlying physical phenomena, but may result from inhomogeneity of the samples, leading to the varied phase angles at low frequencies.

#### **Bode Plots:**

The phase also provides information about the device impedance. For example, a phase of zero indicates that the system is behaving purely resistive, a phase of  $45^{\circ}$  shows that ions have transferred inside the electrode but not reached the end and finally a phase of  $90^{\circ}$  present a purely capacitive behavior. For the electrodes' phases seen in the Bode plots, the phases are getting closer to  $-90^{\circ}$  as the electrodes are more porous (this is with the assumption that all phases start at  $0^{\circ}$ ). More details were discussed in sections 3.3.2 and 3.3.3.

The modeling graphs for all electrodes are presented below:



### **Modeling EIS graphs:**

**Figure B.3.** Nyquist plots from the model for all electrodes. The trends are similar to the corresponding experiments in **Figure 3.17** and **Figure B.1**.



Figure B.4. Zoomed in version of Figure B.3



Figure B.5. Another zoomed in version of Figure B.3

/1.



Figure B.6. Bode plots of all electrodes verifying the experimental trends in Figure 3.18.

The results from all the modeling graphs and their corresponding experiments were presented in **Table 3.3** in section 3.3.3, except for ionic conductivity,  $\chi_1$  and  $\chi_2$  values, which are presented below in Table B.2.

Samples	Tests	Ionic Cond. (κ, S/m)	$\chi_2$ ( $\Omega$ /m) across L	χ <sub>1</sub> (Ω/m) across L
	Model	1.80 x10 <sup>-6</sup>	0.076	$1.10  ext{ x10}^9$
0 %	Exper.	6.26 x10 <sup>-6</sup>	N/A	N/A
	Model	6.75 x10 <sup>-4</sup>	1.28	3.71 x10 <sup>6</sup>
44 %	Exper.	2.05 x10 <sup>-3</sup>	N/A	N/A
	Model	$5.50 \text{ x} 10^{-3}$	0.79	$4.35  ext{ x10}^{5}$
54 %	Exper.	1.10 x10 <sup>-2</sup>	N/A	N/A

Table B.2. All parameters found from experiment and model fit for all samples

11.

		Ionic Cond.	$\chi_2 (\Omega/m)$	$\chi_1 (\Omega/m)$
Samples	Tests	(к, S/m)	across L	across L
	Model	5.20 x10 <sup>-2</sup>	1.20	$4.93 \text{ x} 10^4$
76 %	Exper.	1.64 x10 <sup>-1</sup>	N/A	N/A
	Model	1.0 x10 <sup>-1</sup>	1.25	$1.95 \text{ x} 10^4$
81 %	Exper.	1.73 x10 <sup>-1</sup>	N/A	N/A

Experimental graphs with the corresponding fits are presented for all electrodes:

Pure PPy:



**Figure B.7.** Nyquist and Bode plots of pure PPy compared to the fit from model in equation 3.1 and 3.3, the values shown on the left box at each point present the model values and the ones in the right box show the experimental value. The part in the circle is zoomed in to show the fit.

Looking at Figure B.7, it is found from the Nyquist plot that the experimental and modeling plots are following almost the same trend until the impedance value of 1608  $\Omega$  and frequency of  $6.3 \times 10^{-3}$  Hz. Starting from this frequency, the experimental graph deviates from the model, indicating larger Faradaic reactions that decrease the capacitance. The same analysis as above applies to all the other samples as well except that the parameter values would be different. The



other samples to consider are the 6, and 76 % PPy-deposited CNF samples:

**Figure B.8.** Nyquist and Bode plots of 54 % PPy-deposited CNF compared to the fit from model in equation 3.1. The values in the box to left of each point are the model values and the ones to the right are the experimental values. Here, frequency goes down to 0.0006 Hz.

In the Nyquist plot, the fit and experiment are almost overlapping at the high and intermediate frequency regions, but tend to deviate from each other starting from frequency of  $1.26 \times 10^{-2}$  Hz.



**Figure B.9.** Nyquist and Bode plots of 76 % PPy-deposited CNF compared to the fit from model in equation 3.1. The values in the box to left of each point are the model values and the ones to the right are the experimental values.

As seen from figure B.9, the fit between the model and experiment at high frequency is not well. From the experiment, an almost straight line is seen in this section rather than a semi-circle; hence the parallel surface charge capacitance and charge transfer resistance cannot explain this behaviour. The fit at intermediate frequencies is reasonable for a short period but at lower frequencies the results deviate.

## Ionic Conductivity Graphs: Modeling graphs:

The modeling Nyquist plots for all electrodes are presented in Figure B.11 and the Bode plots are in Figure B.12. These can be directly compared with Figures 3.20 and 3.21.



Figure B.10. Modeling Nyquist plots of all electrodes, similar to experiments (Figure 3.20)



Figure B.11. Modeling Bode plots of all electrodes, similar to experiments (Figure 3.21)
Comparing the plots in Figures B.11 and B.12 with their corresponding experimental results in **Figure 3.10** and **Figure 3.11**, the same trends and explanations apply, which are not repeated here anymore. It should just be noted that the fit from the 76 % is not as good as the other electrodes since the resistance measured for the film is very close to the solution resistance and it cannot be distinguished from the solution resistance.

The experimental plots with their corresponding model fits are presented in Figure B.12 to Figure B.14 as follows:



#### Model and experiment:

**Figure B.12.**Nyquist and Bode plots of pure PPy compared to the fit from model; the frequency range over which the experiment is performed is also from 0.0001 to  $1 \times 10^5$  Hz.



Figure B.13. Nyquist and Bode plots of 54 % sample compared to the fit from model



Figure B.14. Nyquist and Bode plots of the 76 % sample compared to the fit from model

### **B.2.** Rate-Limiting Factors in Ion Transport

The lack of a real intercept at high frequencies may perhaps be due to some parasitic or Faradaic reactions in the electrochemical cell that have created an unexpected behaviour in impedance. It is believed that the unexpected impedance behavior at high frequencies  $(10^5 \text{ Hz to } 0.5 \times 10^3 \text{ Hz})$  is also due to an RC delay caused by RC components inside reference electrode. Using a stainless steel wire connected in parallel to the reference electrode solves this issue. This solution was not applied to the experiments presented here, since it was not understood at the time; hence it can be used in future experiments.

### Expected and measured ionic resistances:

	0 %	44 %	54 %	76 %	81 %
$R_{i\_measured}$ ( $\Omega$ )					
(through both	4472	78.00	10.22	1.14	0.66
pores and PPy)					
$R_{i\_expected}(\Omega)$					
(through	N/A	1.97	1.14	1.34	0.77
electrode pores)					

Table B.3. Expected ionic resistance through pores vs. ionic resistance measured

## Appendix C Einstein and Ion Counting Calculations

Details of Einstein calculations and ion counting results are shown in this appendix.

