Electronic and Structural Effects on the Electrochemistry of Polypyrrole

by

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Abstract

The electrochemical properties of polypyrrole are influenced by a complex interconnection of electronic, structural, and chemical properties of the polymer matrix. These properties were investigated individually in polypyrrole doped with the hexafluorophosphate ion in order to create a complete model of polypyrrole electrochemistry. The electronic conductivity of polypyrrole was investigated through DC conductivity measurements of films in varying oxidation states. The well-known doping induced metal-insulator transition was observed at an electrode potential of -0.1V versus standard calomel electrode (SCE). X-ray diffraction and macroscopic actuation measurements revealed that a structural change begins at the same potential, possibly due to a loss of pi-stacking in the polymer crystals. Electrochemical impedance spectroscopy was performed over a range of oxidation states, and showed that the impedance goes through a sudden transition at -0.1V as well, which is attributed to changes in ionic conductivity. The non-linear dependence of the electronic and ionic conductivity of polypyrrole with oxidation state were included in a finite difference time domain model which simulated potentiostatic charging and discharging of the polymer matrix. The model was able to explain the moving phase front phenomenon during charging of polypyrrole that has been observed in the literature. The front is a shock wave that occurs whenever the polymer is stepped from a state of low to high ionic or electronic conductivity. It also presents an explanation for the redox peaks observed in cyclic voltammograms that does not rely on the Nernst equation, and is therefore more consistent with the electronic nature of polypyrrole.
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Chapter 1

Introduction

Conjugated polymers are a new class of materials that, due to some unique properties, is beginning to find applications in diverse fields. In the neutral state, a conjugated polymer is an innate semiconductor, and in its highly doped state, it is an electronic conductor with a room temperature conductivity of up to $10^5$ S/cm. These, “conducting” polymers have garnered a lot of interest for the potential of combining the field of electronics with the advantages of the polymer industry, including low cost of fabrication and the strength and flexibility of polymers. Applications of conducting polymers in the semi-conducting state currently under development are organic LEDs, transistors, and solar cells.

Conducting polymers have the ability to be doped to a much larger degree than inorganic semiconductors, to a level of 1 charge per 3 monomer units. Also, due to the permeable nature of polymers, conducting polymers may be reversibly doped and undoped. In Figure 1.1, we see the polymer in the neutral, semi-conducting state. Application of an electric potential in an electrochemical cell leads to positive charges on the polymer backbone with ions from the electrolyte penetrating the polymer to balance this charge. Due to this enormous charge storage capacity (100 F/g) [1], conducting polymers are being investigated for use as supercapacitors [2, 3]. The influx of ions also causes a corresponding increase in volume of the polymer matrix, making these materials also suitable for lightweight, linear actuators, or artificial muscles [4, 5].

![Figure 1.1: Reversible doping of conducting polymers: the oxidized film has a positively charged backbone with compensating negative ions in the matrix. These ions cause the film to be swollen with respect to its reduced, neutral state.](image-url)
Polypyrrrole has been the most studied conducting polymer for this application due to its chemical stability, high conductivity and ease of manufacture. Polypyrrrole actuators exhibit peak stresses one hundred times that of mammalian muscle, but fall short of real muscle when it comes to strain and strain rate. Strains of about 5% are typical [6], although recently strains of up to 26% have been recorded [7], and actuation usually occurs at rates of 1 Hz or less [8, 6]. Natural muscle is capable of strains of 20-30% and strain rates of over 100%/s [9]. Despite much progress in the design of conducting polymer actuators, the mechanisms of actuation are still not well understood. While the volume changes have been widely attributed to the flux of ions during redox cycling [10], the full electromechanical response depends on a complex interconnection of the chemical, electrical and mechanical properties. As well, each of these properties depends on the doping level of the film.

![Diagram](image.png)

Figure 1.2: The electrochemical switching properties of conducting polymers are a complex interconnection of chemical, electronic, and mechanical properties [8].

A common factor affecting all of these properties is the structure of the polymer matrix [11, 12, 13, 14, 15, 16]. The evolution of the microscopic structure during actuation is unknown. As well, the structure of polypyrrrole is highly dependent on the conditions in which the film is grown, such as the electrolyte and the deposition temperature, and shows corresponding variation in behavior. In other words, there is a lot of design flexibility. Once we understand the relationship between the structure of the polymer and the electro-chemo-mechanical properties, we may be able to turn this enormous variability into an improved artificial muscle, or supercapacitor, or transistor.
In this thesis, we investigate the electronic, structural and electrochemical properties of polypyrrole doped with the hexafluorphosphate ion, PPy(PF$_6$), as a function of oxidation state. We find that, as expected, all of these properties are correlated; they all experience a sharp transition at an electrode potential of -0.1V versus standard calomel electrode. We use our observations of the non-linear transition in electronic and ionic mobility to create a finite-difference model of the potentiostatic redox that explains a moving phase front phenomena on charging that has been observed in the literature.

Chapters 2 through 4 give some background on the electronic, electrochemical, and structural properties of polypyrrole; Chapter 5 describes the experimental methods used to measure the conductivity, electrochemical impedance, actuation and crystal structure; Chapter 6 describes the electrochemical model used to fit the impedance spectrum, and the time-domain model which simulates potentiostatic steps and the front phenomenon; Chapter 7 describes the results of the experiments and the modeling; and in Chapter 8, we present our conclusions.
Chapter 2

Electronic properties of polypyrrole

2.1 Bandstructure

What distinguishes conducting polymers is the conjugated structure of the backbone; the polymer chain has an alternating single and double bond. Figure 2.1 shows the conjugation in the molecular structure of polypyrrole. The single (sigma) bond has electrons localized between the two atoms, but the double (pi) bond has the electrons in lobes above and below the sigma bond as seen in Figure 2.2.

Figure 2.1: Chemical structure of polypyrrole. The alternating single and double bond makes this polymer a semiconductor.

There is significant overlap of neighbouring pi-bonds, and these electrons are therefore delocalized. In molecules such as benzene, there is complete pi-electron delocalization and the molecule is often drawn not with an alternating single and double bond, but with a delocalized double bond over all the atoms.

Conjugated polymers have one delocalized pi electron per atom, therefore according to band theory they should be intrinsic metals. However, one-dimensional metals are unstable. They undergo a spontaneous dimerization where the bonds alternate long and short. The unit cell becomes twice as long, therefore, a gap opens up and conjugated polymers are intrinsic semi-conductors. This effect is called the Peierls distortion [11]. The bandgap of conducting polymers span the visible spectrum, and are highly chemically configurable.
Figure 2.2: (a) Sigma bonds have most of the electron density between the two nuclei, (b) Pi bonds have electron density above and below the nuclei. Dots represent the nuclei, and the gray ellipses are the electron clouds.

2.2 Doping and the metallic state

Conjugated polymers may be doped just like inorganic semiconductors to become more conducting. Most conducting polymers are p-type, with holes on the backbone of the chain. Since a single bond is longer than a double bond, removing an electron requires a bond-stretching. For this reason, there is strong electron-phonon coupling in conducting polymers. Doping creates charged quasi-particles called solitons, polarons and bi-polarons, formed when a charge polarizes the surrounding lattice, shown in Figure 2.3 [17]. The energy of these states appear in the midgap region.

Figure 2.3: Charge carriers in conducting polymer: (a) soliton, (b) polaron and (c) bipolaron. Dots represent unpaired electrons, and + indicates a positive charge. [17]

For simplicity, the quasi-particles are shown with charges that are localized to one atom, but in fact the quasi-particle exists over approximately 10 monomer units [17]. The charges move easily along the chains at the speed of sound, and less frequently between chains via interchain hopping where the pi orbitals overlap. While
Chapter 2. Electronic properties of polypyrrole

Figure 2.4: Conductivity vs. potential for ClO$_4^-$ doped polypyrrole. There is a sharp, doping induced metal insulator transition at about -0.3V [18].

The polymer is typically 100 times less conductive in the interchain direction, this interchain hopping is very important. Conducting polymers are highly disordered and any disorder along a chain will cause scattering that, in the absence of interchain hopping, would cause complete charge localization. Therefore the three dimensional conductivity depends on both the chain coherence length and the inter-chain hopping probability.

The conductivity as a function of potential for polypyrrole doped with ClO$_4^-$ is shown in Figure 2.4. The conductivity increases dramatically at about -0.3V vs. SCE (standard saturated calomel electrode) or one ion per 10 monomer units [18, 19]. The nature of this doping induced metal-insulator transition is not well understood. Some groups have shown that the Peierls gap decreases with doping level and may actually disappear [20]. Some groups have predicted a metallic state in which the Peierls gap persists and the charges exist in a soliton/bipolaron lattice [21, 22]. While there is no broadly accepted theory for this phenomenon, some consensus exists that the highly doped state is metallic in nature, with a continuous density of states and a well-defined Fermi energy [23].

2.3 Disordered metals

As previously mentioned, there is a high degree of disorder in conducting polymers. Anderson [24] and Mott [25] showed that this results in localization of the states in the band-tails. The energy separating the localized and extended states is called the mobility edge and its location will depend on the magnitude of the disorder potential. This is shown in Figure 2.5.

If the Fermi level exists within the extended states, it will behave like a metal
with band transport, and finite conductivity down to zero Kelvin. If the Fermi level is within the localized states, it will be an insulator and charges will move from localized state to localized state via phonon-assisted variable range hopping. Variable range hopping is characterized by the temperature/conductivity relationship (2.1).

\[ \sigma(T) \propto \alpha e^{-T_0/T} \]  

(2.1)

The conductivity of conducting polymers follows this relationship very well over a range of temperatures down to about 10K. However, the electronic properties of conducting polymers are further complicated by the fact that they are not homogeneous materials; they are made of ordered and disordered regions, as in Figure 4.2, and therefore they may exhibit both band and hopping conduction at any time. Also, there will be different levels of interchain interactions in different regions of the polymer, making the conduction appear one-dimensional in some cases and three-dimensional in others.

The specific morphology and therefore electronic properties depend on a wide range of processing factors. For instance, polypyrrole electropolymerized with the dopant ion \( \text{PF}_6^- \) exhibits band transport and remains metallic down to milli-Kelvin temperatures, whereas when doped with the tosylate ion, it exhibits variable range hopping and has a metal-insulator transition. Also, the conductivity vs. doping curve shown in 2.4 has been measured for numerous counter-ions and the threshold dopant level is highly variable [19, 26, 18, 27].

The electronic properties of conducting polymers are obviously very complicated. The previous discussions have been necessarily oversimplified, but serve to introduce some of the variables in determining the electronic properties of conducting polymer systems. To summarize, they are the:

1. quasi-1D nature of the conductor
2. interchain coupling
3. doping level

4. disorder and morphology of the polymer
Chapter 3

Electrochemistry of polypyrrole

The reversible electrochemical switching of conducting polymers has many potential applications, including supercapacitors, electrochromic windows and displays, and light-weight, muscle-like actuators. In this section, I will review electrochemical principles, experimental techniques, and modeling as they relate to the electrochemistry of polypyrrole.

3.1 The electrochemical cell

The simplest electrochemical cell has two electrodes, an anode and a cathode, in solution separated by an ionically conductive electrolyte. The electrolyte is most commonly a salt in solution, but solid electrolytes like Nafton, and liquid salts like ethylammonium nitrate are also used. Reactions may occur on the interface of the electrodes to produce a voltage (a galvanic cell or battery) or a voltage may be applied between electrodes to drive a chemical reaction (electrolytic cell). In electrochemical experiments, we are often only interested in the potential at one electrode, the working electrode (WE). The other electrode completing the current pathway in solution is called the counter electrode (CE). The potential at the working electrode is monitored with respect to a reference electrode (RE) which has a constant potential. The reference electrode is typically contained in an enclosed glass tube with a saturated solution of the reference electrode redox couple. Electrical contact with the cell is made through a porous plug which is permeable to ions. The current through the reference electrode is negligible, so the effect of the impedance of the reference electrode is insignificant. It is, however, important to place the reference electrode as close to the working electrode as possible when current is running in the cell. The potential at the reference electrode will include the IR drop due to the solution resistance from the working electrode to the reference electrode. This is called the uncompensated resistance. The effect of solution resistance can also be decreased with a high concentration electrolyte. The three electrode cell is shown in Figure 3.1.

3.2 The electrochemical potential and the Nernst equation

The driving force behind an electrochemical reaction is a difference in electrochemical potential, $\mu$, of the reactants and products. The species are in thermodynamic equi-
Figure 3.1: A three electrode electrochemical cell. WE, CE and RE are the working, counter and reference electrode respectively. $R_s$ is the solution resistance, and $R_u$ is the uncompensated resistance.
librium if their electrochemical potentials are equal. The electrochemical potential is the sum of the regular chemical potential, $\mu$ and a term related to the electrical work done by moving a charged species through an electric field.

$$\bar{\mu} = \mu + zF\phi$$  \hspace{1cm} (3.1)

$z$ is the charge number on the species, $\phi$ is the electrical potential, and $F$ is Faraday’s constant. The chemical potential of an electron in a metal is its Fermi energy. Ions in solution follow Maxwell-Boltzmann statistics, and therefore their chemical potential is governed by the law of mass action.

$$\mu = \mu^0 + RT\ln(a)$$  \hspace{1cm} (3.2)

$\mu_0$ is the chemical potential of the species at some standard concentration, and $a$ is the activity. For low concentration solutions, $a$ is usually the concentration of the ion. At higher concentrations, the activity may be corrected for interactions. For the following reversible redox couple

$$R_A \rightleftharpoons P_A + ne^-_A$$  \hspace{1cm} (3.3)

$$R_C + ne^-_C \rightleftharpoons P_C$$  \hspace{1cm} (3.4)

$R$ and $P$ represent the reactants and product at the cathode (C) and anode (A) respectively. If we equate the electrochemical potentials for the above we get

$$\bar{\mu}_R + \bar{\mu}_C + \bar{\mu}_e = \bar{\mu}_{PA} + \bar{\mu}_{PC} + \bar{\mu}_{eA}$$  \hspace{1cm} (3.5)

Expanding the electrochemical potential in terms of its chemical and electrical components and rearranging we get the familiar Nernst equation.

$$E_{cell} = \phi_C - \phi_A = \frac{1}{nF}(\mu^0_P - \mu^0_R - \frac{RT}{nF}\ln\frac{a_P}{a_R})$$  \hspace{1cm} (3.6)

$$E_{cell} = E_0 - \frac{RT}{nF}\ln\frac{a_P}{a_R}$$  \hspace{1cm} (3.7)

From this derivation, we can see that the Nernst equation is only applicable in the following situations:

1. at thermodynamic equilibrium (i.e. zero current).
2. when the law of mass action applies to all of the reagents in the reaction.

The Nernst equation turns out to be of limited use in understanding the electrochemistry of conducting polymers since Maxwell-Boltzmann statistics do not apply to electronic conductors such as conducting polymers, although this has not stopped many researchers from unsuccessfully trying to apply the Nernst equation to these situations.
3.3 Non-equilibrium conditions

When the electrochemical cell is drawing current, the potential will not be the Nernst potential. The relationship between the voltage and current in non-equilibrium conditions is determined by (1) mass transport, or how quickly reagents move to the electrode and (2) kinetics, or how quickly the electron transfer occurs.

