INVESTIGATION OF FREQUENCY-INDEPENDENT IMPEDANCE BEHAVIOR IN CONDUCTING POLYMERS

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By

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ABSTRACT

Biocompatibility and low, frequency-independent impedance are critical in the design of electrodes for bioelectric signal sensing applications. These conditions could be regarded as the minimum requirements in order to ensure the device performance and recorded signal fidelity. While conducting polymers have shown promise for development of sensing and stimulating bio-electrodes, their reactive impedance characteristics which result from slow ionic diffusion and double layer capacitance present challenges for designing reliable devices. Their reactive impedance, introduces a non-linear and ill-behaved high-pass filter that corrupts the recorded signal.

We have fabricated and optimized electrodes modified with a series of poly(heterolenes) that appear to exhibit low impedance which is characterized by non-diffusion-governed behavior in the frequency range relevant for physiological signals. Based on the impedance results obtained for the electrodes we have developed a model for charge transport in the polymer film which does not rely on the incorporation of the well-known Warburg element. A correlation of experimental impedance data with the proposed equivalent circuit and morphological models is also established. Practical implications of these results and preliminary in vivo studies are highlighted.
To

My Family and Friends
Many would, I think, agree with me that, in anyone’s career path, this could be the most exciting moment. However, it is full of uncertainty and nervousness about what the future holds. As I am thinking about the journey ahead, I cannot stop taking a trip back into memory lane and remembering the ups and downs I have experienced during these last few years. By all of this, I am once again reminded about a saying in Kinyarwanda language which goes: “Umutwe umwe wifasha gusara ntiwigira inama”. The saying literally translates: “A single mind may fool itself but it will not wisely advise itself”. The past few years of my graduate education marked the moments of my life when I was neediest. I needed love, wisdom, encouragement, support, the list goes on and on. Fortunately, I have received everything and beyond what I needed from my family, friends and colleagues. Thus, my sincere gratitude goes to all of you who have been there for me.

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SCOPE AND RATIONALE

Conducting polymers, CPs, constitute a novel class of conducting materials. Although CPs are intrinsically poor conductors, their conductivity can be increased upon doping. The tunable conductivity, biocompatibility, and ease of synthesis and processing of CPs make them superior to traditional metal and inorganic semiconductors for a number of applications. In general CPs have attracted considerable interest driven by both scientific curiosity and technological applications.

There is currently compelling evidence that the biocompatibility and dual conductivity of CPs make them suitable candidates for the design of biomedical devices. To date, conducting polymers have shown promise in the design of bio-actuators, tissue engineering, drug delivery systems and implantable devices such as bio-electrodes for bio-signal sensing and stimulation \(^1\). The fabrication and investigation of potential use of a polymer based bio-electrode suitable for sensing bioelectric signals is the central focus of this research.

A polymer based sensing bio-electrode must fulfill two minimum requirements: biocompatibility and the ability to interact with the surrounding tissue in a reliable, predictable fashion. When implanted in the tissue, a bio-electrode can be defined as a heterogeneous system where the polymer film intercalates between an electronic conducting metal and the ionically conducting extracellular fluid or tissue. On a practical basis, its primary function is to ensure intimate electrical communication between the ionic conductor (extracellular or tissue) and electronic conductor (metal substrate attached to the power supply).
The conduction mechanism of a bio-electrode implanted in tissue is characterised by frequency-reactive impedance which results from the charge exchange across its interfaces and the charge transport within the film. This frequency reactive impedance is known to be present in commonly used electrodes such as noble metals and Ag/AgCl. It is often associated with slow diffusional charge transport, charge storage and double layer capacitances. From an electrical point of view, the circuitry of such behavior would not only lead to high impedance at low frequency, it would also act as a high pass filter; a phenomenon that would be detrimental to performance of the device. For reliable acquisition of bioelectric signals, a desirable bio-electrode must not only avoid such impedance drawbacks, it should also exhibit minimal impedance in order to resolve small amplitude bioelectric signals from background noise.

The present work serves as a step toward the goal of fabrication and optimization of a conducting polymer based bio-electrode that can be effectively used for biosignal sensing and stimulation. The research described herein is in part motivated by the results from our laboratory demonstrating that a subset of test electrodes modified with poly(3,4-ethylenedioxythiophene) exhibited interfacial ohmic behavior in vivo within a limited frequency range. Our initial efforts were concentrated on the determination of whether this frequency independent behavior could be reproducibly achieved in poly(3,4-ethylenedioxythiophene) modified electrode in vitro over a wide frequency range; thus providing the ability to fine-tune the parameters leading to ohmic behavior before sacrificing animals for in vivo testing. Chapter 2 is devoted to the
description of various electroanalytical techniques, in particular impedance spectroscopy, which have been employed to characterize our electrochemically synthesized electrodes. In Chapter 3, we report and discuss the results obtained from the investigation of the effects of synthetic parameters such as the film thickness, deposition time, and monomer and counterion concentration on the ohmic behavior of poly(3,4-ethylenedioxythiophene).

Analysis and interpretation of impedance data often requires a quantitative electrical equivalent circuit model. An equivalent circuit model is developed by fitting the experimental impedance data to a theoretical electrical circuit, in which each electrical element stands for an electrochemical process occurring in the system. This approach has become the most commonly used tool for the investigation of conducting polymers. Equivalent circuit models which take into account the porosity of conducting polymer modified electrodes seem to be more prominent in the field. In particular, the transmission line model (TLM) originally proposed and continuously refined by Albery et al. and its various forms became the most generalized equivalent circuits which attempt to address the effects of complex morphological features of polymers. However, the morphological model suggested by our data does not appear to be in congruence with the fundamental basis of the transmission line model.