#### C.1. Einstein Calculations

The Einstein relation is: 
$$D = \frac{\mu_q K_B T}{q}$$
, (C.1)

The mobility is found through the following equation:

$$\mu = \frac{\nu_d(m/s)}{E(V/m)} \Rightarrow (m^2/Vs)$$
(C.2)

The mobility is found through relating it to ionic conductivity as shown in the following steps:

$$i = eNdwv, \tag{C.3}$$

where e is the elementary charge, N is the number of ions per volume, d is the width, w is the thickness, and v is the velocity; here # of ions passing through a volume at 1 second is multiplied by the elementary charge to give the current passing through this volume at every second. The velocity is replaced by the electric field and mobility from equation C.3. The voltage over distance further substitutes the electric field.

$$I = qNA\mu E$$

$$E = V/l$$

$$I = qNA\mu V/l$$
(C.4)

Looking at the electrical side, we have V=IR and  $R = \frac{l}{\sigma_i A}$ . Substituting V/I in place of R in the latter equation, an equation for current is obtained, which can be made equal to the above current equation (C.4).

Hence, we have: 
$$I = \frac{\sigma_i AV}{l}$$
.

Making the two current equations equal, we have:

$$\sigma_i = qN\mu$$
  

$$\Rightarrow \mu = \frac{\sigma_i}{qN}$$
(C.5)

Using this mobility in equation C.1, the diffusion coefficient is found in terms of conductivity:

$$D = \frac{\sigma_i K_B T}{q N q}$$

One sample diffusion coefficient calculation is done for the 44 % electrode as follows: Density of PPy =  $1.5 \text{ g/cm}^3 = 1.5 \text{x} 10^6 \text{ g/m}^3$ 

Density of PPy + CNF =  $6.99 \times 10^5 \text{ g/m}^3$ 

Volume fraction of PPy= Mass fraction of PPy x(density of the whole sample/density of PPy) =  $0.58 \times 6.99 \times 10^5 / (1.5 \times 10^6) = 2.61 \times 10^{-1} \text{ m}^3$ 

N = 0.1 Mx(1-2.61x 
$$10^{-1}$$
)= 7.39x  $10^{-2}$  mol/l = 4.45x $10^{25}$  ions/ m<sup>3</sup>

$$\mu = \frac{6.97 * 10^{-3} (S/m)}{1.602 * 10^{-19} (C) * 4.45 * 10^{25} (ions/m^3)} = 9.40 * 10^{-10} m^2 / Vs$$
$$D_q = \frac{9.40 * 10^{-10} (m^2 / Vs) * 0.025 (V)}{1.602 * 10^{-19} (C)} = 1.47 * 10^8 (m^2 / Cs)$$
$$\Rightarrow D = 9.40 * 10^{-10} (m^2 / Vs) * 0.025 (V) = 2.35 * 10^{-11} m^2 / s$$

The same procedure was used for calculating the diffusion for other samples, except that the volume fraction of polypyrrole is changed and consequently, the number of ions per volume, the mobility of ions and finally the diffusion.

### C.2. Ion Counting Calculations

The number of Fluorine ions was found in chapter 4 and here the number of pyrroles is calculated to further find the pyrroles to  $PF_6^-$  ratio. The current for the area exposed to NMR test is required for pyrrole calculation. This current is found by the following formula: (area under coil x total deposition current)/total deposition area. The total mass of pyrroles can be found by subtracting the CNF mass from the total mass after deposition assuming the large portion of polypyrrole mass is due to monomers or pyrroles. The number of pyrroles from mass calculation is either from the weighed mass or the mass calculated from deposition current. The reason for having two mass values for each electrode is because determining the mass of polypyrrole deposited into the carbon nanofiber is problematic due to the porosity of the samples and their tendency to absorb the solvent (PC). These mass values are presented in Table C.1 along with the current that was used in deposition of the sample used in NMR.

Sample	Pure	44 %	54 %	76 %	Pure CNF
	polypyrrole				
Area (cm <sup>2</sup> )	2.56	2.62	1.91	1.92	1.92
Current $(\mu A)$ for the	319.9	327.9	238.7	239.9	N/A
area used					
Total mass (CNF +	2.79	3.11	1.77	1.13	1.47
PPy) used in NMR					
$(mg) \rightarrow$ calculated					

Table C.1. Properties of the piece of each sample that was used within the NMR coil

The above mass values are found based on the following calculation method and under the assumption that for every 7 electrons, three pyrroles are deposited [17], [71].

Mass of pyrroles used in NMR = ((Deposition current for NMR sample (A) x deposition time (s)  $x3600 \text{ s} / 1.602 \times 10^{-19} \text{ C})/2.3 \text{ e}) \times 67.09 \text{ g}/6.02 \times 10^{23} \text{ molecules}$ 

Total mass = Mass of pyrroles used in NMR + Mass of pure CNF used in NMR

These mass values are then used in calculating the number of pyrroles. The values obtained for the number of pyrroles for both the whole sample and the portion used in NMR are presented in Table C.2 as follows:

Table C.2.	Number of pyrroles calculated from mass and charge for both the whole sample and
for that port	on of the sample used in NMR

Sample	Pure	44 %	54 %	76 %	Pure CNF
	polypyrrole				
# of Pyrroles from	$9.77 \times 10^{19}$	$9.32 \times 10^{19}$	$6.43 \times 10^{19}$	$3.84 \times 10^{19}$	N/A
charge for the whole					
sample					
<b># of Pyrroles from</b>	$1.47 \mathrm{x} 10^{20}$	$1.77 \mathrm{x} 10^{20}$	$2.79 \times 10^{20}$	$2.90 \times 10^{20}$	N/A
measured mass for					
the whole sample					
<b># of Pyrroles from</b>	$2.50 \times 10^{19}$	$2.56 \times 10^{19}$	$1.40 \mathrm{x} 10^{19}$	$9.38 \times 10^{18}$	N/A
charge for the NMR					
sample					
<b># of Pyrroles from</b>	$4.31 \times 10^{19}$	$2.93 \times 10^{19}$	$5.76 \times 10^{19}$	$2.88 \times 10^{19}$	N/A
measured mass for					
the NMR sample					

A sample calculation of these numbers is shown:

- *a)* # of Pyrroles from charge for the 44 % sample:
  - a. Deposition current for the area used in NMR = 0.0003279 A
  - b. Deposition time = 8 hours  $\rightarrow$  28800 s
  - c. Total charge = 0.0003279x28800 = 9.4435 C
  - d. Total electrons transferred =  $9.4435 / 1.602e 19 = 5.8948 \times 10^{19}$  electrons
  - e. # of Pyrroles =  $5.8948 \times 10^{19} / 2.3 = 2.5635 \times 10^{19}$