3.3.1 Mass Transport

The general equation defining flux ($J$) of ions in an electric field is as follows:

$$J = -D \nabla C - \frac{zF}{RT} DC \nabla \phi + Cv \quad (3.8)$$

The first term in Equation 3.8 is the diffusion: $D$ is the diffusion coefficient and $C$ is the ion concentration. The second term is migration: $z$ is the number of charges on the ion, $F$ is Faraday’s constant, $R$ is the gas law constant, and $T$ is the temperature. $zF/RT$ is the Einstein relation for the mobility of an ion in solution. The third term is convection where $v$ is the velocity of the fluid. This is rarely an issue except in cases where the solution is stirred. The total current density in solution will be the sum of the fluxes for each type of ion present in solution.

In the case of an ideally polarizable or blocking electrode, where there are no electrochemical reactions, the electrode in solution acts as an RC circuit as shown in Figure 3.2. The ions move through the solution under the influence of migration and build up in a layer around the electrode with a thickness determined by the concentration of the electrolyte and the applied voltage. This is called the double-layer. The capacitance of a typical double-layer ranges over $0.1 - 0.4 \mu F/cm^2$ [28].

![Figure 3.2](image)

Figure 3.2: (a) An ideally polarizable electrode behaves like an RC circuit. $C_d$ is the double layer capacitance. (b) The double layer capacitance.
Electrochemists typically use a high concentration of electrochemically inactive supporting electrolyte in their experiments to simplify the mass transport equations. This electrolyte will create the double layer and cancel the effect of the electric field in solution. The reactive species in this case acts like the minority carrier in solid state electronics and the dominant mass-transport is diffusion. It is not possible to make this simplification in conducting polymer electrochemistry as there is no supporting electrolyte and migration plays an important role. Therefore many of the equations in electrochemistry textbooks are not applicable to our situation.

3.3.2 Kinetics

The rate constant, $k$, for electron transfer follows an Arrhenius law for thermally activated transfer over an energy barrier of height $E_A$.

\[
k = Ae^{E_A/RT}
\]  

(3.9)

The total rate of a reaction, $\nu$, is the sum of the forward and backward rates

\[
\nu = k_fC_R - k_bC_P
\]  

(3.10)

$k_f$ and $k_b$ are the rate constants for the forward and reverse reaction and $C_R$ and $C_P$ are the concentrations of the reactants and products. Of course a potential can be used to surmount the barrier as well, and this relationship is known as the Butler-Volmer equation.

\[
k_f = k_0e^{-\alpha_f(E-E^0)}
\]  

(3.11)

\[
k_b = k_0e^{(1-\alpha_f)(E-E^0)}
\]  

(3.12)

$k_0$ is the standard rate constant, $\alpha$ is a parameter between zero and one which relates to the symmetry of the activation barrier. It is typically very close to one half. $E$ is the electrode potential, and $E^0$ is the equilibrium potential. Typically if $k_0$ is very large, the kinetics are very fast and the Nernst equation is applicable. The kinetics of polypyrrole electron transfer are very fast due to its metallic characteristics.

3.4 Equivalent circuits

Electrochemical reactions can often be modeled using simple circuit elements [29]. The double layer capacitance is simply a capacitor, although in general the capacitance depends on the potential to some extent, and the solution resistance is a resistor. Other electrochemical processes have similarly been associated with circuit elements. A particularly useful element is the constant phase element (CPE). The CPE is characterized by an impedance with some frequency dispersion:

\[
Z_{CPE} = \frac{1}{(iC\omega)^p}
\]  

(3.13)
A CPE with $p$ equal to 1 is a capacitor. With $p$ equal to a half, the CPE is called a Warburg element. This is the characteristic impedance of semi-infinite diffusion to an electrode and is common when a supporting electrolyte is used to eliminate the effect of migration in the electrochemical reaction. It is also the solution to an RC transmission line. An RC transmission line is shown in Figure 3.5. The resistance and capacitance per unit length are $r$ and $c$ respectively. The impedance of an RC transmission line is determined as follows:

$$I = -\left[\frac{1}{r}\right]\frac{\partial V}{\partial x}$$

(3.14)

$$\frac{\partial V}{\partial t} = -\left[\frac{1}{c}\right]\frac{\partial I}{\partial x}$$

(3.15)

If the spatial derivative of Equation 3.14 is taken and substituted into Equation 3.15 then it is clear that the characteristic equation is indistinguishable from the diffusion equation where $V$ is equivalent to the electrochemical potential difference and the time constant $rc$ equal to $1/D$, the reciprocal of the diffusion coefficient.

$$\frac{\partial V}{\partial t} = -\left[\frac{1}{rc}\right]\frac{\partial^2 V}{\partial^2 x}$$

(3.16)

The RC transmission line is used to model distributed electrodes, such as porous metals.

A rough or inhomogeneous electrode acts like a CPE with $p \approx 0.95$, i.e. like an imperfect capacitor. In electrochemistry, only the smoothest electrodes, such as liquid metals, act like a pure capacitor.

CPE behavior can also physically represent inhomogeneous current distributions, distributions of relaxation times and reaction potentials [29]. It has been applicable not only to electrochemistry, but also to solid-state conduction in inhomogeneous conductors. Many electrochemical circuits have a CPE-like element, which makes it very useful in fitting equivalent circuits, but as there are many physical mechanisms for this behavior, care must be taken in interpreting these models.

Chemical reactions can also be represented as an equivalent circuit element. When equation 3.11 is linearized for small potential, the chemical reaction appears as a resistor. A common equivalent circuit is the Randles circuit, shown in Figure 3.3. $R_S$ is the solution resistance, $C_{DL}$ is the double layer capacitance, $R_{CT}$ is the charge transfer resistance, i.e. the linearized chemical reaction, and $Z_D$ is the Warburg element for diffusion.

### 3.5 Electrochemical methods

The electrochemistry of the working electrode can be investigated by many techniques, a few of which are listed below [28]. All of these techniques give different information about the cell, and are often used in combination to understand the electrode dynamics.
1. Chronoamperometry: potential steps are applied and the transient currents are measured.

2. Potential sweeps and cyclic voltammograms: the current is measured as a function of a linearly varying potential.

3. Potentiometry: the potential of the working electrode is monitored at zero current. This is called the open-circuit potential.

4. Impedance spectroscopy: a small AC potential is applied and the current at that frequency is measured. This gives the complex impedance of the circuit.

These measurements are accomplished by a potentiostat (for controlled potential) or a galvanostat (for controlled current). The impedance analyzer is a combination of a potentiostat and a lock-in amplifier which is used to measure currents down to \( \mu A \). More details about the instrumentation can be found in [28].

These techniques will be discussed in more detail with respect to polypyrrole electrochemistry in Section 3.6, and in the experimental details, Section 5.4.

### 3.6 Electrochemistry of polypyrrole

Since the electronic properties of polypyrrole vary widely with synthesis conditions, it is to be expected that the electrochemical properties do as well. In general, polypyrrole acts as a porous electrode, with no electron transfer between the electrolyte and the polymer.

Consider the redox reaction in a conducting polymer. Since the electrolyte is inert, no electrons are transferred between electrolyte and polymer, however, as the polymer charges, ions must move in or out to maintain electroneutrality. For the charged polymer at equilibrium in a solution with one mobile ion (\( X^- \)) the balanced
equation is [30]

\[(PPy)_n^+ + X_P^- \rightleftharpoons (PPy)_n + X_S^- \] (3.17)

\(X_P^-\) is the ion in the polymer matrix, \(X_S^-\) is the ion in solution, and \((PPy)_n\) is a chain of \(n\) pyrrole units. If we equate the electrochemical potentials in this reaction, we get

\[\mu((PPy)_n^+) + RT \ln(a_{X_P^-}) - F\phi_{X_P^-} = \mu((PPy)_n) + RT \ln(a_{X_S^-}) - F\phi_{X_S^-} \] (3.18)

When the film is highly reduced and has localized states, this equation results a quasi-Nernst equation [30], but with a range of energy states. However, at higher doping, ESR measurements have shown that there is more and more interaction between charged species [31] leading to a 3D metallic state and a Fermi-Dirac distribution. That means there is a negligible difference in electrochemical potential of the polymer with addition of one electron. Therefore, the law of mass action (and the Nernst equation) is not applicable. In this case,

\[E = \phi_{WE} - \phi_{X_S^-} = \frac{RT}{F} \ln \frac{a_{X_P^-}}{a_{X_S^-}} + (\phi_{WE} - \phi_{X_P^-}) \] (3.19)

where \(\phi_{WE}\) is the working electrode potential. The first term is the Donnan potential, \(E_D\) [28]

\[E_D = \frac{RT}{F} \ln \frac{a_{X_P^-}}{a_{X_S^-}} = \phi_{X_P^-} - \phi_{X_S^-} \] (3.20)

The Donnan potential exists on the polymer/solution interface and results from the Maxwell-Boltzmann distribution governing the ion statistics; it exists at any semi-permeable membrane that separates different solute concentrations. This potential will contribute to the apparent impedance of the surface. Taking the activities to be the concentrations (0.05M in the solution, and up to 5M in the oxidized film), the Donnan potential is approximated at about 100mV. This is just an order of magnitude estimation because the ion activities will be very different in the polymer and in the solution due to the different solvation and the dilute approximation that the activity is equal to the concentration is not accurate at 5M.

The second term of equation 3.19 is the potential difference between the polymer chains and the ions which is caused by the charge separation of the polymer and ionic phase. This potential can be described by an effective capacitance, \(V = Q/C\). Metallic polypyrrole acts like a capacitor with a large internal surface area [32]. The effective capacitance depends on the electronic properties of polypyrrole as a function of potential, but is relatively independent of potential when the polymer is in the metallic state [33, 34]. The potentials from equation 3.20 are shown in Figure 3.4.

The above argument takes into account only the electrochemistry, however we also know that the polymer expands and contracts with oxidation and reduction. An extra term may be added to equation 3.18, \(\Delta\mu_{conf}\), which refers to the difference in chemical potential from the expanded to contracted conformations. This term is often neglected as much smaller than the other two terms, but some groups [35, 36]
Chapter 3. Electrochemistry of polypyrrole

Figure 3.4: The potentials through the polymer system. $\phi_{WE}$ is the working electrode potential, $\phi_P$ is the potential of the ions in the polymer matrix, $\phi_S$ is the potential of the bulk solution, $\phi_C$ is the capacitive potential, and $\phi_D$ is the Donnan potential.
feel that the conformational energy may play a large role in some cases. In addition, there is the change in solvent-polymer interactions [37], and most importantly, the extremely large change in electron transport of the polymer film from the reduced to oxidized state; conductivity changes of 4 to 8 orders of magnitude have been recorded [38, 19, 26].

It is clear that the thermodynamics of this system are quite complicated, with all of these effects undoubtedly occurring at the same time. It is for this reason that traditional electrochemical analysis has failed for these polymers. Conducting polymers show irreversibility and hysteresis in voltammograms [35, 39]; they have transfer coefficients, \( \alpha \), as defined in Equation 3.11, of approximately 0.1 as opposed to 0.5 for normal electrodynamics [40]; the activity coefficients derived from the Nernst equation are unphysical [30].

Electrochemical impedance spectroscopy has had some success explaining the electrochemical behavior of conducting polymer electrodes in the conducting state. Equivalent circuits have concentrated on the mass-transport of ions as the rate limiting step, and typically employ a finite transmission-line element (Figure 3.5). This element could represent a distributed electrode [32, 34, 41, 42] or a finite diffusion element [43, 44], as the differential equations for these physical situations are identical (3.16). Polypyrrole in the oxidized state acts like a two-phase system of conductors (the polymer and the electrolyte) with both a capacitive component and a diffusive component as seen in Equation 3.19. Which controls the mass transport will depend on the local concentration and electric field distributions. Typically, the transmission line model does not fit exactly. The better the fit, the more involved the circuit model [34], making the physical meaning ambiguous.

![Figure 3.5: The finite transmission line is a model for a porous electrode or a finite diffusion problem.](image)

As expected from the transmission line model, the long time-scale impedance generally appears RC-like, with a very large capacitance; under a potential step, the current decays exponentially. On the other hand, from the highly reduced state, application of a potential step has been observed to create phase fronts between the oxidized and reduced regions that move at constant velocity away from the electrode. The current does not decay exponentially, but is approximately constant until the phase front reaches the end of the film (Figure 3.6) [45, 46, 47]. This can also be seen directly in thin films due to the electrochromic effect in conducting polymers which causes a color change under electrochemical switching (Figure 3.7) [48, 47].
This behavior cannot be explained by the homogeneous ion-limited transmission-line model. In the reduced state, the electron transfer is also important.

![Graph](image)

Figure 3.6: Phase fronts caused by potentiostatic oxidation of polypyrrole in the insulating state. The current is constant until the front reaches the end of the film [47].

There are many suggestions for the cause of the front including the kinetics of charge transfer at the conducting interface [47], and a change in conformational energy [36]. Many models explaining these fronts have arisen [49, 47, 45, 48, 50] involving both continuum and microscopic models. So far, these models have been qualitative rather than quantitative, due to the difficulty in separating the effects of ionic and electronic mobilities, and the difficulty of measuring certain parameters such as the ionic diffusion coefficient.

From the fully oxidized state, the film to reduces fairly evenly due to the metallic nature of the film. However, it is very difficult to reduce all the way; up to 10% of the dopants may remain in a film reduced by an electrode at one end [38]. This has been explained via percolation theory [38], with small metallic islands being separated by insulating regions at the percolation limit.

These experiments will be discussed in more details in Section 7.4.
Figure 3.7: The absorbance \( A = -\log(I/I_0) \), \( I_0 \) is the intensity of the incident beam, and \( I \) is the transmitted intensity) of red light along the length of the film is detected by a linear bank of photodiodes, designated 1-14 on the plot. 1 is closest to the electrode, and 14 farthest away. The photodiodes clearly show the front moving along the strip of polypyrrole. [47].
Chapter 4

Structure of polypyrrole

The structure of polypyrrole is investigated by means of x-ray diffraction and macroscopic actuation measurements. X-ray diffraction (XRD) uses the interference of elastically scattered photons off of a periodic lattice of atoms to probe the structure of crystalline matter. This technique is very common in chemistry and materials science for evaluating crystal structures [51, 52] so a complete review will not be provided; however, there are some significant differences when using this technique to look at polymers [53, 54]. This chapter will give a brief review of the principles of x-ray diffraction, and then discuss principles particular to organic crystals and polypyrrole in particular. The last section will discuss the macroscopic actuation of polypyrrole.

4.1 X-ray interactions with matter

X-rays interact with matter in three different ways:

1. the photoelectric effect
2. Compton scattering
3. coherent scattering

The photoelectric effect occurs when a photon is absorbed by an atom and the atom releases this energy in the form of an ionization electron. They may also release any remaining energy in the form of x-ray fluorescence. The photoelectric effect is the principal cause of absorption in materials and increases with Z, the number of electrons in the constituent atoms. As polymers are generally composed of low atomic number atoms, the absorption is very small.

Compton scattering is elastic scattering of a photon with a loosely bound electron in the outermost shell of an atom. The photon gives up some of its energy to the electron, therefore the energy of the outgoing photon will be longer in wavelength than the incoming photon. Compton scattered photons are typically filtered out in modern diffractometers. Scattering is also proportional to the number of electrons in the material, therefore polymers are also weak scatterers of x-rays.

Coherent scattering is a phenomenon which can only occur in ordered materials. The photon scatters elastically from an electron, losing none of its energy and retaining its phase. The momentum change of the photon is absorbed by the entire
crystal, instead of an individual electron. This is similar to the principle of crystal momentum in solid state electronics.