**b)** # of Pyrroles from mass for the 44 % sample:

a. # of Pyrroles = (pyrroles mass in NMR xAvogadro's) / (pyrrole's mass)

 $= (0.003268 \times 6.02 \times 10^{23}) / (67.09) = 2.9326 \times 10^{19}$ 

b. pyrroles mass in NMR = (total mass used in NMR – CNF mass used in NMR) x pyrrole's mass / (pyrrole's mass + (PF<sub>6</sub><sup>-</sup> mass)/3)

 $= (0.00588 - 2.5771 \times 10^{-4}) \times 67.09 / (67.09 + 48.32136) = 0.003268 \text{ g}$ 

c. CNF mass used in NMR = total mass used in NMR x deposition current /(whole sample mass after deposition)

$$= 0.00588 \times 0.001193 / 0.02722 = 2.5771 \times 10^{-4} \text{ g}$$

Comparing the number of pyrroles from both methods, it is found that the number of pyrroles from mass calculation is 1.14 times the number found from charge. This difference may be due to some error in mass calculation for the sample used in NMR; the solvent from that sample may have not been removed thoroughly before weighing, which that contributes to increase in the mass. Any change in mass, changes mass of pyrroles used in NMR and hence the number of pyrroles. The other values for other samples can be seen and compared from Table C.3.

Number of Fluorine ions from NMR is calculated as follows for the 54% sample as an example:

$$\frac{\# ofFinTeflon}{S_{teflon}} = \frac{\# ofFinCNF / PPy}{S_{PF6}}$$

$$= \frac{18.4e - 5}{32153.2634 * 2.137} = \frac{\# ofFinCNF / PPy}{580.8786}$$
(C.6)

Values for other samples at different soaking times and conditions are shown as ratios of Pyrrole to  $PF_6^-$  in Table C.3:

<b>Table C.3.</b> Pyrrole to PF <sub>6</sub> <sup>-</sup>	ratios for all samples	at different conditions	s using the Teflon	standard
(0.0046 g);				

	<b>Ratio</b> = $\#$ of Pyrroles/ $\#$ of $PF_6^-$ ions
PPy sample 1	
Dry	5.06
After soaking in PC for 20 sec	1.62
After soaking in PC overnight	3.31
PPy sample 2 (current sample)	
After Cycling	1.05
After Ionic Conductivity test	7.50
After soaking overnight in PC	2.55
PPy/CNF 44 % sample 1: # of pyrrol	es: $4.689 \times 10^{18}$ for area of 0.48 cm <sup>2</sup>
After Cycling	2.25
After cycling and soaking 10s in PC	2.67
After cycling and soaking overnight in PC	3.65
After cycling and soaking overnight	in PC:
44 % sample 2	164.87
54 % sample	89.67
76 % sample	20.67
Pure CNF	N/A

Looking at the Table, the ratios obtained after overnight soaking for all samples is higher than before soaking except for PPy sample 2. The smaller ratio indicates higher # of PF<sub>6</sub><sup>-</sup> ions

after overnight soak, which may be explained due to reasons previously mentioned for the inconsistency of ratios. For all the other samples, though, the ratio after overnight soak is higher indicating the loss of some  $PF_6^-$  ions. In order to clarify the mystery in loss of  $PF_6^-$  ions, various NMR tests were done before and after soak in PC.

Based on what was explained about various standards, ratios obtained for NaBF<sub>4</sub> or Na<sub>2</sub>HPO<sub>4</sub> standards are shown:

Table C.4. Pyrrole to  $PF_6^-$  ratios for all samples using phosphorous tests or using  $NaBF_4$  standard

	44 %	54 %	76 %					
	Soaked in Pure PC	Soaked in Pure PC	Soaked in Pure PC					
Ratio from phosphorous test (Na <sub>2</sub> HPO <sub>4</sub> standard, # of Phosphorous $\rightarrow$ 1.4x10 <sup>-6</sup> moles for 0.0140 g solution in capillary) used								
After 10 sec soak	61.94		73.49					
Ratio using NaBF <sub>4</sub> s moles for 0.02201 g	tandard, # of I solution in cap	Fluorine → 1.7 illary	′608x10 <sup>-6</sup>					
After 10 sec soak	29.65	160.67	23.75					
After 1 CV in the 2 <sup>nd</sup> round of tests 10 sec soak in PC	N/A	21.53	N/A					
After 1 CV in the 2 <sup>nd</sup> round of tests Overnight soak in PC	N/A	4.92	N/A					

For the tests done with NaBF<sub>4</sub> standard, after performing some electrochemical tests on the 54 % sample,  $PF_6^-$  ions are inserted back in since the ratio decreases to 21.53 from 160.67. The

ratio decreased further to 4.92 after more ions are re-inserted. This value contradicts the values obtained for other experiments; the ratio is smaller after overnight soak, indicating large number of  $PF_6^-$  ions in the sample. For other tests the ratio was higher, indicating less number of  $PF_6^-$  ions. This small ratio could indicate that some ions were immobile in the sample before soaking and after that they started moving; hence another test, namely decoupling is performed to validate that. Our NMR experiments would not observe signals from  $PF_6^-$  ions that are immobilized and not able to tumble rapidly. This is because dipole-dipole couplings between the Fluorine nuclei would broaden the  $PF_6^-$  NMR signals.

## Appendix D EIS and IC Modeling Derivation

#### **D.1. Details of Modeling Derivation**

#### Warburg Impedance:

Warburg impedance is also referred to as Warburg element and it is represented as  $Z_W = A_W/(j\omega)^{0.5}$ , where  $A_W$  is Warburg coefficient, j is the imaginary unit and  $\omega$  is the angular frequency. The transmission line that is used in this thesis represents the same behaviour, except that it uses series of resistors and capacitors to show this behaviour rather than using a box showing  $Z_W$  element. The transmission line is used to explain the complicated electrochemical reactions for a complex structure where the calculation of real and imaginary components is also complicated. Using the transmission line, it is easier to split the calculation into elementary steps or in other words use a cumulative calculation of the electrode impedance. It should be noted that the phase associated with the original Warburg region is 45°, but for our case, if we vary the capacitance values along our transmission line, our Warburg region may have varied phases.

### **D.1.1. EIS Modeling**

The circuit similar to Figure 3.13 is shown in Figure D.1 as follows:



**Figure D.1.** The same circuit as Figure 3.20, except that the resistors are per length and are called  $\chi_1$  and  $\chi_2$ ; capacitors are shown as  $\zeta(\Omega)$ .