The intensity of coherent scattering from an atom depends on the scattering angle. To begin with, x-ray scattering by an electron occurs preferentially in the forward and reverse direction. Also, since the electrons surrounding an atom occupy a finite amount of space, photons scattered from the sum total of electrons in an atom become incoherent at larger angles. Both of these effects are taken into account in the atomic scattering factor (also called the form factor), $f$, which describes the scattering as a function of angle for each atom. Lighter elements have atomic form factors that drop off more rapidly with angle. In organic crystals, this leads to a limited range of angles where diffraction peaks may be observed.

## 4.2 Interference

In crystalline material, interference of scattered radiation from the sum of the atoms in the lattice causes a finite number of sharp diffraction peaks. This is described by Bragg’s Law, illustrated in Figure 4.1. The x-rays diffract off of two sets of planes separated by a distance, $d$, and interfere at infinity. It is clear that constructive interference occurs only for those angles, $2\theta$, where

$$n\lambda = 2d\sin\theta$$

(4.1)

$n$ is the diffraction order, $\theta$ is the angle of incidence on the planes, and $\lambda$ is the wavelength of the photon. A more general way of expressing the interference relationship...
is with the Laue formulation:

\[ \mathbf{k} - \mathbf{k}_0 = \mathbf{K} \]  

(4.2)

where \( \mathbf{k} \) and \( \mathbf{k}_0 \) are the incoming and outgoing wavevectors respectively and \( \mathbf{K} \) is one of the reciprocal lattice vectors.

In crystals with an \( n \)-atom basis, the intensity of a diffraction peak corresponding to a particular reciprocal lattice vector, \( \mathbf{K} \), is modified not only by the atomic scattering factor, but also by the structure factor, \( S \), which incorporates the interference of photons diffracted from each atom in the basis.

\[ S_{\mathbf{K}} = \sum_{j=1}^{n} f_j \exp(i\mathbf{K} \cdot \mathbf{d}_j) \]  

(4.3)

### 4.3 Intensity corrections

The previous section represented the ideal x-ray diffraction pattern. In a real x-ray diffraction experiment, the intensity of the peaks is modified by other factors as well. These corrections must be made in order to do a quantitative structure evaluation.

In a powder specimen, where all orientations of the crystal are equally represented, the multiplicity of the planes must be taken into account. For instance, in a cubic lattice, the \((100)\), \((010)\), \((001)\), \((100)\), \((010)\), and \((001)\) have equivalent angles of reflection so the multiplicity of this reflection is 6.

The intensity of the diffracted x-rays is also affected by the geometry of the measurement apparatus. XRD of polymers is normally done in transmission mode as the absorption and the scattering in polymers is very weak. The ideal polymer thickness for maximum signal is \(1/\mu\), where \( \mu \) is the linear absorption coefficient. The intensity as a function of angle must be modified to reflect both the difference in diffraction volume for different angles, and the difference in absorption.

The width of the x-ray peak is a convolution of the actual peak width and width of the slits in the diffractometer apparatus.

The Lorentz factor is a correction for the density of reciprocal lattice points near the Ewald sphere. Reciprocal lattice vectors that cross the Ewald sphere at normal incidence will produce a peak that is less intense than one which crosses at grazing incidence. For a powder sample which takes on all orientations at once, \( L \) is equal to:

\[ L = \frac{1}{\sin 2\theta \sin \theta} \]  

(4.4)

In addition, the incident x-rays are normally unpolarized, but upon scattering with electrons acquire a polarization proportional to \( P \):

\[ P = \frac{1}{2}(1 + \cos^2 \theta) \]  

(4.5)
These two factors are normally combined to form the co-called \( LP \) factor.

For polymers above their glass transition temperature, the temperature below which molecular motions are frozen out, the chains will have a random component to their crystal spacings due to thermal vibrations. The intensity of the peaks will be decreased by the temperature factor (4.6). The width of the peaks are unaffected [53, 54].

\[
TF = \exp(-2M)
\]  

where \( M \) depends on the angle since the relative displacement of a crystal dimension, \( a \), will be smaller for larger crystal dimensions, i.e. smaller angle.

\[
M = B \sin^2 \theta / \lambda^2
\]

B is a factor characterizing the magnitude of the thermal displacements.

### 4.4 Polymer crystals

Polymer crystals are never perfectly ordered, therefore they rarely experience sharp diffraction peaks like inorganic crystals. This next section deals with the morphology of polymers and its effect on the x-ray pattern.

Polymers form ordered structures that are unlike the perfect crystals formed by atomic and molecular solids. Due to

1. constraints imposed by covalent intrachain bonding
2. weak Van der Waals or hydrogen bonding interchain interactions, and
3. the large configuration space, i.e. large entropy, of a flexible polymer chain

polymers form structures that are often partially crystalline and partially amorphous [31].

There are two broad types of polymer crystal structure, depending on the persistence length of the chains. Lamellae, shown in Figure 4.2, are formed by stiffer polymers, this is the the commonly accepted crystal model for conjugated polymers [11]; and fringed mycelles, in Figure 4.3, are typically formed by very flexible polymers such as polyethylene. Both polymer systems show both crystalline and amorphous regions.

Also, even within a polymer crystal there tends to be a lot of disorder. Polymers are subject to lattice distortions of the first and second kind [55]. Lattice distortions of the first kind are random deviations from the ideal lattice points, such as you would get from thermal vibrations. For this reason, they are often called “frozen in thermal displacements”. The effect of this type of distortion is just the temperature
Figure 4.2: Stacked lamellae [31]

Figure 4.3: Fringed mycelles [31]
factor, (4.6). Distortions of this type are very common, as polymers rarely reach thermodynamic equilibrium during annealing.

Distortions of the second kind are also called paracrystalline distortions. Paracrystals have no long range order. They have lattice spacings that have some variation from cell to cell. This type of disorder is characterized by

\[ g = \frac{\Delta d}{d} \]  

(4.8)

where \( d \) is the lattice spacing. The effect of this type of disorder is both a decrease in intensity, \( I \), with diffraction order, \( h \), and an increase in the width, \( \delta b \), of the diffraction peaks. The intensity goes as

\[ I = \exp\left(-2\pi^2 g^2 m^2\right) \]  

(4.9)

and if the width is defined as

\[ \delta b = \frac{\int (I(b) - I_0)db}{I_{\text{max}}} \]  

(4.10)

where \( b \) is equal to \( 1/d \) and \( I_0 \) is the background, then the width goes as

\[ \delta b = \frac{(\pi gh)^2}{d} \]  

(4.11)

This type of disorder is also responsible for the fact that polymer crystals are typically very small. The small size of the crystals results in an increase in the width of the peaks, and a decrease in the height but these do not change with peak order. The height of a diffraction peak with size \( L \) goes as \( L^2 \), and the width is characterized by the Scherrer equation:

\[ \delta b = \frac{1}{L} \]  

(4.12)

Equations (4.11) and (4.12) are combined to give the total effect of the micro-paracrystals on the width of the diffraction peaks. If three or more orders of reflection are observed, it is possible to separate the effects of the size and the distortions. However, this is rarely the case for conducting polymers. Only one order of reflection is typically observed with as-grown polypyrrole, which sets a minimum for the disorder factor, \( g \), of about 25%.

4.5 XRD of Polypyrrole

The x-ray diffraction pattern of an as-grown sample deposited using the method outlined in Section 5.1 is shown in Figure 4.4. The large amount of disorder inherent in the polypyrrole matrix means the x-ray peaks are broad and the higher order peaks are severely damped. Nogami [56] provided the first interpretation of this pattern.
Since four peaks are not enough to define the unit cell, the polymer was first stretch-aligned. Stretch-aligning accomplishes two things: (1) the amount of order in the sample is improved, especially in the stretch direction, which increases the number of observed peaks, and (2) the crystals become anisotropic, with the chains aligned in the stretch direction. With prior knowledge of the monomer-monomer spacing along the chain length, $b = 7.3 \text{Å}$, and the size of the dopant ions, some deductive reasoning led to the unit cell shown in Figure 4.5. The lattice spacings are $a$, $b$, and $c$ equal to $11.8 \text{Å}$, $7.3 \text{Å}$, and $3.75 \text{Å}$ respectively, and the angle, $\alpha$, is equal to $65^\circ$. For a monoclinic cell such as this, the reciprocal lattice vectors are

$$a^* = \frac{2\pi}{a} \hat{z}, \quad b^* = -2\pi \frac{c_x \hat{y} + c_y \hat{x}}{b c_y}, \quad c^* = \frac{2\pi}{c_y} \hat{y}.$$  

The length of $b^*$ is $1/b \sin \alpha$. The face-to-face stacking distance is $3.4 \text{Å}$ and has been found to be very consistent for polypyrrole, regardless of the dopant ion. It is believed that the chains are closely stacked in this direction due to pi-stacking in the oxidized state. Pi-stacking is a phenomenon where unpaired electrons in the pi-orbitals are shared by ring molecules stacked on top of one another, in a type of weak covalent bond, and is thought to be important for conduction.

The amorphous peak from Figure 4.4 corresponds to an intermolecular distance of $4.5 \text{Å}$. It was found to be completely amorphous, even under stretching and has been attributed to the amorphous regions of the polymer [56]. The interchain spacing $a$, has been experimentally correlated to the ion size [14, 15].

Nogami also used the Scherrer equation (4.12) to evaluate the size of the crystallites in the film. They found that the crystal size in the direction of the polymer chain was less than $20 \text{Å}$, or 3 times the chemical repetition length. In our opinion, this is not a reasonable number for the crystal size, especially considering the large conductivity of the film. We propose instead that the polymer is paracrystalline. Paracrystallinity results in peaks with increasing width and decreasing amplitude with diffraction order, which is qualitatively observed in Nogami’s stretch aligned samples. In no direction were a full three orders observed, therefore we cannot determine with certainty the size and disorder parameters. Paracrystalline distortion also explains why in the unstretched film we only see the first order peaks; the unstretched film is more disordered and all higher orders are suppressed.

From the observed diffraction orders in Nogami’s experiment, we can infer the amount of disorder in the different crystal directions. For a stretch aligned film in the horizontal direction, equatorial peaks are of the form $(0k0)$ and meridional peaks are $(h0l)$. The peaks that would be expected for the proposed unit cell and the actual peaks observed are listed in Table 4.1. You can see that many diffraction peaks are missing. This could mean that this is a poor model for the unit cell, but there are other possible reasons for missing peaks.

As Nogami et. al. noted, the $(020)$ peak could be missing due to the structure factor. The structure factor of polypyrrole has not yet been analyzed to the best
Figure 4.4: X-ray diffraction pattern of electrodeposited PPy(PF$_6$) showing the $a^*$, $b^*$, and $c^*$ reciprocal lattice vectors and the amorphous peak.
Figure 4.5: The proposed unit cell for polypyrrole [56]. The rings are displayed edge on using rectangles. The chain length direction is \textbf{b}; the chains are close packed in the ring face to face direction, \textbf{c}; and ions are situated between chains with flat rings, in the \textbf{a} direction.

of our knowledge. The fact that a third order peak is observed in this direction indicates a high degree of order in the stretch direction as we would expect. The missing meridional peaks are (200), (101), (201), (102) and (202). These are all higher orders with a component in the \textbf{a}^* direction (ring-ion-ring), and it is likely that these peaks are missing due a large amount of paracrystalline disorder in this direction. Also note that the (100) peak has a much smaller amplitude than the other first order peaks. Figure 4.4 does not apply the LP intensity correction from Section 4.3; when it is applied we see that the actual amplitude of the \textbf{a}^* peak is about 40 times smaller than the \textbf{c}^* peak. The small size of this peak relative to the others is also consistent with a large degree of disorder. The presence of the (002) diffraction peak, however, indicates increased order in the ring face-face direction, which is consistent with strong pi-pi stacking interactions.

It is clear that there is some ambiguity in the diffraction pattern of polypyrrole and other unit cells have been proposed. There have been both experimental and theoretical studies indicating a helical structure may be possible. TEM images of polypyrrole suggest that individual chains of electrodeposited PPy may form helices, whereas in the bulk, a more disordered structure is evident [57]. Electron diffraction shows small crystallites surrounded by amorphous material, and a hexagonal structure that was attributed to helices [58]. Quantum chemical simulation have shown that a molecular conformational change may be an actuation mechanism in polypyrrole, going from a planar, pi-stacking conformation in the oxidized state, to a helical or bent structure in the neutral, reduced state [59].

The deposition conditions, including the temperature [16], the deposition current
Table 4.1: Diffraction orders for stretch-aligned polypyrrole

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Orders Expected</th>
<th>2θ</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equatorial</td>
<td>(010)</td>
<td>13.4</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>(020)</td>
<td>26.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(030)</td>
<td>40.8</td>
<td>×</td>
</tr>
<tr>
<td>Meridional</td>
<td>(100)</td>
<td>7.5</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>(200)</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(001)</td>
<td>26.2</td>
<td>×</td>
</tr>
<tr>
<td></td>
<td>(101)</td>
<td>27.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(201)</td>
<td>30.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(002)</td>
<td>53.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(102)</td>
<td>54.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(202)</td>
<td>56.3</td>
<td></td>
</tr>
</tbody>
</table>

[60], and the counter-ion [14, 61, 11] all influence the structure and this in turn affects the conductivity [11] and electrochemical properties [13] of the polymer. For example: electrodepositing at low temperatures and low current densities typically results in more crystalline films, which are denser, stronger and have higher conductivity; the conductivity of the film is related to the counter-ion size as the chains are forced to be farther apart with large ions in the matrix; using small, symmetrical counter-ions like PF$_6^-$ or ClO$_4^-$ results in a fairly isotropic structure, whereas with flat ring counter-ions like the tosylate ion (TsO) the polymer chains prefer to lie flat on the substrate.

### 4.6 Actuation of polypyrrole

The structural changes in polypyrrole are not fully understood. As discussed in Section 1, the redox process involves a combination of electrical, chemical, and structural changes including ionic motion, polymer chain diffusion and possibly a change from the planar structure to the helical structure.

For volume changes on time-scale of seconds, it has been shown by electrochemical quartz crystal micro-balance (EQCM) [62] measurements and through the bending beam method [10, 46] that the volume changes are associated with the mass-transport of ions into the polymer. EQCM gives the mass and stiffness of a film deposited on a resonant crystal, and the bending beam method measures very small volume changes by attaching the polymer film to a compliant electrode and measuring the changes in curvature of the bilayer strip due to actuation.

Models of actuation that treat the polymer as a viscoelastic material with a forcing term proportional to the number of ions exchanged with solution (or equivalently, the charge moved) have been fairly successful for these time scales [63, 64, 65]. Equation 4.13 describes the strain, $\epsilon$, caused by the passage of charge $\rho$ under a stress $\sigma$ when
only one ion is mobile in the film.

\[ \epsilon = \sigma \left( \frac{1}{Y} - \frac{1}{Y'} \right) + \alpha \cdot \rho \]  

(4.13)

\( Y \) and \( Y' \) are the Young’s moduli in the initial and final states, and \( \alpha \) is some constant of proportionality incorporating the size of the ions and their solvation shell, as well as the effects of osmosis \([66]\). It is important to incorporate changes in the stiffness of the polymer. Depending on the solvent, the Young’s modulus can change by over a factor of two \([67]\). This may be because in the oxidized state the film has pi-stacking, and in the reduced state, it would not. The increased interactions caused by pi-stacking would be expected to make the film stiffer. Dynamic models must include the electrochemistry of the polymer as well as the mechanical swelling.

There are, however, some effects which are not so easy to explain. For instance, sometimes the chemical effects cannot be ignored. The solvation of the film changes with oxidation state \([68]\), in general being more soluble in the oxidized state and the solvent and counter-ion interactions can affect the mobility of ions in the polymer \([69, 10]\). Also, when the polymer is held for a time in the neutral state, the polymer chains undergo a conformational change to a more compact state, regardless of whether the anions or cations are mobile in solution \([10, 36]\). This is exemplified by a reversal in actuation that occurs for polypyrrole doped with dodecylbenzene sulfonate (DBS\(^{-}\)) \([10]\). The DBS ion is very bulky, and does not move during actuation. Under reduction, sodium ions in the solution enter the polymer and cause an initial expansion of the polymer. After the current has stopped, however, the polymer begins a slow contraction which does not seem to saturate on the time-scale of 10 minutes.

In addition, polypyrrole undergoes an irreversible change in the first cycle. The first cycle of polypyrrole is characterized by much larger redox peaks in cyclic voltammograms \([39]\) and a particularly sharp front \([48]\). We have also observed an irreversible loss in charge capacity. This is called the first scan effect in the literature and it is thought to be caused by polymer relaxation \([36]\).

---

\(^1\)Note, \( E \) is the normal symbol for the Young’s modulus. \( Y \) has been used to prevent confusion with the cell potential which is denoted \( E \) throughout the text.
Chapter 5

Experimental methods

In this thesis, we investigate the change in electronic, electrochemical and structural properties as a function of oxidation state. We attempt to correlate these interrelated effects to develop a comprehensive model of the electrochemistry of polypyrrole actuators.

The sections in this chapter are as follows:

Section 5.1 The general procedure for electrodepositing polypyrrole is described.

Section 5.2 The apparatus for polymer redox is described.

Section 5.3 The conductivity of the polymer is measured as a function of oxidation state.

Section 5.4 The electrochemistry of polypyrrole is investigated through electrochemical impedance spectroscopy and through chronoamperograms.

Section 5.5 The structure of the polypyrrole is investigated through x-ray diffraction and macroscopic actuation measurements.

5.1 Deposition

Polypyrrole can be grown either chemically or electrochemically. Electrochemical deposition results in films with the highest conductivity and the best mechanical strength. Polypyrrole is polymerized through electrochemical oxidation of the pyrrole monomer. Oligomers form in solution and precipitate onto the electrode where they nucleate growth of the polymer. Figure 5.1 shows the synthesis reaction.

Polypyrrole is grown in the doped or oxidized state. The doping level in as-grown polypyrrole is approximately one charge per three monomers [11]. The electrodeposited film is black and appears smooth and shiny on the electrode side and slightly rougher with a “cauliflower” type morphology on the solution side.

The polymer system chosen for this study is polypyrrole doped with the hexafluorophosphate ion, PPy(PF$_6$). It is electrodeposited onto the working electrode from a solution of 0.06M distilled pyrrole, 0.05M tetraethylammonium hexafluorophosphate (TEA·PF$_6$) and 1%vol distilled water in propylene carbonate (reagents from Sigma-Aldrich) [14]. The solution is deoxygenated by bubbling with nitrogen before and during growth. The deposition solution should be as pure as possible to prevent
Figure 5.1: The electrochemical reaction for deposition of polypyrrole

Figure 5.2: The electrochemical cell for deposition of polypyrrole
side-reactions that could lead to defects in the polymer. All reagents were used as received, except for the pyrrole, which was distilled frequently to remove oligomers that form spontaneously in the presence of light and oxygen. The distilled pyrrole was stored under nitrogen after distillation in the freezer.

The choice of electrode material is key. Polypyrrole does not nucleate well on many metals, including stainless steel, and indium tin oxide (ITO). The best results have been achieved on glassy carbon, platinum and titanium [16]. The surface quality of the electrode is also very important. Ideally, the surface should be mirror smooth for uniform nucleation.

To obtain free-standing films, a glassy carbon crucible is used as the working electrode. The crucible is polished first with 1 \( \mu \)m diamond spray and then with jeweler’s rouge. The surface is microscopically smooth but has some macroscopic bumps which do not seem to adversely affect the growth. The counter electrode is a copper foil which has been sanded to remove oxides. The reaction occurs at a constant current of 0.125 mA/cm\(^2\) (the potential is approximately 0.7V vs. SCE) and a temperature of -35 to -40°C for 8 hours to obtain a thickness of approximately 22 \( \mu \)m. The thickness and the conductivity of the film vary by about 20% over the surface of the crucible. The deposition apparatus is shown in Figure 5.2.

### 5.2 The redox cell

Figure 5.3 shows the electrochemical cell used for all redox cycling experiments.

A non-aqueous Ag/Ag\(^+\) reference electrode is used to control the potential. The reference electrode consists of a silver wire in a glass tube with 0.01M AgClO\(_4\) and 0.05M TEA-ClO\(_4\) in propylene carbonate. The reference electrode solution is separated from the cell solution with a porous plug. This is only a quasi-reference electrode; the potential changes slowly with time due to electrolyte exchange with the cell. For calibration, the potential of the reference electrode was frequently tested against a standard calomel electrode (SCE) in an aqueous medium. From now on, all potentials will be quoted versus the SCE, as this is a true reference electrode. Polypyrrole has an electrochemical potential of (0.4 ± 0.03)V vs. SCE in its fully-oxidized, as-grown state. In the fully reduced state, with no ions in the matrix, the film has a potential of -0.8V vs. SCE.

The counter electrode is carbon fiber paper. Carbon-fiber paper experiences no electrochemical degradation in the range of potentials used. However, due to the much larger capacitance of polypyrrole than carbon-fiber paper, the voltage at the counter electrode will be much larger than at the working electrode, therefore there is likely some electrolyte degradation at the counter electrode. The solution is replaced often to make sure that these reactions do not contaminate the sample.

The solution used for cycling is 0.05M TEA-PF\(_6\) in acetonitrile. The solution is bubbled in nitrogen to eliminate parasitic reactions with oxygen. Acetonitrile has the advantage of a much lower boiling point than propylene carbonate. Films dry
Figure 5.3: The electrochemical cell for redox cycling. The working electrode is polypyrrole, the counter electrode is carbon fiber paper and the reference electrode is Ag/Ag⁺.

quickly and can be characterized soon after cycling.

All electrochemistry is performed with a Solartron SI 1287 galvanostat/potentiostat (http://www.solartron.com/), controlled by the CorrWare software package (http://www.scribner.com/).

5.3 Conductivity

It was shown in Section 2.2 that the conductivity of polypyrrole is a sigmoidal function of doping level. The transition level and shape of the conductivity varies greatly from polymer to polymer. In this experiment we measure the conductivity of PPy(PF₆) as a function of oxidation state.

The conductivity of free-standing films is measured with the four point probe shown in Figure 5.4. It is important to use a 4-point resistance measurement because the conductivity of polypyrrole is very high, and the contact resistance is typically large. The probe is composed of four parallel gold wires attached to a glass slide. This provides good contact over the entire width of the polypyrrole strip. Leads are connected to a Hewlett-Packard 34401A multimeter in 4-pt resistance mode. Good contact between the gold wires and the polypyrrole was ensured by placing the polypyrrole between the probe and a cover slide, and applying pressure with a metal clip.
Film thickness, $t$, is measured with a micrometer. This undoubtedly compresses the polypyrrole somewhat, but by tightening the micrometers until the ratcheting mechanism slips, we ensure that the compression is consistent from one film to another.

The film width, $w$, and length, $L$ are measured with calipers. The conductivity of the as-grown films is approximately 300S/cm.

The films are known to exhibit a memory effect in some situations; the electrochemical history of the film affects its current properties. To investigate whether there is a memory effect in the conductivity of PPy(PF$_6$), we prepare three sets of films in identical oxidation states, $E$, between fully oxidized and fully reduced, but with different histories. The electrochemical procedure for each set is summarized in Table 5.1. The final step in each set is holding the film potentiostatically at $E$ until the current has decayed to zero.

<table>
<thead>
<tr>
<th>Set</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>potentiostatic at $E$ until stabilized</td>
</tr>
<tr>
<td>2</td>
<td>potentiostatic at -0.8V, 40 minutes; potentiostatic at $E$ until stable</td>
</tr>
<tr>
<td>3</td>
<td>$(20 \text{ min } -0.8V, 20 \text{ min } 0.4V) \times 2$; potentiostatic at $E$ until stable</td>
</tr>
</tbody>
</table>

Table 5.1: Procedure for preparing films in different oxidation states measurement of conductivity and x-ray diffraction
It is very difficult to completely reduce the free-standing film; the conductivity of the film decreases to the point that the voltage drop along the film length is large, and further reduction stops. To get a more even reduction, the free-standing film was sandwiched in between a stainless steel plate covered with carbon-fiber paper on the polypyrrole side and a stainless-steel mesh as shown in Figure 5.5. The carbon-fiber paper is necessary because stainless steel has very poor electrical contact to polypyrrole. Carbon fiber paper provides the best, most consistent electrical contact to polypyrrole with a contact resistance of approximately 2Ω. The stainless-steel mesh has a open area of 70% and was used only to provide mechanical contact between the carbon-fiber paper and the polypyrrole. In this way, there is good electrical contact over the whole area of the polymer and ion movement is not impeded; the potential across the polymer is much more uniform, and greater reduction is possible.

In this geometry, there is still some inhomogeneity in film reduction causing the conductivity to vary over different regions of the film. At high doping levels, the resistivity of the film is fairly uniform, but at low doping, it can vary by a factor of three over the film. This is because at low doping levels, the resistance increases exponentially; therefore, a small change in doping level causes a much larger difference in conductivity. The conductivity of each film was therefore averaged over its length. These films were then subjected to x-ray diffraction to determine the structural evolution with oxidation state. The procedure for x-ray diffraction is described in Section 5.5.1.

A complete and even reduction can only be attained from very uniform films that are reduced on the substrate upon which they were deposited. It was decided, however, that free-standing films would be used for this experiment as all of the films could be from the same crucible deposition, reducing variation between films, and the initial conductivity could be measured before redox to eliminate films that were of poor quality.

5.4 Electrochemistry

5.4.1 Electrochemical impedance spectroscopy

Impedance spectroscopy is done with a Solartron SI 1260 Impedance/Gain-phase Analyzer in conjunction with the SI 1287 Electrochemical Interface. At high frequencies, the impedance of the Ag/Ag⁺ reference electrode has a capacitive component. Therefore, for impedance spectroscopy measurements, the reference electrode is placed in parallel with a 1µF capacitor in series with a platinum wire in contact with solution. This decreases the capacitive impedance of the reference electrode. The data was collected and analyzed using the ZPlot software package. This package includes a complex nonlinear least squares (CNLS) fitting package for fitting the three dimensional complex impedance data, $Z(\omega)$.

For impedance measurements, it is desirable to have a thin layer of polypyrrole
Figure 5.5: The working electrode for reduction of free-standing films. The film is sandwiched in between a carbon-fiber paper electrode and a stainless steel mesh. This ensures good contact over the whole film area.

on a conductive substrate. The conductive substrate assures a constant oxidation level over the film volume. The film-on-substrate geometry also reduces the RC time constant of the film, and correspondingly the measurement time. The film is deposited for 30 minutes onto a working electrode consisting of 300 nm of gold evaporated onto atomically smooth silicon with a chromium layer to promote adhesion. Otherwise, the polypyrrole deposition conditions are exactly as described in Section 5.1.

The impedance of a single film was measured over the range of polypyrrole oxidation states. The procedure is as follows:

1. After deposition, the film is rinsed in pure acetonitrile and placed in the redox cell.
2. A cyclic voltammogram is performed to relax the film.
3. The film is soaked in acetonitrile overnight to ensure complete solvent exchange.
4. The film is held at 0.4V until the current has stabilized.
5. The impedance is measured with the DC potential from 4 and a 25mV AC potential over the frequency range of 100KHz to 0.1Hz.
6. Repeat 4 and 5 for DC potentials from 0.4V to -0.8V.

For a direct comparison of impedance at different oxidation states, it is important to use the same film and to disturb the cell as little as possible. The series resistance
will depend on the exact placement of the reference electrode, and the film parameters such as the capacitance and resistance may not be perfectly repeatable from one deposition to another.

5.4.2 Potentiostatic redox and fronts

In Section 3.6, we discussed some interesting phenomena that have been observed in the potentiostatic reduction and oxidation of polypyrrole that cannot be explained via the transmission line impedance models: from fully reduced, a sufficiently oxidizing potential results in moving phase fronts, and from oxidized to fully reduced, the film reduces evenly but full removal of the ions is not possible. We investigate these phenomena through cyclic volammograms and chronoamperograms of free-standing films and films in the film-on-substrate geometry.

5.5 Structure

5.5.1 X-ray diffraction

5.5.1.1 Potentiostatic redox in acetonitrile

The same free-standing films that were prepared in different oxidation states for the conductivity measurements in Section 5.3 were used for measuring the microscopic structure via x-ray diffraction.

The apparatus for the x-ray diffraction measurement is shown in Figure 5.6. Wide angle x-ray scattering (WAXS) patterns are obtained with a Bruker AXS - D8 Advance diffractometer with a Sol-X SiLi EDX detector. The source is Cu Kα radiation with wavelengths of 1.5406 Å and 1.5444 Å. The beam is divergent, and collimated with 3 sets of slits. The films are measured in transmission mode, i.e. the sample is always perpendicular to the incident radiation, while the detector is scanned over 2θ to pick up the diffraction peaks. The sample is placed in a vacuum chamber with Kapton windows at a pressure of approximately 100mTorr to eliminate unwanted low angle scattering from air. The noise amplitude with the sample chamber under vacuum is negligible. Additionally, to increase the signal to noise, each film is folded over once to get double the thickness. This thickness is unfortunately still well below the optimum thickness of 1/µ (µ is the linear absorption coefficient of polypyrrole). The WAXS patterns are normalized by the thickness of the film.

5.5.1.2 Galvanostatic redox in propylene carbonate

Initial x-ray diffraction measurements were done on films cycled galvanostatically in a propylene carbonate redox solution. It was later decided that this technique is less accurate than cycling potentiostatically; the IR drop may lead to non-uniformities in the film oxidation state due to variations in contact resistance and film thickness that
Chapter 5. Experimental methods

Figure 5.6: The x-ray diffraction apparatus
wouldn’t occur in potentiostatic cycling where the current drops to zero. Nevertheless, we include these measurements here because of differences we observed in cycling with propylene carbonate versus acetonitrile which may be important.