This circuit is the modified Warburg circuit (a transmission line is used in place of only one element as was shown above) that was referred to in the text of the thesis (chapter 3) so many

times. Instead of the resistors shown in **Figure 3.20** in section 3.3.2, resistances per unit length  $(\Omega/m)$ ,  $\chi_1 \rightarrow \text{ionic resistance and } \chi_2 \rightarrow \text{electronic resistance are used, which represent the local ohmic drop at each intersection point depending on transport properties. Also, in place of capacitors and leakage resistors, <math>\zeta(\Omega)$  is used, which represent the capacitance per length (F  $\rightarrow$  s/ $\Omega$ m) in parallel with the leakage resistance ( $\Omega m$ ) and the result divided by length. The thickness can be multiplied by  $\zeta(\Omega)$  to account for the exchange of electrical charge at the interface all along the thickness and at each of the circuit intersection points. Therefore, the dimensional unit of elements linking electrical and ionic resistances would be  $\Omega m$ .

The ac. impedance equation of this circuit is derived through calculating the response of the transmission line to a small AC potential step [44]. The derivation process is outlined as follows:

$$\frac{\partial \phi_1}{\partial x} = -i_1 \chi_1 \rightarrow i_1 = \frac{-1}{\chi_1} \frac{\partial \phi_1}{\partial x} \rightarrow derivative \Rightarrow \frac{\partial i_1}{\partial x} = \frac{-1}{\chi_1} \frac{\partial^2 \phi_1}{\partial x^2}$$
(D.1)

$$\frac{\partial \phi_2}{\partial x} = i_2 \chi_2 \rightarrow i_2 = \frac{1}{\chi_2} \frac{\partial \phi_2}{\partial x} \rightarrow derivative \Rightarrow \frac{\partial i_2}{\partial x} = \frac{1}{\chi_2} \frac{\partial^2 \phi_2}{\partial x^2}$$
(D.2)

$$\partial i_1 = C \frac{\partial \eta}{\partial t} \rightarrow \partial i_1 = C_v A dx \frac{\partial \eta}{\partial t} \rightarrow \frac{\partial i_1}{\partial x} = C_v A \frac{\partial \eta}{\partial t}$$
(D.3)

$$\partial i_2 = C \frac{\partial \eta}{\partial t} \rightarrow \partial i_2 = C_v A dx \frac{\partial \eta}{\partial t} \rightarrow \frac{\partial i_2}{\partial x} = C_v A \frac{\partial \eta}{\partial t}$$
(D.4)

Where  $\eta = \varphi_1 - \varphi_2$ ,  $\varphi_1 \otimes \varphi_2$  are potentials at the bottom and top lines at each intersection respectively,  $\chi_1$  and  $\chi_2$  are resistances per unit length,  $i_1$  is the current in the bottom line and  $i_2$  is the current in the top line, dx is the infinitsimal thickness and finally C<sub>v</sub> is the capacitance per volume [50].

Making equations D.1, D.2, D.3 and D.4 equal and converting to lapalace domain, we get the following:

$$\frac{\partial^2 \eta(x,s)}{\partial x^2} = C_v As(\chi_1 + \chi_2) \eta(x,s) = \frac{1}{\zeta A dx} As(\chi_1 + \chi_2) \eta(x,s),$$
(D.5)

where  $\zeta = 1/\text{LsC}_L$ , or  $\zeta = \frac{R_l}{L \times (1 + R_l s C_L)}$ , if there is leakage present. Here,  $C_L$  is the capacitance per unit length (F/m), which when divided by width physically represents the double layer capacitance formed when negative ions (PF<sub>6</sub>) from the solution come close to the positive ions on the backbone of the polymer. The R*l*, which is the leakage or Faradaic resistance ( $\Omega$ m), is 142 explained via the transfer of charge through the interface, or some consequent reactions at the interface (Faradaic reaction), which is the rate-limiting factor in discharging of the capacitor. The leakage is both used in the circuit for EIS and ionic conductivity (next chapter). When we apply electric potential, two processes occur at electrodes: (1) Accumulation of ions (e.g.  $PF_6^-$ ) near the electrodes (creation of double layers) to balance the positive charge on the backbone and (2) transfer of charge through the interface (Faradaic reaction) [91], [92]. This transfer that leads to discharging of the capacitor, is explained as a leakage resistance, which can slow down the discharging if its value is high enough. The time required for discharging can be found by multiplying the leakage resistance by the capacitance. The discharge happens at low frequencies where the capacitance is open and the Faradaic reaction starts draining out some charge. At high frequencies when the capacitance is short, all the charges go through the shorted line and the leakage resistance does not really play any role.

Using characteristic equation (a polynomial equation obtained from linear differential equations with constant coefficients),  $\eta(x,s)$  in equation D.6, can be solved as follows:

$$\eta(x,s) = A(s)e^{-\sqrt{C_v As(\chi_1 + \chi_2)x}} + B(s)e^{\sqrt{C_v As(\chi_1 + \chi_2)x}}$$
(D.6)

Using equations (D.1) and (D.2) and the circuit, we see that  $i_1(0) = 0$  and  $i_2(L) = 0$  and  $i_1(0) = -\frac{1}{\chi_1} \frac{\partial \eta}{\partial x} |_0; i_2(L) = \frac{1}{\chi_2} \frac{\partial \eta}{\partial x} |_L$ . Using this as a boundary condition, the following is found:  $-\frac{1}{\chi_1} \frac{\partial \eta}{\partial x} |_0 = \frac{1}{\chi_2} \frac{\partial \eta}{\partial x} |_L$ 

Solving this equation using  $\frac{\partial \eta(x,s)}{\partial x}$  in equation (D.5), gives the equation for the coefficients A(s) and B(s) seen in equation D.6:

$$A = \frac{B(\chi_1 e^{\sqrt{s\alpha L}} + \chi_2)}{\chi_1 e^{-\sqrt{s\alpha L}} + \chi_2} \rightarrow A = \gamma B, \text{ where } \gamma = \frac{(\chi_1 e^{\sqrt{s\alpha L}} + \chi_2)}{\chi_1 e^{-\sqrt{s\alpha L}} + \chi_2} \text{ and } \alpha = C_{\nu} A(\chi_1 + \chi_2),$$

where  $\gamma$  is the coefficient relating 'A' and 'B' and is defined as above and  $\alpha$  represents the expression used under the square root in equation D.6.