The electrochemical cell was the same as in Figure 5.3 but with a propylene carbonate solution instead of acetonitrile. After deposition, the film is left on the crucible and cycled from fully oxidized (as-grown doping level) to fully reduced and back at a constant current of \( \pm 0.125 \text{mA/cm}^2 \), the same as the deposition current. Full reduction is observed by a sharp increase in the magnitude of the working electrode potential, and occurs at a charge of approximately 1 in 3 monomers. Further reduction causes the film to degrade and therefore the period of the current square wave is chosen to bring the film just short of this point. After cycling, some of the film was removed from the crucible in this re-oxidized state, rinsed with propylene carbonate, and left to dry for x-ray diffraction measurements. The remainder of the film was returned to the redox solution where the film was fully reduced again at approximately 0.125mA/cm\(^2\) to determine the total charge in the film. This is an indirect measurement of the area of the remaining polypyrrole, which is difficult to determine otherwise. The film was then reoxidized to a charge corresponding to 2/3 of the full reduction charge. Some of the film was removed in this oxidation state for x-ray diffraction. This procedure was repeated to produce films in oxidation states of \( \frac{3}{2}, 1, \frac{2}{3}, \frac{1}{2}, \frac{1}{3} \) and 0 times the fully oxidized charge, \( Q \). The \( Q, \frac{1}{2}Q \) and 0 films come from one deposition, and the \( \frac{2}{3}Q \) and \( \frac{1}{3}Q \) come from a different deposition, and the \( \frac{3}{2}Q \) from yet another. The x-ray patterns from different depositions are very consistent, so comparing different depositions should be acceptable.

The films were air-dried for several days to remove the propylene carbonate, which has a high boiling point of 240°C. The x-ray diffraction procedure is identical to that above, except that 10-20 films are stacked together, so the signal to noise is much higher.

5.5.2 Actuation

The actuation is measured using an Aurora Scientific Muscle Lever 300B-LR (www.aurorascientific.com/). The actuation apparatus is shown in Figure 5.7. Electrical contact to the free-standing film is made with gold wire wrapped around a piece of carbon-fiber paper that is held in contact with the polymer by a fixed bottom clamp. The top of the polymer is attached to a lever which applies a constant stress with a sensitive rotary motor and measures displacements down to 1/100\(^{th}\) of a millimeter via a capacitive displacement meter.

The voltage, stress and strain under electrochemical cycling were recorded simultaneously.
Figure 5.7: The actuation apparatus
Chapter 6

The electrochemical model of polypyrrole

The transmission line model discussed in Section 3.6 is a good physical description of the charging of a distributed capacitor such as polypyrrole. It was previously stated, however, that this simple model does not quantitatively fit the equilibrium impedance. There are a few reasons for this:

1. The model assumes that the unit surface capacitance (the double layer) is the same as the unit volumetric capacitance. It is not at all obvious why this should be true. It is conceivable that the double layer capacitance would be much greater than the volumetric capacitance since the volumetric capacitance is limited by the space for ions in the matrix, whereas the surface capacitance may have a diffuse layer of ions extending into solution as well. Also, the Donnan potential will appear as an enhanced RC surface component.

2. The polypyrrole capacitance has some frequency dispersion; it acts like a constant phase element (CPE). There are many physical mechanisms suggested for this effect [29]. In general, a medium with charge transport that exhibits a range of potentials or time constants will exhibit this effect. In the case of polypyrrole, this is fairly intuitive. Ionic transport occurs in a disordered medium with a spatial variation of diffusion coefficients; at short time scales the capacitance will seem smaller than at long time scales because ions haven’t had time to diffuse into the more convoluted parts of the polymer. Another physical model of the CPE is a branched transmission line. The main migration path will be in the film thickness direction, however the ions move microscopically in all directions, so this model is also applicable.

3. The model assumes there is no potential drop across the polymer, whereas we know the potential drop can be significant in the reduced film.

4. The model assumes that the transport properties are homogeneous throughout the film which is clearly false when fronts occur. The clearly separated oxidized and reduced regions in front-type charging will have very different mobilities.

If the transmission line model is modified to include a surface capacitance and a constant phase element dispersion, it fits the electrochemical impedance spectroscopy data from Section 5.4.1 quite well. For a thin film of polypyrrole on a conductive
substrate, the polypyrrole resistance can be neglected as it is always lower than the ionic resistance, except perhaps in the highly reduced state. In the case of a small AC potential at equilibrium, the transport properties are probably quite homogeneous, so \( Z \) is not a problem either. The complex impedance for this model is [70]:

\[
Z = R_S + \left( (i\omega C_{DL})^{P_s} + \frac{1}{R_{DL} + Z_{TL}} \right)^{-1}
\]

(6.1)

\[
Z_{TL} = \frac{R_{PPy}^2 + R_{ion}^2}{\lambda (R_{PPy} + R_{ion})} \coth(\lambda)
\]

(6.2)

\[
\lambda = ((R_{PPy} + R_{ion}) \cdot (i\omega C_V)^P)^{1/2}
\]

(6.3)

In this equation, \( Z_{TL} \) is the impedance of the transmission line, not including the double layer, \( R_{ion} \) and \( R_{PPy} \) are the total ionic and polypyrrole resistances, \( C_V \) is the total volumetric capacitance, \( L \) is the thickness, \( R_{DL} \) and \( C_{DL} \) are the resistance and capacitance of the double layer, and \( p \) and \( p_s \) are the CPE dispersion parameters for the bulk and the surface respectively, and should be close to 1. This model was fit to the impedance data at varying oxidation states.

We may also modify the transmission line model to incorporate the finite conductivity of polypyrrole, and furthermore, the change in conductivity with oxidation state that was discussed in Section 2. The conductivity of polypyrrole becomes important when electrical contact to the film is made at only one end, rather than over the entire area. A change in the ionic conductivity with oxidation state is also possible due to macroscopic swelling and contraction of the film, and may be incorporated in the model. The measurement of these parameters is discussed in Section 7.1 and 7.2. In this model, the oxidation state at any position in the film is represented by the charge on the capacitive component in that location. This can lead to inhomogeneities in the transport properties, and even moving phase fronts.

We recognize three different experimental geometries that have produced front-like responses and three different transmission line models to describe them. These are shown in Figure 6.1. The first geometry, (a) [36], is a thin-film on a conductive substrate. The ions and the electrons both move in series, parallel to one another. This is the transmission line from equation 6.1. For simplicity the CPE has been changed into a capacitor \( (p = 1) \) and the double layer capacitance is the same as the volumetric capacitance. The double layer only affects the short-time response and is not a major concern in a time domain model.

The second geometry, (c) [45, 46, 47, 71], is a free-standing film with an electrode attached at one end. The main electronic and ionic pathways are perpendicular to one another. The ions move in parallel over the area of the film, and the electrons move in series along the length of the film. This model is obviously a simplification as the transmission-line charging through the thickness is ignored, but it will be sufficient at longer time scales, especially when the polymer resistance becomes large.
Chapter 6. The electrochemical model of polypyrrole

The third geometry, (e), was devised by Smela et. al. [48]. It involves a thin polymer film on a conducting substrate, which is covered by an ion-blocking polymer on the top. In this way, ions may enter the polymer only from the sides. This geometry is the exact opposite of the free-standing film geometry: the ions move in series along the film length and the electrons move in parallel through the thickness.

The impedance of a transmission line with variable resistance cannot be determined analytically, so a finite difference routine was constructed to solve for the time-domain response when a potential step is applied. The basic algorithm is as follows:

1. Internal parameters are the film dimensions; the capacitance per unit length along the transmission line (c); the polypyrrole and ionic resistance per unit length ($r_{PPy}$ and $r_{ion}$), both of which may be functions of the charge on the capacitive element at position $i$; and the series resistance ($R_S$) which includes the solution resistance and the contact resistance between the working electrode and the polypyrrole.

2. Input parameters are the initial and final voltage in the step potential ($V_0$ and $V_f$). This is absolute voltage, not versus reference. $E = 0V$ is the fully reduced state (no charge on the capacitive elements) and $E = 1.2V$ is the fully oxidized state.

3. A transmission line circuit is constructed with a finite number of elements, $N$. $N$ is chosen such that the solution converges, and is different for the three geometries.

4. $V_0$ is used to determine the initial steady state charge on each of the capacitors, $q_i(t = 0) = cV_0$. The charges are used to determine the initial resistance of the polypyrrole and ions at position $i$.

5. The instantaneous current in each branch of the transmission line is calculated based on the impedance from 4 and the step potential, $V_f$. This calculation is shown in Appendix B. The charge on the capacitors is changed by an amount $q_i(t + dt) = q_i(t) + i_i(t)dt$.

6. The resistances are updated based on the new charges $q_i(t)$.

7. 5 and 6 are repeated until the current decays to zero and the system has attained equilibrium.

Appendix A contains the Matlab code used to simulate a potentiostatic step in the free-standing film geometry. The programs for the other experimental geometries are very similar, with minor changes for the differences in impedance, and of course the effective capacitances and resistances in the circuit model, $c$ and $r$, will change depending on the geometry. For example, in case (a), $c$ represents the capacitance
Figure 6.1: The circuit models for the three experimental geometries: thin film on a substrate (a)&(b), free-standing film (c)&(d), and Smela geometry (e)&(f). $c$, $r_{PPy}$ and $r_{ion}$ are the unit capacitance, polypyrrole and ionic resistances. $R_S$ is the series resistance including the solution resistance and the contact resistances.
per unit thickness, integrated over the area, and in (c) and (e), $c$ is the capacitance per unit length, integrated over the width and the thickness.

Note that the stability of this code is a function of the ratio of $dt$ to $N$; if we double $N$, we must halve $dt$ and the length of the simulation increases by approximately 4. There is therefore a practical limitation on the ability of this model to simulate a continuum transmission line. However, $I(t)$ at the values of $N$ chosen for each geometry was found to vary slowly with $N$, leading us to believe that the simulations are accurate.
Chapter 7

Results

7.1 Conductivity

![Graph showing conductivity as a function of oxidation state for polypyrrole films.](image)

Figure 7.1: The conductivity as a function of oxidation state for polypyrrole films reduced potentiostatically from as-grown (circles), films that were fully reduced then reoxidized (x's), and films that were cycled from oxidized to reduced twice (triangles).

The conductivity of the films prepared as described in Section 5.3 is shown in Figure 7.1, and the resistivity is shown in Figure 7.2. The as-grown conductivities of all of the films were fairly uniform at $(270 \pm 25)$ S/cm. The conductivity as a function of oxidation state appears generally sigmoidal for each set of films, in agreement with the literature for polypyrrole doped with other ions. There is an inflection point at around -0.1V which signifies the transition from the conductive to the non-conductive state. Notably, none of the reoxidized films recovered the high, as-grown conductivity. The films that were reduced for 40 minutes and then reoxidized suffered the greatest loss in conductivity, more than the cycled films that were held at -0.8V for twenty minutes at a time, for a total time of 40 minutes. It appears that the time spent at
Figure 7.2: The resistivity as a function of oxidation state for polypyrrole films reduced potentiostatically from as-grown (circles), films that were fully reduced then reoxidized (x’s), and films that were cycled from oxidized to reduced twice (triangles).
low potentials causes an irreversible loss in conductivity. It is possible that the small parasitic current that occurs at low potentials may be causing damage to the film, but this is unlikely as experiments where films were cycled to -0.7V, with a similar parasitic current, showed no decrease in conductivity even after four square wave cycles. Molecular relaxations at low potentials may also be the cause of the decrease in conductivity; this is investigated in Section 7.3.

It is easier to see the low potential conductivity from Figure 7.2. The maximum resistivity measured in this experiment was approximately 2Ω/cm. This is lower than the resistivity measured when the film was reduced directly on the deposition substrate, which was about 86Ω/cm. The sandwich geometry is not able to exhaustively reduce the film, probably due to insufficient electrical contact to the substrate.

The charge capacity also sees a decrease corresponding to the time held at very reducing potentials. The charge versus oxidation state for the three sets of films is shown in Figure 7.3. The charge as a function of potential is fairly linear for each set, as we’d expect for a distributed capacitor, but they each have different slopes. The charging was determined from the integrated current from the redox, minus the small parasitic current. The charge capacity and the conductivity are obviously related, although not in a simple, linear way.

Figure 7.3: The charge as a function of oxidation state for polypyrrole films reduced potentiostatically from as-grown (circles), films that were fully reduced then reoxidized (x’s), and films that were cycled from oxidized to reduced twice (triangles)
7.2 Electrochemical impedance spectroscopy

A thin film of polypyrrole was deposited on a gold electrode for electrochemical impedance spectroscopy (EIS). A cyclic voltammogram (CV) was first performed to relax the structure. The voltage is ramped up and down between the vertex potentials of 0.4V and -0.8V with a rate of change of $\alpha = 25mV/s$. The CV of a capacitor is simply a rectangle with current

$$I = C\alpha$$  \hspace{1cm} (7.1)

The resistance of the circuit will lead to an exponential decay to the equilibrium current in Equation 7.1. A Faradaic reaction is characterized by a peak in the CV. The current ramps up exponentially as the voltage approaches the standard potential of the reaction, and then decreases as the reaction becomes mass-transport limited. In a typical electrochemical cell, you will see both Faradaic and capacitive currents. The derivation of the electrochemistry of polypyrrole from Section 3.6 has, however, treated the polymer as a capacitor with no Faradaic reactions. The CV shown in Figure 7.4 shows that this is in general correct. However, a large cathodic peak is seen on the first cycle only, accompanied by a corresponding loss of charge. This is the most likely cause for the first cycle decrease in conductivity and capacitance seen in the previous section. Subsequent cycles show a fairly capacitive response, with no distinct redox peaks. The linear region observed on switching toward anodic potentials at $-0.8V$ is a result of the front-type of response where the current is proportional to the voltage, $dI/dt = \alpha$, that was discussed in Section 3.6. The switching at the positive vertex follows an exponential decay as expected. The capacitance calculated from the CV is approximately 20mF.

The electrochemical impedance spectrum was then found for oxidation states from 0.4V to -0.6V using the methods outlined in Section 5.4.1. The impedance spectrum could not be found at -0.8V due to a large parasitic current that occurs on the gold substrate at this potential and causes delamination of the film. The complex impedance can be expressed as

$$Z = Z' + iZ''$$  \hspace{1cm} (7.2)

or

$$Z = |Z| e^{i\phi}$$  \hspace{1cm} (7.3)

The data is plotted equivalently in two different ways: the complex impedance plots ($Z'$ vs. $Z''$) are shown in Figure 7.5 and the Bode plots ($|Z|$ and $\phi$ vs. frequency) for the same data is shown in Figure 7.6. These methods of looking at the data are complementary and are both used frequently by electrochemists.

The complex impedance plot gives some direct information about the circuit elements in the cell. For instance, at high frequencies we see a semi-circle above the real axis. The semi-circle is a result of a parallel RC element in the circuit and at such high
frequencies may be identified with the double layer capacitance. The intercept with the real axis at high frequencies is the series resistance of the circuit. At low frequencies, a vertical line in this plot would represent a large series capacitor $Z = 1/i\omega C$. The low-frequency response of the data, however, shows an almost vertical line with some dispersion. This is modeled as a constant phase element, $Z = 1/(i\omega C)^p$ and is explained by the convoluted structure of the polymer which results in a range of time constants for ionic penetration into the matrix.

From the Bode plot, we get a better idea of the magnitudes of the components of the circuit model. From this plot, it seems that the time constant of the film decreases with decreasing potential. We can also directly see the CPE effect, the low frequency phase of the film at -0.6V has an angle that is saturating at $-60^\circ$ rather than $-90^\circ$ as we’d expect for a pure capacitor.

It is important to fit to the full complex impedance as a function of frequency. The complex nonlinear least squares algorithm originally developed by R. Macdonald was used [29] to fit the data to the model described by Equations 6.1 to 6.3.

The polypyrrole conductivity as measured in Section 7.1 shows that the polymer resistance will be negligible compared to the ionic resistance until at least -0.7V. The ionic conductivity is typically less than 0.1S/cm in solution, and would be expected to be much less than this in the polypyrrole matrix. These measurements justify the use of Equation 6.1 which neglects the polypyrrole resistance.
Chapter 7. Results

Figure 7.5: The complex impedance of polypyrrole as a function of oxidation state. The frequency range is 0.1Hz to 100KHz.

There is insufficient data to fit all of the parameters, so we choose a fixed value for $p_s = 0.9$, which is a reasonable value for a rough electrode.

The complex impedance fits for two oxidation states are shown in Figure 7.7 to demonstrate the goodness of the fit. There are some non-idealities which are not handled by the model. You can see from Figure 7.7a) that the high frequency response is not perfectly fit by this model. This could be due to the assumption that the high frequency motions are entirely caused by the double-layer charging, neglecting the possibility of high frequency motions of the ions in the volume. Also, Figure 7.7b) shows that the data starts to diverge from the fit at low frequency. This is because of the small parasitic currents caused by electrochemical breakdown of the solvent that occur at low potentials. The fit parameters for all of the data are tabulated in Table 7.1.

The largest changes in the electrochemical impedance with oxidation state are in the capacitance and exponent of the CPE, plotted in Figure 7.8. These parameters have a sigmoidal shape with a transition at approximately -0.1V, similar to the DC conductivity of polypyrrole in Figure 7.1. It does not appear that the polypyrrole resistance is directly the cause of this transition as the ionic resistance is still dominant at these potentials and the fit of the series resistance with oxidation state does not show this type of variation. The low frequency capacitance is fairly constant with oxidation state, as demonstrated by the constant current over the entire potential
Figure 7.6: The Bode plot of the complex impedance of polypyrrole as a function of oxidation state

<table>
<thead>
<tr>
<th>$E$ (V)</th>
<th>$R_S$ (Ω)</th>
<th>$R_{ion}$ (Ω)</th>
<th>$C_V$ (mΩ)</th>
<th>$p$</th>
<th>$R_{DL}$ (Ω)</th>
<th>$C_{DL}$ (μF)</th>
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<tr>
<td>0.4</td>
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<td>12 ± 1</td>
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<td>13.5 ± 0.2</td>
<td>51 ± 4</td>
</tr>
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<td>27 ± 2</td>
<td>12 ± 1</td>
<td>0.92 ± 0.01</td>
<td>14.0 ± 0.3</td>
<td>52 ± 4</td>
</tr>
<tr>
<td>0.0</td>
<td>16.84 ± 0.08</td>
<td>46 ± 2</td>
<td>8.3 ± 0.5</td>
<td>0.90 ± 0.01</td>
<td>12.7 ± 0.3</td>
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</tr>
<tr>
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<td>38 ± 2</td>
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<tr>
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<td>28 ± 3</td>
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<td>0.28 ± 0.04</td>
<td>0.693 ± 0.005</td>
<td>8.8 ± 0.8</td>
<td>28 ± 3</td>
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Table 7.1: Fit parameters for the electrochemical impedance spectrum of polypyrrole vs. oxidation state
Figure 7.7: The transmission line fit to the electrochemical impedance spectrum; (a) $V_{DC} = 0.4$V, and (b) $V_{DC} = -0.6$V.

region of the cyclic voltammogram in Figure 7.4. This is sensible as the total internal surface area of the film should not change with oxidation state. The capacitance as calculated from the CV is slightly larger the capacitance from the EIS of the oxidized film, and is a truer representation of the DC capacitance. It is more likely that the change in CPE parameters is related to changes in ionic mobility. Changes in the structure of the polymer would undoubtedly affect the ionic diffusion coefficients. For example, if the film were to contract due to removal of ions, the short timescale diffusion coefficient, reflected in $C$, would be expected to decrease. The diffusion may also become more restricted, elongating the distribution of diffusion coefficients with time and causing and increase in $p$. This result highlights the limitations of a lumped parameter continuum model in characterizing a heterogeneous, atomistic process. The physical mechanism of the CPE in heterogeneous electrodes has not been well defined in this case. Nuclear magnetic resonance has the ability to measure diffusion coefficients as a function of frequency, and may enable us to identify the source of the CPE behavior.

The surface capacitance is sigmoidal in shape as well, as it is obviously related to the volumetric capacitance. In the oxidized state $C_S$ is equal to 30$\mu$F/cm$^2$ which is well within the range of 10-40$\mu$F/cm$^2$ typical for the double layer. This validates the interpretation of the RC semi-circle as the double-layer capacitance.

The ionic resistance in the film does not seem to vary progressively with oxidation
Figure 7.8: The fit values of the volumetric parameters, (a) $C_V$ and (b) $p$ as a function of oxidation state. Both show the sigmoidal variation with oxidation state characteristic of the polypyrrole conductivity.
state, nor does the series resistance. At very high frequencies, the impedance of the reference electrode and the leads serves to obscure the intercept with the real axis, and the high frequency fit is simply not good enough to determine the series resistance to the accuracy required to see a change in resistance for such a thin film.

We also investigated the effect of deposition time on the fit parameters. Polypyrrole was deposited on gold for 5 minutes using the method from Section 5.4.1. The film was rinsed in propylene carbonate and immediately put in a redox solution of 0.05M TEA-PF$_6$ in propylene carbonate and the impedance was measured at 0V versus the open-circuit potential. The same film was then returned to the deposition solution for another 5 minute deposition. In this way the impedance of the film was attained for depositions of 5 minutes to 30 minutes. Using the same film assured minimal variation in parameters as the electrode area and deposition current were the same each time. It was important to use propylene carbonate for the redox solution as it is unclear what effect the solvent exchange would have on the deposition. There is no consistency with respect to the reference electrode position in each case, so no conclusions can be made about the series resistance. The fit parameters are listed in Table 7.2 and $C_V$ and $C_S$ are plotted in Figure 7.9. The volumetric capacitance $C_V$ varies linearly with deposition time as expected. The double-layer capacitance increases with deposition time until the 20 minute deposition. This is most likely due to the evolution of the surface morphology, which starts out smooth and eventually becomes “cauliflower-like” in appearance [16]. The ionic resistance does not evolve linearly as might be expected. This could be because the density of the film does not remain constant through the deposition. The film starts out less dense, and then fills in with further deposition. Also, the ionic resistance is much higher in this film than in the previous film that was investigated in acetonitrile redox solution. Since the ions are accompanied by a solvation shell, it is reasonable that the solvent affects the ionic resistance.

<table>
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<tr>
<th>$t_{dep}$ (min)</th>
<th>$R_{ion}$ (Ω)</th>
<th>$C_V$ (mF)</th>
<th>$p$</th>
<th>$R_{DL}$ (Ω)</th>
<th>$C_{DL}$ (µF)</th>
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<td>0.884 ± 0.007</td>
<td>81 ± 1</td>
<td>141 ± 6</td>
</tr>
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</table>

Table 7.2: Fit parameters for the electrochemical impedance spectrum of polypyrrole vs. deposition time.
7.3 Structure

7.3.1 Anisotropy

As-grown films from the crucible were stacked 10 films thick and measured in transmission mode with no vacuum in a Rigaku 300 X-ray Diffractometer. The angle of incidence of the x-rays with the film normal was varied from $0^\circ$ and $46^\circ$. Variations in the x-ray patterns were observed, as shown in Figure 7.10. The scattering intensities were scaled by the spot size of the beam on the sample at each angle, which goes as $1/\cos \theta$, where $\theta$ is the angle between the film normal and the incident x-rays.

In polymer physics, this anisotropy is called texture. According to the Nogami model of the crystal structure of polypyrrole, Figure 4.5, the $c^*$ peak represents the ring face to face distance, perpendicular to the chain direction. This peak varies strongly with the angle of incidence, being weakest when the beam is perpendicular to the film surface. The $a^*$ peak is not visible, and the $b^*$ peak, the di-pyrrole length along the chain direction, is largest when the beam is perpendicular to the film. The anisotropy in this direction appears smaller only because the angle is smaller, therefore the reciprocal lattice point is closer to the Ewald sphere. The large peak is truly isotropic as would be expected for an amorphous peak. The small decrease in this peak intensity is probably due to absorption in the polymer which is quite small.

The observed anisotropy indicates that the chains are preferentially aligned per-
Figure 7.10: X-ray diffraction of polypyrrole at different incident angles showing anisotropy in the electrodeposited films. Black through pink lines represent angles between the film normal and the incidence angle of 0, 10, 20, 30, 40 and 46°. \( b^* \) is the di-pyrrole length, \( A \) is the amorphous peak, and \( c^* \) is the distance between face to face pyrrole rings. The \( a^* \) peak is at approximately 5° but cannot be seen due to scattering from air.
perpendicular to the deposition electrode. This has been previously observed in [72]. This is in contrast to deposition with flat organic ring counter-ions where the crystals show a high degree of anisotropy, with the chains parallel to the electrode surface and the nearly isotropic nature of the PPy(ClO$_4$) film [61]. The increased order associated with the texture of the film is related to the improved electrical properties of the PPy(PF$_6$) film.

For determining the structure as a function of oxidation state, we measure the film at normal incidence only and we assume that the texture of the film does not change with oxidation state. This is not necessarily true in the case of potentiostatic reductions over long time scales where macroscopic motions of the polymer are possible, and future work must include texture measurements.

At low angles, there is a large amount of scattering that obscures the $a^*$ peak. This is from air scattering, and demonstrates the need to do these measurements in a vacuum. A background air pattern can be obtained without a sample, but direct background subtraction is complicated by the fact that some of this air-scattered radiation is absorbed and re-scattered when the polymer is in place.

### 7.3.2 Galvanostatic redox in propylene carbonate

The actuation during galvanostatic redox in a propylene carbonate solution from fully oxidized to fully reduced is shown in Figure 7.11. From fully oxidized, or a doping level of 100%, the film initially contracts with expulsion of ions. The actuation is fairly linear with charge, as we would expect from the model in Equation 4.13. The potential decreases linearly with charge as well, showing that the film acts like a capacitor. At a charge of approximately 50%, there is a kink in the potential versus doping level; this is the metal-insulator transition charge. At this doping level, the actuation reverses direction, and begins to expand with further reduction. This is contrary to the postulated swelling mechanism for actuation but may be explained by a change in Young’s modulus with oxidation state. Upon reoxidation, the film actuation exactly reverses. The result is a double-peak in the actuation cycle.

The x-ray diffraction pattern of polypyrrole films produced by galvanostatic cycling is shown in Figure 7.12. The patterns have been fitted to four Gaussian functions and a background consisting of a constant diffuse scattering and a small-angle component, which has the form of the LP factor (equations 4.4 and 4.5). The fit parameters are listed in Table 7.3. The LP factor generally results from uncorrelated, low-density scatterers. The source of the small angle scattering is still unknown. It does not appear in the as-grown film, as shown in Figure 7.13, and does not seem to be correlated with the doping level, so it may be related to the initial relaxation of the film. Density variations resulting from small crystalline and amorphous regions could also produce such scattering.

Figure 7.14 shows the fits for the length of $a$ and the intensity of the amorphous peak, the only parameters to experience significant change with oxidation state. $a$ is the ring-ion-ring distance in the Nogami model of the polymer crystal structure,
Figure 7.11: The actuation during galvanostatic redox in propylene carbonate. The charge on the polymer, the potential and the strain are shown. A kink in the voltage profile indicates the metal-insulator transition of polypyrrole, and is correlated to a reversal in actuation direction.
Figure 7.12: The x-ray diffraction patterns of polypyrrole films cycled in propylene carbonate versus oxidation state. From top to bottom the oxidation state is 3/2Q, Q, 2/3Q, 1/2Q, 1/3Q, 0, where Q is the fully oxidized charge. The background has been subtracted.
Figure 7.13: X-ray diffraction of fully oxidized polypyrrole in the as-grown state and after one galvanostatic cycle show a very similar pattern, except for an increased low angle scattering in the cycled film.
therefore it is this length that would be most likely to change if the ions are removed from the crystals during actuation. There is a large degree of uncertainty in the fits due to the fact that the overlapping Gaussians are not fully resolved, but there appears to be a net contraction in a, and a minima at a doping level of approximately 50%. This may correspond to the minima in the actuation profile, however the correlation between the actuation and the crystal dimension is not obvious at all. It seems wide angle x-ray scattering is not giving us the complete microscopic picture of actuation in polypyrrole.

![Graphs showing length and amplitude changes with doping level.](image)

Figure 7.14: Fits of the length of a (a), and the amplitude of the amorphous peak (b) with oxidation state. The other parameters did not exhibit any statistically significant change.

The intensity of the amorphous peak also experiences a transition at about 50% doping. This transition may have more to do with changes in solvation than in polymer structure however. Figure 7.15 and 7.16 show that at least part of the amorphous peak could be due to unevaporated propylene carbonate in the polymer. Figure 7.15 shows that the amorphous peak grows when the film is wet, and Figure 7.16 shows that pure propylene carbonate has a peak at the exact location of the
<table>
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<th>Peak</th>
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<th>A (CPS)</th>
<th>w (degrees)</th>
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<td>4.3 ± 0.8</td>
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</tbody>
</table>

Table 7.3: Fit parameters for x-ray diffraction patterns of polypyrrole cycled in propylene carbonate versus oxidation states. Peak 1, 2, 3, and 4 are the a*, b*, amorphous and c* peaks respectively.
amorphous peak. This would also explain why this peak was still isotropic after stretching as observed in [56]. Even fully amorphous polymers tend to align under stretching, but solvent would remain isotropic.

![Graph showing X-ray diffraction](image)

**Figure 7.15**: X-ray diffraction of a reduced film that was air dried and wet with pure propylene carbonate. The wet film has a much larger amorphous peak.

The high boiling point of propylene carbonate makes it difficult to dry the films completely, which is one reason for choosing acetonitrile for cycling in the next series of experiments. However, the amorphous peak intensity of the air-dried films remains unchanged for films dried for two days versus three months, therefore it is likely that solvent-polymer interactions are involved, as well as a high boiling point.

If a portion of the amorphous peak is simply solvent, then the change in intensity of the amorphous peak under reduction could be due to a change in solvent affinity with oxidation state. We know that the polymer-solvent affinity is greater in the oxidized state [68]. A polar solvent such as propylene carbonate or acetonitrile will tend to dissolve charged species (salts), but not neutral species - i.e. likes dissolve likes.

Another possibility is that the amorphous peak is due to ions, which take up amorphous positions in the polymer. This possibility will be discussed in the next section.
7.3.3 Potentiostatic redox in acetonitrile

In this section, the films we describe were deposited in propylene carbonate, left to dry naturally, then cycled potentiostatically in acetonitrile using the method outlined in Section 5.5.1.1. It is worth pointing out some of the differences between this method and the previous method.

First, the oxidation states produced galvanostatically are less accurate than those produced potentiostatically due to inhomogeneities in thickness and contact, uncertainties in the film volume, and the effects of parasitic current which could not be subtracted using this method. In the potentiostatic method, the inhomogeneities are less important as the current eventually drops to nearly zero, and the film is at equilibrium. Another difference between this method and the potentiostatic method is the duration of time at a certain potential. The potentiostatic method holds the film at a certain potential for a sustained amount of time, which may lead to long timescale molecular relaxations, whereas the galvanostatic method has the film at the desired potential for very little time before the signal is turned off. And of course, acetonitrile evaporates very quickly, and will have a different affinity for the polymer. All of these differences are likely responsible for the differences in x-ray diffraction patterns that are observed in this measurement.