The expressions 'A' and 'B' can be substituted back in equation (D.6) and in the derivative of that equation as well. Using the boundary conditions explained above, the expression for  $i_1(L)$  and  $i_2(0)$  can be found as follows:

$$\begin{split} i_{1}(0) &= -\frac{1}{\chi_{1}} (B\sqrt{s\alpha}(-1+1)) = 0 \\ i_{1}(L) &= -\frac{1}{\chi_{1}} (B\sqrt{s\alpha}(\frac{\chi_{2}(e^{\sqrt{s\alpha}L} - e^{-\sqrt{s\alpha}L})}{\chi_{1}e^{-\sqrt{s\alpha}L} + \chi_{2}})) \\ i_{2}(L) &= \frac{1}{\chi_{2}} (B\sqrt{s\alpha}(-1+1)) = 0 \\ \Rightarrow i_{T}(L) &= i_{1}(L) + i_{2}(L) = i_{1}(L) + 0 = i_{1}(L) \\ i_{2}(0) &= \frac{1}{\chi_{2}} (B\sqrt{s\alpha}(\frac{\chi_{2}(e^{\sqrt{s\alpha}L} - e^{-\sqrt{s\alpha}L})}{\chi_{1}e^{-\sqrt{s\alpha}L} + \chi_{2}})) \\ \Rightarrow i_{T}(0) &= i_{1}(0) + i_{2}(0) = 0 + i_{2}(0) = i_{2}(0) \end{split}$$
(D.7)

The further steps required for finding the total potential are briefly outlined:

$$\Delta \Phi_t = -\chi_1 \int_L^0 i(x) dx \tag{D.8}$$

This equation presents the change in potential across the thickness considering the ionic resistance per length and the current going through those resistances. Further the current at each vertical branch in the circuit is found by calculating the potential over impedance at each branch:

$$di(x) = -\frac{\eta(x,s)}{\zeta} dx \rightarrow$$

$$i(x) = -\frac{1}{\zeta} \int_{L}^{x} \eta(x,s) dx \rightarrow -\frac{1}{\zeta} \int_{L}^{x} (B\gamma e^{-\sqrt{s\alpha L}} + Be^{\sqrt{s\alpha L}}) dx$$
(D.9)

After integration, i(x) is found to be as follows:

$$i(x) = -\frac{B}{\zeta\sqrt{s\alpha}} (-\gamma e^{-\sqrt{s\alpha}x} + \gamma e^{-\sqrt{s\alpha}L} + e^{\sqrt{s\alpha}x} - e^{\sqrt{s\alpha}L})$$

$$i_2(0) = i_1(L) = i_T = \frac{1}{\zeta} \int_0^L \eta(x,s) dx =$$

$$-\frac{B}{\zeta\sqrt{s\alpha}} (-\gamma e^{-\sqrt{s\alpha}x} + \gamma e^{-\sqrt{s\alpha}L} + e^{\sqrt{s\alpha}x} - e^{\sqrt{s\alpha}L}) =$$

$$-\frac{B}{\zeta\sqrt{s\alpha}} (-\gamma + \gamma e^{-\sqrt{s\alpha}L} + 1 - e^{\sqrt{s\alpha}L})$$
(D.10)

Substituting i(x) in equation (8), we get the following for  $\Delta \Phi_t$  (total potential):

$$\Delta \Phi_{t} = \frac{-B\chi_{1}}{\zeta\sqrt{s\alpha}} \left(\frac{\gamma}{\sqrt{s\alpha}} - \frac{\gamma e^{-\sqrt{s\alpha}L}}{\sqrt{s\alpha}} + \frac{1}{\sqrt{s\alpha}} - \frac{e^{\sqrt{s\alpha}L}}{\sqrt{s\alpha}} + L\gamma e^{-\sqrt{s\alpha}L} - Le^{\sqrt{s\alpha}L}\right)$$
(D.11)

Now, using equations (D.10) and (D.11), the total impedance can be found through ohm's law:

$$Z_{\text{total}} = \frac{\Delta \Phi_t}{i_T}$$

After doing the algebra, the final equation for impedance ( $\Omega$ ) of the circuit is found to be the following:

$$Z = \frac{L^*(\chi_1\chi_2)}{\chi_1 + \chi_2} [1 + \frac{2 + \frac{(\chi_1^2 + \chi_2^2)}{\chi_1\chi_2}}{v\sinh(v)}]$$
(D.12)  
where  $v = L^* \sqrt{\frac{1}{\xi}(\chi_1 + \chi_2)} = L \times \sqrt{\frac{jwC_L(\kappa + \sigma)}{A\kappa\sigma}} = L \times \sqrt{\frac{jwC_v(\kappa + \sigma)}{\kappa\sigma}}$  and  $L = \text{thickness}$ 

If leakage is also included, then we have:  $v = L \times \sqrt{\frac{(1 + jwC_L R_l)(\kappa + \sigma)}{R_l A \kappa \sigma}}$ 

This equation can also be re-expressed in terms of  $\sigma_{electronic}$ ,  $\kappa$  ( $\sigma_{ionic}$ ) and  $C_v$ :

$$Z = \frac{L}{A \times (\sigma + \kappa)} \left[1 + \frac{2 + (\frac{\sigma}{\kappa} + \frac{\kappa}{\sigma}) \cosh(L \times \sqrt{\frac{(1 + R_l j w C_v A)}{\sigma \kappa A R_l}} (\sigma + \kappa))}{(L \times \sqrt{\frac{(1 + R_l j w C_v A)}{\sigma \kappa A R_l}} (\sigma + \kappa)) \sinh(L \times \sqrt{\frac{(1 + R_l j w C_v A)}{\sigma \kappa A R_l}} (\sigma + \kappa))}\right]$$
(D.13)

This impedance is the modified Warburg and was further added to the charge transfer resistance:

$$Z_s = Z + Rct$$

Then  $Z_S$  was calculated in parallel to the double layer capacitance at high frequency:

$$Z_{dl} = 1/j_W C_{dl}$$

$$Z_{total} = (Z_{dl} \times Z_s)/(Z_{dl} + Z_s)$$
(D.14)

Finally, this impedance was added to the solution resistance  $(R_s) \rightarrow Z_{\text{final}} = Z_{\text{total}} + R_s$ . The impedance in equation D.14 was simulated in Matlab to get the Nyquist and Bode plots and to be compared to the corresponding experimental results. It was found through simulations that the electronic conductivity is so high compared to the ionic conductivity that it can be ignored at times. If this is the case, the modified Warburg impedance equation reduces down to the following as  $\sigma \rightarrow \infty$ :

$$Z1 = \sqrt{\frac{R_l}{\kappa A.(1 + R_l j w C_v A)}} . \operatorname{coth}(L \times \sqrt{\frac{(1 + R_l j w C_v A)}{\kappa A R_l}})$$
(D.15)

Considering the solution and charge transfer resistance as well as the double layer capacitance as above, equation D.15, we then have:  $Z_s = Z1+Rct$ ,  $Z_{dl} = 1/jw C_{dl}$ ,  $Z_{total} = (Z_{dl}xZ_s)/(Z_{dl}+Z_s)$  and finally  $Z_{final} = Z_{total} + R_s$ 