The actuation during potentiostatic cycling in acetonitrile is very different than the actuation observed in propylene carbonate (Figure 7.11). The actuation during

Figure 7.16: X-ray diffraction of pure propylene carbonate. The sharper peak at 22° is due to the sample holder.
a potentiostatic square wave from fully oxidized to fully reduced is shown in Figure 7.17. Under reduction, the film first experiences a very small contraction, which may be due to motion of ions. The film then begins to expand in a way that does not seem correlated with the current. The expansion continues long after the current has stopped, signifying that it is unrelated to ionic movement, and may be a molecular relaxation. In both the galvanostatic and potentiostatic reductions we observe a double peak, although in the potentiostatic case one peak is very small.

![Graphs of potential, current, and strain over time](image)

Figure 7.17: The actuation during potentiostatic redox in acetonitrile. The potential, the current and the strain are shown. The actuation shows only a small contraction on reduction, followed by a larger expansion which does not appear to depend on the current or the movement of ions.

There is a large, unrecoverable contraction in the first cycle, of up to 10%. This is probably related to the loss in charge on the first cycle, and the displacement of propylene carbonate. After this contraction, actuation at potentials less than -0.1V is insignificant, even though there is significant current flow. The motion of ions does not appear to cause significant actuation.

The wide-angle x-ray patterns are shown versus oxidation state in Figure 7.18, for
the films reduced once (a), reduced then reoxidized (b), and cycled twice (c). The patterns were normalized by the as-grown thickness of the sample. One of the first things to notice is the difference between the 0.4V film in Figures 7.18(a) and (b), shown together in Figure 7.19. The reoxidized film shows the same increased small angle scattering as in the propylene carbonate cycled film, but it does not recover a large amorphous peak like it does in propylene carbonate. This could signify that a large part of the amorphous peak is due to propylene carbonate. Propylene carbonate was displaced from the polymer upon reduction in the same manner as we saw in Figure 7.14, but since it is reoxidized in acetonitrile which evaporates quickly, the peak height does not grow substantially upon reoxidation.

The fits are very poor because of overlapping and unresolved peaks in some of the reduced states. No patterns are recognizable in the fits, so they are not included here. Also, the total scattering intensity of each film does not seem to be correlated to its oxidation state, possibly due to differences in crystallinity or sample positioning from film to film. Yet if we look at the relative peak heights and positions in each film, there are some patterns common to all three sets of film that are recognizable by eye.

1. The amorphous peak decreases in intensity with more cathodic potentials. This occurs even for the set (b) and (c) films where the propylene carbonate should have been fully displaced by acetonitrile.

2. The crystal peaks do not change at all until a transition at about -0.1V.

3. At -0.1V, the $a^*$ peak begins to increase and broaden. It completely dominates the $b^*$ peak which can no be longer resolved at all. After this initial large increase, the $a^*$ peak shrinks again, being smaller in the fully reduced state than the fully oxidized state.

4. Peak $c^*$ begins to decrease with respect to the amorphous peak after -0.1V, eventually becoming the same height as the amorphous peak in the fully reduced state.

5. All of the peaks are smaller in the reduced state than the oxidized state.

It is clear that there are some significant, reproducible structural changes during redox. The fact that the crystalline peaks do not seem to change until a certain potential, while the amorphous peak decreases monotonically from fully oxidized to fully reduced means that the reduction initially proceeds without changing the crystal structure. Perhaps initially the ions are removed from the amorphous regions. This makes some sense as the ions will be held in the crystals by the crystal energy and will require more energy to remove than in the amorphous regions. The potential where the crystals begin to change also seems to be correlated with the conductivity and the electrochemical impedance as measured in Sections 7.1 and 7.2. The three properties of structure, conductivity and electrochemistry are obviously related.
Figure 7.18: The x-ray diffraction patterns of polypyrrole cycled potentiostatically in acetonitrile as a function of oxidation state. (a) The first reduction, (b) the first reoxidation, and (c) cycled twice from oxidized to reduced. From top to bottom the potentials are 0.4, 0.16, -0.08, -0.32, -0.56 and -0.8V.
According to Nogami, the shortest distance in the crystal, the c\textsuperscript{*} peak, is the ring face-to-face distance. As we discussed previously, the close packing in this direction is a result of pi-stacking, which is a relatively strong interaction where electrons are shared between two adjacent oxidized rings. Pi-stacking does not occur in the neutral state because there are no excess electrons to share. The decrease in the amplitude of this peak upon reduction could be due to loss of pi-stacking, with an accompanying decrease in order. A decrease in pi-stacking would explain many other observations as well:

- Expansion on reduction: The crystals would not be held together as strongly and the polymer would expand in a gel-like manner.

- A decrease in Young’s modulus

- A decrease in conductivity on reduction: The pi-stacking is important for the conductivity because it facilitates conduction between chains, and can result in full three-dimensional delocalization. It would be useful to measure the temperature dependence of the conductivity in different oxidation states, as we may observe a transition from three-dimensional to one-dimensional conductivity due to this change in structure. A loss of pi-stacking may also be visible in electron spin resonance experiments.
• An irreversible decrease in conductivity with prolonged cathodic potentials: The expansion of the film during reduction appears to continue without saturating. After long reductions, the film does not contract completely when the potential is reversed, and does not recover its conductivity. Perhaps some pi-stacking bonds are not re-formed.

The uncertainty on the central angle of the \( \alpha^* \) peak is too large to say whether the ring-ion-ring distance is changing with oxidation state as expected from motion of the ions. What is observed is a drastic change in peak amplitude and breadth of this peak, first increasing, then decreasing. A possible explanation is presented based on the movement of ions.

NMR results have indicated that the mobility of the PF\(_6^-\) ions is very high, even in the dry film [73]. The diffraction pattern of the ions would be amorphous in this case, similar to a liquid. Based on the total charge in the oxidized film and its volume, the ion concentration in the oxidized state is approximately 5M. Assuming a completely isotropic distribution of ions, the average radial distance between ions is calculated to be 4.3 Å. This is very close to the observed \( d \) for the amorphous peak, 4.5 Å, so it is very plausible that part of this peak is due to the ions. As the film is reduced, the ionic density would decrease, and the peak would spread toward lower angles, and eventually disappear from the pattern. This may be the cause of the apparent increased height and breadth of peak \( \alpha^* \): the actual \( \alpha^* \) peak remains relatively unchanged as seen from the fully oxidized and fully reduced pattern, but the amorphous ionic peak overlaps with this peak causing it to look larger. This hypothesis could be tested by measuring the evolution of the x-ray pattern under reduction of a stretch-aligned film. Under stretching, the crystalline peaks, \( \alpha^* \), \( b^* \) and \( c^* \) become anisotropic, whereas the ionic peak, due to the high ionic mobility, would remain isotropic under stretching. This would allow a separation of the effects of the amorphous polymer, the ions and the polymer crystals.

The film reduced galvanostatically did not show this change in peak \( \alpha^* \) midway between fully oxidized and fully reduced, even though the patterns for the fully reduced films produced galvanostatically and potentiostatically are very similar. The comparison of these two methods is difficult because of differences in the electrochemical method and the solvent. It is possible that the changes in \( \alpha^* \) seen in the potentiostatic method are caused by polymer relaxations that occur only under sustained potentiostatic redox. A comparison of films actuated quickly and films held potentiostatically for long times in the same solvent would provide more information.

Unfortunately due to the poor crystallinity of the film, we are unable to directly correlate the structural changes to the actuation mechanism and because of this, we are also unable to determine which model of the polymer structure is correct, the planar or the helical model. Stretch aligning the films may improve the order to a degree that the peaks may be resolved with confidence. Another option is to use pyrrole oligomers (10s of monomer units) instead of polymers (10 000 monomer units) for future measurements. Oligomers tend to be more crystalline than the full polymer.
structure.

Although it cannot be fully explained at this point, it is clear that some sort of rapid structural change occurs at a potential of -0.1V. -0.1V is the metal-insulator transition point of the polymer, and a transition point for the electrochemical impedance. It is no surprise that these properties are related - the structure will influence the ionic conductivity through the diffusion coefficient and the electronic conductivity through overlapping electronic orbitals. It also seems clear that the actuation mechanism is much more complicated than the simple swelling model of actuation would suggest, especially during sustained reduction. Effects of solvent affinity, chain-chain interactions and pi-stacking, and possibly molecular relaxations at sustained potentials were observed.

7.4 Model validation

In this section, the implications of the electrochemical model proposed in Section 6 are investigated, and compared to data when it is available. The three experimental geometries are discussed.

7.4.1 Free-standing film geometry

The transmission line in Figure 6.1c) is modeled using a sigmoidal dependence of the electronic conductivity of polypyrrole on the oxidation state. The free parameters $\sigma_{\text{max}}$, $\sigma_{\text{min}}$, $Q_0$ and $w$ which are the conductivity in the oxidized state, the conductivity in the reduced state, the transition charge between conductive and non-conductive regimes, and the width of the transition. This function is plotted in Figure 7.20 with the parameters 100S/cm, 0.01S/cm, 0.5$Q_{\text{max}}$, 0.05$Q_{\text{max}}$ respectively. $Q_{\text{max}}$ is the charge on the polymer in the fully oxidized state, which is determined by the capacitance of the film and the voltage difference between oxidized and reduced, 1.2V.

$$\sigma = \frac{\sigma_{\text{max}} - \sigma_{\text{min}}}{1 + e^{-(Q-Q_0)/w}} + \sigma_{\text{min}}$$  \hspace{1cm} (7.4)

This function is not a perfect fit to the measured conductivity in Figure 7.1, but is closer to the conductivity measurements in the literature. It is likely that inhomogeneities in reduction contributed to error in the measurement described in Section 7.1. A more accurate conductivity measurement should be obtained by reducing the film directly on the deposition substrate, or measuring the conductivity in-situ using impedance spectroscopy. Efforts to do this measurement are on-going.

The other physical parameters in the model are the film dimensions, and the ionic impedance parameters: the volumetric capacitance, $C_V$, and the ionic resistance in the solution, $R_S$, and the film, $R_{\text{ion}}$. Note that in this model, the thickness direction is not modeled as a transmission-line, but simply as a series RC element. This could be rectified in future versions of the model. The incremental values of the impedance...
Figure 7.20: The conductivity is modeled as a sigmoidal function of the charge parameters are calculated by the code from the bulk values above. Bulk values can be measured via impedance spectroscopy.

The simulation parameters that discretize the time and space dimensions are also important. $N$ is the number of spatial elements, and $dt$ is the time step. If $dt$ is too large then the simulation does not converge. If $N$ is too small, the simulation converges, but not to the correct answer. At low $N$, the discrete nature of the simulation is apparent, with current spikes for each element.

A potential step to 0.4V from the fully reduced state at -0.8V is simulated with the model parameters listed in Table 7.4. The chronoamperogram is shown in Figure 7.21 and the charge, $Q(x,t)$, is shown in Figure 7.22. The moving phase front is clearly visible from Figure 7.22. A front is caused by a sudden transition from a non-conductive to a conductive state of the polymer, therefore it exist whenever the film is stepped to potentials above the metal-insulator transition potential. These results can be compared with the experimental results of Tezuka et. al. [39] in Figures 3.6 and 3.7. The experimental data qualitatively agrees with the model. The charge is proportional to the absorbance due to the electrochromic effect [39], and both show a sharp front between oxidized and reduced. The current is relatively constant with time until the front hits the end of the film, where it has a discontinuity in the slope and then decays exponentially. Since the film parameters for this experiment were not available from the literature, modeled parameters were fit parameters from my own films. The films used in the literature are much thinner than these films,
which explains why the time constants of the modeled and experimental data are dissimilar. Also, in the experimental data, we see a surface RC component at short timescales which is not present in the simulation. It was found in the electrochemical impedance modeling from Section 7.2 that the surface capacitance was not the same as the volumetric capacitance per unit thickness, and this had to be incorporated in the transmission line to get the correct high-frequency response. This component out for simplicity in the time-domain model, so it is not surprising that the model is inaccurate at short times.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>width</td>
<td>0.59 cm</td>
</tr>
<tr>
<td>length</td>
<td>2.5 cm</td>
</tr>
<tr>
<td>thickness</td>
<td>10 µm</td>
</tr>
<tr>
<td>$R_{ion}$</td>
<td>65 Ω</td>
</tr>
<tr>
<td>$C_V$</td>
<td>120 mF</td>
</tr>
<tr>
<td>$\sigma_{max}$</td>
<td>250 Ω cm$^{-1}$</td>
</tr>
<tr>
<td>$\sigma_{min}$</td>
<td>0.001 Ω cm$^{-1}$</td>
</tr>
<tr>
<td>$Q_0$</td>
<td>$0.5 \times Q_{max}$</td>
</tr>
<tr>
<td>$w$</td>
<td>$0.05 \times Q_{max}$</td>
</tr>
<tr>
<td>$N$</td>
<td>100</td>
</tr>
<tr>
<td>$dt$</td>
<td>0.05 s</td>
</tr>
</tbody>
</table>

Table 7.4: Test parameters for modeling potentiostatic steps

Johansson et. al. [45] find that the fronts move at a velocity proportional to the current, which is also true of the model. They also show that the current and the width of the front depends on the voltage, and the front disappears at low overpotentials, 7.23. We simulate this in Figure 7.24 and show agreement.

If the cell is open-circuited when a front is in progress, the front has been found to dissipate in a diffusion-like manner [74]. This may be modeled as well, with the extra boundary condition that the total current is zero and the voltage is left to drift. The experimental data shown in Figure 7.25 and the modeled data in Figure 7.26 are extremely similar.

On reduction in the free-standing film geometry, the model predicts that the film will reduce quite evenly because of the highly conductive nature of polypyrrole in the metallic state. The current is shown in Figure 7.27 to decay very quickly. However, after the current has reached equilibrium, we see from Figure 7.28 that there is a large amount of residual charge. Tezuka et. al. observe this in [38], and postulate that the discharging stops with a large amount of charge left in the polymer because conductive islands in the polymer are disconnected from one another at a percolation threshold. They assume that the polymer exists locally in one of two states, conductive and non-conductive. Figure 7.28 tells a different story. According to the model, there
Figure 7.21: The modeled chronoamperogram on charging from fully reduced to fully oxidized.

Figure 7.22: The modeled charge, $Q(x,t)$, on oxidizing from fully reduced.
Figure 7.23: The experimental chronoamperograms showing how the fronts change with applied over-potential [45].
Chapter 7. Results

Figure 7.24: The modeled chronoamperograms showing how the fronts change with applied over-potential. Curves a-e are for over-potentials of 1.2V, 0.8V, 0.6V, 0.5V and 0.45V.

Figure 7.25: The observed front dissipation on open-circuiting the electrochemical cell [74]. The curves e-l are in order of increasing time.
is a small region around the electrode which becomes very resistive, causing a large potential drop in this area which prevents further reduction. This is more consistent with the physical picture of the doping-induced metal-insulator transition discussed in Section 2, where the local conductivity of the polymer is a continuum caused by changes in the bandstructure of the polymer with doping [23]. The model predicts that the conductivity of the film not directly around the electrode will remain quite conductive after reduction, whereas according to the percolation model, the entire film should be very resistive. This could be verified experimentally.