The model in equations D.13 and D.15 give almost the same fits since electrical conductivity is so high compared to ionic conductivity in equation D.13, that it has small effect. Another factor that can be considered for ion transport in the polymer films in the 3-electrode configuration is the diffusion of ions from both sides of the film, since the film has no backing as mentioned before. To account for the two-sided diffusion, two transmission lines, the same as the one used here, should be in parallel and then the charge transfer resistance, double layer capacitance and finally solution resistance can be added to the parallel configuration. For this purpose, initially any of equations D.12 or D.13 or D.15 were found for each side of the sample up to half of the thickness, meaning all the thickness values used in these equations should be divided by half. Then we would have two equivalent transmission line equations for each side that can be calculated as being in parallel:

$$Z_{R} = \frac{L \times (\chi_{1}\chi_{2})}{2\chi_{1} + \chi_{2}} [1 - 2 \times (\frac{\chi_{1}}{\chi_{2}} (\frac{1 - \cosh(v_{1/2})}{v_{1/2}\sinh(v_{1/2})}))]$$
  

$$Z_{L} = \frac{L \times (\chi_{1}\chi_{2})}{2\chi_{1} + \chi_{2}} [1 - 2 \times (\frac{\chi_{1}}{\chi_{2}} (\frac{1 - \cosh(v_{1/2})}{v_{1/2}\sinh(v_{1/2})}))]$$
(D.16)

where 
$$v_{1/2} = \frac{L}{2} \times \sqrt{\frac{2}{\zeta \times L}(\chi_1 + \chi_2)}$$

$$Z_{total} = Z_R \parallel Z_L = \frac{Z_R \times Z_L}{Z_R + Z_L}$$
(D.17)

Then the final impedance was found by adding the other parts of the circuit ( $R_{ct}$ ,  $C_{dl}$  and  $R_s$ ) to equation D.17 similar to what was done in equation D.14.

As mentioned in section 3.2.3, a 2-D model was developed to check for any improvements in the fits. The circuit model is presented in **Figure D.2**.



**Figure D.2.** Same circuit as **Figure 3.20** and Figure D.1 is repeated in parallel along the length. Re, which is the electronic resistance along the length is also included

If model in **Figure D.2** was to be used, then the same approach for solving the 1D transmission line would have been used, except that now the electronic resistor along the length would also be considered and the circuit would be solved for a finite case along the length as shown (2D transmission line):

$$Z_2D = \sqrt{\text{Re} \times Z} \cdot \text{coth}(Length \times \sqrt{\frac{\text{Re}}{Z}}), \qquad (D.18)$$

where Re is the resistance along the length as in **Figure D.2**. and Z is the impedance found in equation D.14. This model did not seem to give good fits as mentioned before and the values

obtained for the main parameters, as before, were not reasonable. Therefore, the results from all the other models except this one were shown.

### **D.1.2.** Ionic Conductivity Modeling

Same derivations as the EIS modeling, except that the boundary conditions are different, as well as some process after applying the boundary conditions, which are outlined below:

So, similar to the EIS section, we have the equation for  $\eta(x,s)$ :

$$\eta(x,s) = A(s)e^{-\sqrt{C_v As(\chi_1 + \chi_2)x}} + B(s)e^{\sqrt{C_v As(\chi_1 + \chi_2)x}}$$
(D.19)

Using the boundary conditions, the equation for the total current, which is equal to i1 at zero and L, is found to be the following:

$$i_T(0) = i_T(L) = i_1(0) = i_1(L) = \frac{1}{\chi_1} \frac{\partial \eta(L)}{\partial x} = \frac{B\sqrt{s\alpha}(e^{\sqrt{s\alpha}L} - e^{-\sqrt{s\alpha}L})}{\chi_1(1 - e^{-\sqrt{s\alpha}L})}$$
(D.20)

Further, the total potential is found as shown in equation D.21:

$$\Delta \Phi_t = -\chi_1 \int_{L}^{0} i_1(x) dx \tag{D.21}$$

This equation presents the change in potential across the thickness considering the ionic resistance per length and the current going through those resistances. Further the current at each vertical branch in the circuit is found by subtracting the potential over impedance at each branch from the total current at one end (e.g. at point L):

$$i_{1}(x) = i_{T}(L) - \left(-\frac{1}{\zeta} \int_{L}^{x} \eta(x, s) dx\right)$$
  

$$\eta(x, s) = B(\gamma e^{-\sqrt{s\alpha}x} + e^{\sqrt{s\alpha}x})$$
(D.22)

Here, the  $\eta(x,s)$  equation is substituted in the  $i_1(x)$  equation and the following is obtained:

$$i_{1}(x) = \frac{B\sqrt{s\alpha}}{\chi_{1}}(-\gamma e^{-\sqrt{s\alpha}L} + e^{\sqrt{s\alpha}L}) + \frac{B(-\gamma e^{-\sqrt{s\alpha}x} + \gamma e^{-\sqrt{s\alpha}L})}{\zeta\sqrt{s\alpha}} + \frac{B(e^{-\sqrt{s\alpha}x} - e^{-\sqrt{s\alpha}L})}{\zeta\sqrt{s\alpha}}$$
(D.23)

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Substituting  $i_1(x)$  in equation (D.21), we get the following for  $\Delta \Phi_t$  (total potential):

$$\Delta \Phi_{t} = -B\sqrt{s\alpha} \times L \frac{(e^{-\sqrt{s\alpha L}} - e^{\sqrt{s\alpha L}})}{1 - e^{-\sqrt{s\alpha L}}}$$

$$-\frac{\chi_{1}B}{\zeta_{5}\alpha} (\frac{4 - 2e^{\sqrt{s\alpha L}} - 2e^{-\sqrt{s\alpha L}}}{1 - e^{-\sqrt{s\alpha L}}}) - \frac{\chi_{1}BL}{\zeta_{5}\alpha} (\frac{e^{\sqrt{s\alpha L}} - e^{-\sqrt{s\alpha L}}}{1 - e^{-\sqrt{s\alpha L}}})$$
(D.24)

Now, using equations (D.23) and (D.24), the total impedance can be found through Ohm's law:

$$Z_{\text{total}} = \frac{\Delta \Phi_t}{i_T(L)}$$

After doing the algebra, the final equation for impedance of the circuit is found to be the following:

$$Z = \frac{L \times (\chi_1 \chi_2)}{\chi_1 + \chi_2} [1 - 2 \times (\frac{\chi_1}{\chi_2} (\frac{1 - \cosh(v)}{v \sinh(v)}))]$$
(D.25)  
where  $v = L \times \sqrt{\frac{1}{\xi} (\chi_1 + \chi_2)} = L \times \sqrt{\frac{jwC_L(\kappa + \sigma)}{A\kappa\sigma}} = L \times \sqrt{\frac{jwC_v(\kappa + \sigma)}{\kappa\sigma}}$ and  $L =$ thickness

This equation can also be re-expressed in terms of  $\sigma$ electronic,  $\kappa$  ( $\sigma$ ionic) and Cv:

(D.26):

$$Z = \frac{L}{(\sigma + \kappa)\pi r^{2}} \left[1 - 2 \times \left(\frac{\sigma}{\kappa} \left(\frac{1 - \cosh(L \times \sqrt{\frac{(1 + R_{l} jwC_{v}A)}{\sigma\kappa AR_{l}}}(\sigma + \kappa)}\right) - \frac{1 - \cosh(L \times \sqrt{\frac{(1 + R_{l} jwC_{v}A)}{\sigma\kappa AR_{l}}}(\sigma + \kappa)})\right)\right]$$

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### Appendix E Charging Time Constant Along Length vs. Along Thickness

The charging time constant along length is found through the following:

Initially the electronic resistance along length should be compared to ionic resistance along thickness, if  $R_i \gg R_e$ , then charging time constant along length is calculated and compared to the one along thickness: tau =  $R_eC_{total} \times (L_{diff}/L_{total})$ . The diffusion length ( $L_{diff}$ ) considers the amount by which the ions are penetrated through the thickness of the sample compared to the total thickness.

$$L_{diff}(f) = \sqrt{\frac{D}{w}}$$
  
$$\tau_L(f) = \frac{R_e \times C_{total} \times L_{diff}(f)}{L}$$

## Appendix F Specific Capacitance From Measured Masses

The specific capacitance values with masses calculated based on charge were found in section 3.1, but those based on measured masses are presented here. From Table F.1, it is seen that the specific capacitance values from the measured masses are decreasing among the porous samples going from the 44 % to the pure CNF sample, but the one for the 44 % sample is more compared to the pure PPy. The decrease in the specific capacitance values is because the decrease in the measured PPy mass going toward more porous samples is not accounted for due to perhaps containing electrolyte inside, which adds to the mass.

Sample	0 %	44 %	54 %	76 %	81 %	Pure CNF
Weight <sub>PPy+CNF</sub> (g) after deposition (measured)	0.011 ± 0.0067	0.027 ± 0.0036	0.035 ± 0.0016	0.037 ± 0.0017	$0.050 \pm 0.0028$	0.0018 ± 0.0011
Specific Cap. (measured weight): C <sub>PPy+CNF</sub> /g <sub>PPy-added</sub> (F/g)	81.97 ± 1.14	101.52 ± 3.77	35.40 ± 1.41	23.17± 2.29	15.01 ± 1.24	6.7 ± 0.9

Table F.1. Specific capacitance calculated based on measured masses of CNF/PPy electrodes

The charged-based calculations were done in two ways; one considering only the PPy mass grown in each case and the other including the mass of doping ions ( $PF_6^-$  ions) along with PPy masses (the more doped the sample, the higher the mass and the lower the specific capacitance assuming close raw capacitance values). Sample calculations are done for the 44 % sample as an example:

Mass of PPy only (no PF<sub>6</sub><sup>-</sup> mass, independent of oxidation state) = ((Deposition current for the whole sample (A) x deposition time (s) x 3600 s /  $1.602 \times 10^{-19}$  C) / # of  $\bar{e}$  per pyrrole) x mass of pyrroles (2 hydrogen gone)/ $6.02 \times 10^{23}$  molecules =

 $(0.0012 \text{ A x 8 h x 3600 s / } 1.602 \text{x} 10^{-19} \text{ C}) \text{ x } (1/2.3 \text{ }\bar{\text{e}}) \text{ x 65.09 g x } (1/6.02 \text{x} 10^{23} \text{ molecules}) = 0.01 \text{ g}$ 

→ Specific capacitance =  $\frac{2.00 \ mA}{0.010 \ g} \sim 198.4 \ F/g$ 

**Mass of PPy only (with PF\_6 mass) =** Mass of PPy only (no  $PF_6$  mass) + Mass of  $PF_6$  =

 $0.01 + (0.01 \text{ g} / \text{mass of 4 pyrroles}) \text{ x molar mass of } PF_6^- = 0.01 + (0.01 \text{ g} / 260.4 \text{ g}) \text{ x } 144.97 \text{ g} = 0.01 \text{ g} + 0.0057 \text{ g} = 0.0157 \text{ g}$ 

→ Specific capacitance = 
$$\frac{2.00 \ mA}{0.0157 \ g} = 127.39 \ F/g$$

It should be noted that the doping level of the samples is indicated by the oxidation state (asgrown values shown in Table 3.1) of the electrodes at the time of mass measurement. The doping level of the as-grown oxidized state is one dopant ( $PF_6^-$ ) for every 3 to 4 monomers (pyrroles) and 2.3ē per pyrrole or 7ē or 9ē for each monomer amount respectively.

A sample calculation (equation F.1) is shown for the 44 % sample and the other electrodes follow the same calculations.

$$C_{raw\_measured} = Current / scan \ rate = \frac{2.00 \ mA}{1 \ mV/s} = 2.00 \ F$$

$$C_{v\_CNF+PPy}(volumetric \ capacitan \ ce) = \frac{2.00 \ F}{2.56 \times 10^{-8} \ m^3} = 7.81 \times 10^7 \ F/m^3$$

$$C_{raw\_measured} / mass_{PPyMeasured} (specific \ capacitan \ ce) = \frac{2.00 \ F}{0.0197 \ g} = 101.52 \ F/g , \quad (F.1)$$

$$C_{raw\_measured} / mass_{PPy\_ch \ arg \ eBased\_with PF_6} (specific \ capacitan \ ce) = \frac{2.00 \ F}{0.0157 \ g} = 127.39 \ F/g$$

where Craw\_measured is the total capacitance and Cv\_CNF+PPy is the volumetric capacitance.

The average of the maximum and minimum current for the 44 % sample on the CV graph of **Figure 3.4** is found (2 mA) and divided by the scan rate (1 mV/s) to give the raw capacitance. Further, the volumetric capacitances are found by dividing the capacitance of each electrode by the volume of that electrode. Lastly, the specific capacitance, which only considers the mass of PPy in each electrode, is found by dividing the total capacitance of CNF/PPy samples by the amount of PPy content (gram) they have. A complete version of Table 3.1 is shown in Table F.2.

Table F.2. Basic characteristics of the	sample
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Sample	0 %	44 %	54 %	76 %	81%	91%
Mass <sub>PPy+CNF</sub> (g) after deposition (calculation excluding PF <sub>6</sub> mass)	0.011	0.010	0.007	0.004	0.004	0.0045
Mass <sub>PPy+CNF</sub> (g) after deposition (calculation including PF <sub>6</sub> <sup>-</sup> mass)	0.016	0.016	0.011	0.006	0.006	0.0045
Specific Cap. (calculated mass excluding PF <sub>6</sub> <sup>-</sup> mass): C <sub>PPy+CNF</sub> /mass <sub>PPy-</sub> <sub>added</sub> (F/g)	123.1 ± 19.2	198.4 ± 31.8	158.3 ± 25.4	180.8 ± 23.6	185.1 ± 25.9	6.7 ± 0.9
Specific Cap. (calculated mass including PF <sub>6</sub> mass):	80.0 ± 9.6	127.4 ± 15.3	101.7 ± 12.3	116.2 ± 15.0	118.9 ± 14.9	6.7 ± 0.8
$C_{PPy+CNF} / mass_{PPy-added} (F/g)$						
Oxidation state as grown (V)	0.62	0.68	0.56	0.53	0.47	N/A

The volumetric capacitance values were plotted against porosity in section 3.1.2 and here they are plotted against the calculated mass of PPy.



**Figure F.1.** The volumetric capacitance of each electrode is plotted against the charged-based mass of PPy

# Appendix G Comparison of Parameters Between All Electrodes

Results from all methods are compared in this appendix.

The ionic diffusion, ionic conductivity and diffusion time from all methods for all electrodes are compared here (Table G.1).

**Table G.1.** Comparing diffusion, ionic conductivity and charging time constant of all samples

 from ionic from both experiment and model

Sample	Test	Diffu (m <sup>2</sup> /s	sion Coefficient )	Test		Ionic Conductivity (IC), (κ, S/m)	τ (s) (diffusion time across thickness)
Pure PPv	Exper.	NMR	$(3.31 \pm 3.1) \times 10^{-13}$		Model	1.0 x10 <sup>-6</sup>	$1.57 \text{ x} 10^4$
(0%)		IC	$(3.37 \pm 0.35) \times 10^{-14}$	IC	Exper.	$(6.26 \pm 0.23) \text{ x10}^{-6}$	$(5.81 \pm 1.03)$ x10 <sup>3</sup>
	Model	IC	1.25 x10 <sup>-14</sup>	EIS	Model	1.8 x10 <sup>-6</sup>	$6.53  ext{ x10}^3$
					Exper.	$(6.26 \pm 0.23) \times 10^{-6}$	N/A
44 %	Exper.	NMR	$(5.08 \pm 3.8) \times 10^{-12}$	IC	Model	12.8 x10 <sup>-3</sup>	18.56
		IC	$(2.63 \pm 0.18) \times 10^{-11}$		Exper.	$(2.05 \pm 0.04) \times 10^{-3}$	$156 \pm 22$
	Model	IC	2.21 x10 <sup>-10</sup>	EIS	Model	6.75 x10 <sup>-4</sup>	194.18
					Exper.	$(2.05 \pm 0.04) \times 10^{-3}$	N/A
	Exper.	NMR	$(1.92 \pm 0.50) \times 10^{-11}$	IC	Model	1.90 x10 <sup>-2</sup>	4.65
54 %		IC	$(1.97 \pm 0.17) \text{ x10}^{-10}$		Exper.	$(1.10 \pm 0.03) \times 10^{-2}$	$11.22 \pm 1.60$
	Model	IC	4.75 x10 <sup>-10</sup>	EIS	Model	5.50 x10 <sup>-3</sup>	16.86
					Exper.	$(1.10 \pm 0.03) \times 10^{-2}$	N/A

Sample	Test	Diffusion Coefficient (m <sup>2</sup> /s)		Test		Ionic Conductivity (IC), (κ, S/m)	τ (s) (diffusion time across thickness)
	Exper.	NMR	$(1.01 \pm 0.5) \times 10^{-10}$	IC	Model	8.00 x10 <sup>-2</sup>	1.3
76 %		IC	$(6.23 \pm 0.45) \times 10^{-9}$		Exper.	$(1.64 \pm 0.05) \text{ x}10^{-1}$	$0.86 \pm 0.12$
	Model	IC	7.39 x10 <sup>-9</sup>	FIS	Model	$5.20 \text{ x} 10^{-2}$	1.18
					Exper.	$(1.64 \pm 0.05) \text{ x}10^{-1}$	N/A
	Exper.	NMR	N/A	IC	Model	$1.70 \text{ x} 10^{-1}$	0.62
81 %		IC	$(7.48 \pm 0.57) \text{ x10}^{-9}$		Exper.	$(1.73 \pm 0.23) \text{ x}10^{-1}$	$0.47 \pm 0.06$
	Model	IC	N/A	FIS	Model	1x10 <sup>-1</sup>	0.20
				LIS	Exper.	$(1.73 \pm 0.23) \text{ x10}^{-1}$	N/A
	Exper.	NMR	$(1.10 \pm 0.05) \times 10^{-10}$	IC	Exper.	$(1.78 \pm 0.07) \text{ x}10^{-1}$	$0.020 \pm 0.001$
91 %		IC	$(6.49 \pm 0.04) \text{ x}10^{-8}$	EIS	Model	N/A	N/A
	Model	IC	N/A	]	Exper.	$(1.78 \pm 0.07) \text{ x}10^{-1}$	N/A

## Appendix H Solution Resistance Approximation

Method for finding solution resistance on the front and backside of the electrode is explained here.

In order to find a fixed solution resistance for all electrodes assuming a working to reference electrode (WE to RE) distance of  $\sim 2 - 3$  mm, and to check the likelihood of a 1-sided or 2-sided diffusion, the solution resistance on both sides of the working electrode is measured in EIS configuration. Knowing whether the diffusion is from both sides or one side can determine if the CV time constant values have to be multiplied by 4 before being compared to ionic and solution time constants. The procedure for performing the solution resistance experiments is outlined below:

A reference electrode is included up to step 5

- Placed the RE, WE and counter (CE) electrodes in the solution, so that the distance between the RE and WE is ~ 2 - 3 mm and the distance between CE and WE is ~ 1.2 -1.6 cm (these are the distances I had used in my EIS experiments before; except that for pure PPy I had the RE and WE electrode distance to be ~ 1 cm).
- Brought the WE to a potential of ~ 0.24 V similar to what I had before for my EIS experiments
- 3) Covered the front side (side facing the reference and CE) of the WE with a kapton tape so it is not conducting and measured the impedance (applied 10, 30 and 40 mV potentials and frequency range of 10 Hz to 1e5 Hz to be similar to what I had used for my EIS experiments before).
- Uncovered the front side and covered the back side (side facing against the RE and CE) and repeated the procedure in step 3
- 5) Uncovered both sides and measured the potential again
- 6) Repeated everything without RE

Two sample Bode plot results are presented when the front and the backsides are covered. These are for the case that a RE is used. Front side covered:



Figure H.1. Bode plot of the solution resistance from the back of the electrode



Backside covered:

Figure H.2. Bode plot of the solution resistance from the front of the electrode

Other values found for other cases with and without RE are presented in the following table:

**Table H.1.** Front, back and both sides resistance values for both the cases where a reference electrode is used in the impedance measurements and when it is not used

	With RE	No RE
$R_{f}(\Omega)$	30.7	128.8
$R_{b}(\Omega)$	306.6	376.5
R (both sides of WE uncovered) (Ω)	28.5	126.8