Obviously much more work is required to validate this model with experimental data of our own. This has not been done yet due to the difficulty of exhaustively reducing the film. However, a cyclic voltammogram has been obtained with a free-standing film and simulated using measured and fit parameters. The simulation is compared with the data in Figure 7.29 and shows a close fit. The model parameters are listed in Table 7.5. Values are all in reasonable agreement with expectations. The shape of the CV, and especially the anodic peak, depend strongly on the shape of the conductivity-charge relationship, and greater agreement would undoubtedly result from an accurate measurement of this quantity. It is curious that the anodic peak decreases with cycling, signifying perhaps a change in the conductivity-charge relationship over time.

The fact that this model produces peaks in the cyclic voltammogram has impor-
Figure 7.27: The modeled chronoamperogram on reducing from fully oxidized.

Figure 7.28: The modeled charge, $Q(x,t)$, on reducing from fully oxidized.
### Table 7.5: Fit parameters for the cyclic voltammogram of a free-standing film

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td>65Ω</td>
</tr>
<tr>
<td>$C$</td>
<td>$120mF$</td>
</tr>
<tr>
<td>$\sigma_{\text{max}}$</td>
<td>$200\Omega^{-1}cm^{-1}$</td>
</tr>
<tr>
<td>$Q_0$</td>
<td>$0.75 \times Q_{\text{max}}$</td>
</tr>
<tr>
<td>$w$</td>
<td>$0.07 \times Q_{\text{max}}$</td>
</tr>
<tr>
<td>CV rate</td>
<td>$5mV/s$</td>
</tr>
</tbody>
</table>

Figure 7.29: The modeled versus measured CV of a free-standing film
tant implications. Peaks in a cyclic voltammogram normally signify an electrochemical reaction. In the normal electrochemical reaction, there is electron transfer from the electrolyte to the electrode. The peaks are caused by the Maxwell-Boltzmann statistics and the mass-transport equations governing the electrolyte. In the charging of polypyrrole, however, there is no electron transfer with the electrolyte and the polymer itself does not obey Maxwell-Boltzmann statistics. The mass-transport equations however are still important. The model presented in this section produces the observed peaks in the cyclic voltammograms and is more consistent with the electronic nature of the polymer.

7.4.2 Smela geometry

Smela et. al. simulated the geometry from Figure 6.1e) with polypyrrole doped with dodecylbenzenesulfate, PPy(DBS). A thin film of polypyrrole was deposited on a gold electrode, and a transparent ion-blocking polymer was patterned over top of the film so that ions can enter the film only through the sides. In this geometry, the ionic resistance is unambiguously the largest contribution to the charging impedance, as the path-length of the ionic current through the film length is 500 times longer than the path-length of the electrons through the thickness of the film. They observed fronts through the electrochromic effect on reduction only.

![Figure 7.30: The charge modeled using the Smela geometry with a non-linearity in ionic conductivity. (a) is a step potential from 0.4V to -0.8V and (b) is from -0.8V to 0.4V](image-url)
Figure 7.31: The electrochromic front observed in the Smela geometry [48]

The model circuit for this geometry is shown in Figure 6.1f). This circuit is incapable of producing fronts from changes in the polypyrrole electronic conductivity. Phase-fronts are created when a non-linearity exists in the series conductivity only. Also note that the observed fronts occur on stepping from the conductive to non-conductive states, which is also not consistent with the model.

A non-linearity in the ionic conductivity, however, would produce the observed effect in this model. In PPy(DBS), the DBS$^{-}$ ion is very large and immobile in the film. On electrochemical redox, it is the much smaller Na$^{+}$ cation that enters and leaves the film in order to balance the charge. The diffusion coefficient of the ions is assumed to be larger in the expanded state, in this case the reduced state, and changes non-linearly with oxidation state. This is a reasonable assumption, as it has been shown by electrochemical spectroscopy (Section 7.2) and x-ray diffraction (Section 7.3) that the electrochemical impedance and the polymer structure are correlated with changes in polypyrrole conductivity. A moving front occurs from oxidized to reduced because the ionic conductivity goes from low to high, exactly analogous to the oxidation of polypyrrole in the free-standing film geometry. The ionic conductivity in the model goes from 0.01S/cm in the oxidized state to 0.1S/cm in the reduced state, a change of only 10 times. The modeled charge on reduction and oxidation is shown in Figure 7.30. A front is seen on discharging in Figure 7.30a) and the diffusive looking charging is shown in Figure 7.30b). The front observed by Smela et al. is shown in Figure 7.31 for comparison.
Figure 7.32: The experimental chronoamperograms for films in the conductive substrate geometry. A free-standing film was placed in the sandwich working electrode and reduced at -0.8V (a), and then reoxidized (b) at 0.4V.
7.4.3 Thin film on a conductive substrate geometry

The chronoamperograms for oxidizing and reducing a free-standing film of PPy(PF$_6$) in the sandwich working electrode (Figure 5.5) is shown in Figure 7.32. This data was obtained while cycling films for x-ray diffraction and conductivity measurements. There is clearly a front causing flattening of the oxidizing current, while the reducing current looks exponential. In this geometry, there is electrical contact over the entire area of the film. The electrons and ions move in series, parallel to one another. The circuit model for this geometry is shown in Figure 6.1b). A front may be created by either a non-linearity in the electronic or ionic resistance, however, the polypyrrole conductivity is higher than the ionic conductivity for all but possibly the most reduced potentials, therefore the front observed in this geometry is probably due to changes in the ionic conductivity. This data could not, however, be fit with a sigmoidal ionic conductivity. It is unclear what the ionic conductivity as a function of oxidation state should look like, and what effect the electronic conductivity may have. In the future, electrochromic measurements of PPy(PF$_6$) in the Smela geometry may give us this information, and possibly independent diffusion measurements performed using NMR.
Chapter 8

Conclusions

The electronic, structural and electrochemical properties of polypyrrole doped with the hexafluorophosphate ion, PPy(PF$_6$) were investigated in this study. We find, predictably, that these properties are intimately correlated.

- The electronic conductivity was found to experience a rapid conductivity change at -0.1V vs. the standard calomel electrode (SCE). It is a sigmoidal function of oxidation state, going from approximately 300S/cm in the fully oxidized state to 0.5S/cm in the reduced state.

- X-ray diffraction showed that at this same potential, the crystal structure of the polymer began to change. Observed changes may represent a loss of pi-stacking, which would affect the conductivity due to reduced interchain charge-hopping, and possibly a conversion from three-dimensional to one-dimensional conduction. This may also be the reason for an observed reversal in actuation: the film first contracts during reduction due to the expulsion of ions, then expands due to loss of pi-stacking.

- Electrochemical impedance spectroscopy measurements demonstrated that the impedance undergoes a sudden transition at -0.1V vs. SCE as well. The largest change in the impedance was in the low-frequency dispersion of the constant phase element, which models a distributed capacitor. This was attributed to a change in the mass-transport of ions in the polymer, which could be brought about by changes in the structure of the matrix.

A finite difference time-domain model of the potentiostatic charging of polypyrrole was created to include the non-linear changes in conductivity that were observed. The model was able to simulate chronoaomerograms and the electrochromic effect, which is a direct measure of the local oxidation state in the film. By modeling a potentiostatic step with a sigmoidal dependence of polypyrrole conductivity with oxidation state, we were able to simulate the moving phase front phenomenon on charging from a very reduced state that has been observed by many groups. Also, by simulating different experimental geometries, we were able to prove that the ionic conductivity must change non-linearly with oxidation state as well. Using this model, cyclic voltammograms with redox peaks were also produced. This is significant as it presents an explanation of the redox peaks that does not rely on the Nernst equation, and is therefore more consistent with the electronic nature of polypyrrole.
Much more work is required to elucidate the exact nature of the correlations between the electronic, structural and electrochemical properties that we observed. All of these properties have noticeable effects on the electrochemistry of polypyrrole, and we must seek to understand the entire system if we are to design conducting polymers that make use of dynamic charging and discharging, as in actuators and supercapacitors. Conducting polymers are a new class of materials that are not yet fully understood. We must be prepared to embrace different methodologies and formalisms to deal with their unique nature. Increased collaboration between physicists, electrochemists and engineers would be very beneficial to the field. Due to the very complex nature of this system, numerical modeling, especially at the microscopic level, will be an important tool.
Bibliography


[73] J. Tso and C. Michal. Unpublished NMR results showing the diffusion of PF$_6^-$ ions in dry polypyrrole films is similar to their diffusion in solution.

Appendix A

The Matlab code for modeling potentiostatic steps

This section contains the Matlab code for modeling a potentiostatic step in the free-standing film geometry. The other geometries are very similar, with minor changes to the resistance matrix, M, and the film dimensions.

```matlab
function sigma = conductivity(sigmax,sigma0,Q0,w,Q)
    \% function sigma = conductivity(sigmax,sigma0,Q0,w,Q)
    \% A sigmoidal conductivity profile with Q 
    \% Input parameters:
    \% sigmax -> conductivity at low doping 
    \% sigma0 -> conductivity at high doping
    \% Q0 -> the metal-insulator transition charge 
    \% Q -> the width of the transition 
    \% Q -> the charge at which to calculate sigma 
    \% Output parameters:
    \% sigma -> the conductivity 
    sigma = (sigmax-sigma0)./(1+exp(-(Q-Q0)/w))+sigma0;

function [tv,iv,Qm,Rm] = potentiostatic_length(V0,V,Qv)
    \% function [tv,iv,Qm,Rm] = potentiostatic_length(V0,V,Qv)
    \% Simulates a potentiostatic step on a film attached to an electrode 
    \% at one end. 
    \% Input parameters:
    \% V0 -> initial potential 
    \% V -> final potential
    \% Qv (optional) -> a vector of charges. If this is defined,
    \% it is used instead of V0 to define the initial conditions of
    \% the circuit model. 
    \% Output parameters:
    \% tv -> time vector 
    \% iv -> current vector, i(t)
    \% Qm -> matrix of Q(t,x) of the film 
    \% Rm -> matrix of R(t,x) of the film
```
% Some parameters
%---------------------------------------------------------%

% the total potential range of the polymer is -0.8V to
% +0.4V vs. SCE. It is simpler to define it as 0 to Vmax = 1.2V
Vmax = 1.2;

Rs = 65; % solution resistance (Ohms)
C = 0.012; % volumetric capacitance of the film (F)

% Film dimensions in cm
L = 2.5;
width = 0.59;
thick = 0.0010;
A = width*thick; % cross-sectional area of the film

N = 100; % number of elements to split up film
Rsi = Rs*N; % incremental solution resistance
Ci = C/N; % incremental capacitance

% initial charge on the incremental capacitors, based on V0 and C
Qi = Ci*V0;
% maximum charge on incremental capacitors, based on Vmax and C
Qmax = Ci*Vmax;

% Conductivity parameters. The conductivity is a sigmoidal function
% of Q that is defined by the max/min conductivity, the transition
% charge, and the transition width. See conductivity.m for definition.
sigmamax = 200; % S/cm
sigmamin = 0.01;
sigma_width = 0.05*Qmax; % width of the transition
Qt = 0.5*Qmax; % position of metal-insulator transition

% time parameters
dt = 0.05; % time increment in seconds
tmax = 30; % total time in seconds
maxsteps = ceil(tmax/dt); % number of time steps

% initialize vector variables
if nargin < 3 % if Qv is not defined
Appendix A. The Matlab code for modeling potentiostatic steps

Qv = Qi*ones(N,1); % Qv is defined by V0 as above
end

Vv = V*ones(N,1); % voltage vector is set by the step potential
% resistance vector is set by conductivity parameters and the initial
% charge on the capacitors
Rv = (L/N)./conductivity(sigmamax,sigmamin,Qt,sigma_width,Qv)/A;
iv = []; % initialize current vector
Qm = Qv; % initialize the charge matrix

% The simulation
%--------------------------------------------------------------------%
%%% jj is the time-step
for jj = 1:maxsteps
% M is the matrix that must be solved to get the spatial component of
% the simulation. The derivation is in Appendix B.
% M = zeros(N,N); % initialize
for ii = 1:N
    M(ii:N,ii:N) = M(ii:N,ii:N) + Rv(ii)*ones(N-ii+1,N-ii+1);
end
for ii = 1:N
    M(ii,ii) = M(ii,ii) + Rsi;
end
bv = (Vv - Qv/Ci)*dt;
% Solve for dQ(x), the charge passed in each incremental capacitor.
% M*dQv = bv
dQv = M\bv;

% The total current is calculated and stored for each time step
iv(jj) = sum(dQv)/dt;

% The new charge at each incremental capacitor, Q(x,t)
Qv = Qv + dQv;

Qm = [Qm,Qv]; % Store the charge

% update the resistance of the polypyrrole, R(x), based on the
% oxidation state, Q(x,) for the next step
Rv = (L/N)./conductivity(sigmamax,sigmamin,Qt,sigma_width,Qv)/A;
end
% create the time vector and the resistance matrix, R(x,t)
tv = linspace(0,tmax,maxsteps);
Rm = (L/N)./conductivity(sigmamax,sigmamin,Qt,sigma_width,Qm)/A;

% plot i(t) and the R(x,t)
figure(1)
hold on
plot(tv,iv*1000,'k');
xlabel('time(s)');
ylabel('current (mA)');
figure
imagesc(tv,linspace(0,L,N),Qm/Qmax);
colorbar
xlabel('time (s)');
ylabel('x (cm)');
title('Q')
Appendix B

Calculating the instantaneous current distribution

In this section, we demonstrate how to calculate the instantaneous current distribution of a transmission line. As an example, we take the \( N = 4 \) branch circuit in Figure B.1. We equate the voltage drops across each branch of transmission line, and solve for the current. The calculations are shown on the next page. The matrix calculations can be easily adapted for any length of transmission line.

Figure B.1: The transmission line model for the free-standing film geometry
Appendix B. Calculating the instantaneous current distribution

\[
V = (i_1 + i_2 + i_3 + i_4)(R_S + r_1) + q_1/c + i_1 r_{ion}
\]

\[
V = (i_1 + i_2 + i_3 + i_4)(R_S + r_1) + (i_2 + i_3 + i_4)r_2 + q_2/c + i_2 r_{ion}
\]

\[
V = (i_1 + i_2 + i_3 + i_4)(R_S + r_1) + (i_2 + i_3 + i_4)r_2 + (i_3 + i_4)r_3 + q_3/c + i_3 r_{ion}
\]

\[
V = (i_1 + i_2 + i_3 + i_4)(R_S + r_1) + (i_2 + i_3 + i_4)r_2 + (i_3 + i_4)r_3 + i_4 r_4 + q_4/c + i_4 r_{ion}
\]

In matrix notation:

\[
\begin{pmatrix}
V - q_1 \\
V - q_2 \\
V - q_3 \\
V - q_4
\end{pmatrix} =
\begin{pmatrix}
R_S + r_1 + r_{ion} & R_S + r_1 & R_S + r_1 & R_S + r_1 \\
R_S + r_1 & R_S + r_1 + r_2 + r_{ion} & R_S + r_1 + r_2 & R_S + r_1 + r_2 \\
R_S + r_1 & R_S + r_1 + r_2 & R_S + r_1 + r_2 + r_3 + r_{ion} & R_S + r_1 + r_2 + r_3 \\
R_S + r_1 & R_S + r_1 + r_2 & R_S + r_1 + r_2 + r_3 & R_S + r_1 + r_2 + r_3 + r_{ion}
\end{pmatrix}
\begin{pmatrix}
i_1 \\
i_2 \\
i_3 \\
i_4
\end{pmatrix}
\]