The transmission line model assumes a macrohomogeneous structure which can generally be modeled by parallel one dimensional ionic and electronic conduction rails interconnected by capacitors. Our morphological model suggests a two adjacent macrohomogeneous layers. A model which is more consistent
with our proposed morphology and impedance data is described in Chapter 4. The proposed model is further discussed and tested against simulated data (under conditions that may not necessarily be experimentally accessible) in Chapter 5; thus establishing the validity of its simplified form.

The insights gained from Chapters 3, 4 and 5 suggest that it may be possible to achieve ohmic behavior in other polymer types. While it is clear that ohmic behavior originates from a two-layer morphology, the role of chemical nature of the monomer (ethylenedioxythiophene) in imparting this unique frequency-independent impedance cannot be excluded. The role of the monomer identity can be at the level of electropolymerization (leading to the two-layer morphology) or at level of charge transport processes in the film (affecting the charge carrier pathways). To investigate these possibilities, chemically related monomers were electrosynthesized under our optimum conditions and the films were investigated for ohmic behavior. In particular, the role of heteroatom and backbone have been investigated. These results are reported in chapter 6.

Although the real life application aspects of our electrodes remain to be investigated, our results demonstrate evidence of frequency-independent impedance behavior in polymer based electrodes (both \textit{in vitro} and \textit{in vivo}). The achievement of frequency-independent impedance behavior in conducting polymer modified electrodes (CPMEs) is an important step towards the materialization of CPMEs for biomedical applications. To the best of our knowledge, this behavior is not predicted by any of the previously proposed models. This suggests that a self-consistent picture of impedance theory which
accurately addresses a wide range of experimental results constitute an invaluable addition to the field.

The present work is only a step towards the development of an effective bio-electrode for stimulation and sensing bio-electric signals. It is meant to bring new insights into the fabrication and optimization of polymer based electrodes which can effectively overcome currently known impedance and frequency filtering drawbacks. This may offer an alternative approach to tackle some of the current practical challenges encountered in the field. Future directions and practical outlook of this research is highlighted in Chapter 7.
References


CHAPTER 1
INTRODUCTION TO CONDUCTING POLYMER MODIFIED ELECTRODES

1.1. Historical Background of Conducting Polymers

Often referred to as “synthetic metals”, conducting polymers constitute a new class of organic material capable of conducting electricity because of their alternating single and double bonds along the backbone chain (Figure1.1). Although conducting polymers are intrinsically poor conductors, their conductivity can be increased dramatically over a wide range by doping them \(^1\).

As the name indicates, conducting polymers are large organic macromolecules which have the unique ability to conduct electricity. A detailed historical account of the evolution of conducting polymer field has been given by Inzelt \(^2\). In summary, the notion of conducting polymers surfaced in the scientific community in the mid 1800s when Letheby—then at the College of the London Hospital—first reported electrochromic properties of polyaniline \(^3\). However, polyaniline was not recognized as a polymer since the concept of polymeric macromolecules was not fully embraced by the scientific community until after the work of Staudinger on polymeric materials \(^4\),\(^5\).

Another early discovery in the field has been reported by an Austrian group in mid 60s, who observed high conductivity in iodine-doped polypyrroles \(^6\),\(^7\),\(^8\),\(^9\). They reported resistivity values ranging between 1-200 ohms/cm, which is comparable to those achieved even after three decades of intensive research in conducting polymers. Surprisingly, this innovative discovery received little attention from the scientific community. The lack of interest may have been a
result of the fact that very little was known about the electropolymerization and conduction mechanisms in amorphous materials. The conduction in amorphous materials was not critically discussed until the work of Mott \(^\text{10}\) which brought new insight into the conductivity mechanism in amorphous structures.

The discovery of iodine-doped polyacetylene by Alan J. Heeger, Alan G. McDiarmid and Hedeki Shirakawa \(^\text{11}\) is often regarded as the beginning of the field of conducting polymers. In their breakthrough article titled “Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, \((\text{CH})_x\)” the authors reported over seven orders of magnitude increase in the conductivity of polyacetylene and change of color upon the exposure of the polymer and its uptake of halogen vapors (in the case of iodine). The changes were dependent upon the extent of halogenations (currently known as doping level).

The discovery of conducting polyacetylene earned Heeger, McDiarmid and Shirakawa the Nobel Prize in Chemistry for “The discovery and the development of conducting polymers” in 2000. This discovery and subsequent efforts have advanced our understanding of conducting polymer structure, resulted in improved syntheses, and increased our understanding of conduction mechanisms in the polymer films.

Another groundbreaking step in the field was made by Diaz et al. who reported the ability to electrochemically synthesize polymer films on metal electrodes for the first time \(^\text{12}\). The control over the electropolymerization offered by electrochemical methods has led to increased efforts in the investigation of
the charge transport mechanism in the film. Although significant progress has been made over the last few decades and appreciable knowledge has been attained, results found in the literature indicate that, a unifying model that provides an accurate picture is still needed. A summary of work devoted to the development of such a model is briefly reviewed in section 1.3.

1.2. Electrical Conduction in the Solids and a Particular Case for Conducting Polymers

Generally speaking, intrinsic electrical properties of any solid material fall under one of the four categories depending on its electronic band structure and inherent conductivity: insulator, semi-conductor, conductor and superconductor (intrinsic superconductors are less popular than the other categories). From a material property point of view, atoms in a solid crystal interact with their neighbors. For example, a metal cube composed of $N$ atoms has $N$ atomic orbitals which overlap in 3-dimention to form a continuum of $N$ molecular orbitals. These orbitals overlap to form two separate electronic bands—the conduction and valence bands (Figure 1.2). For conductors such as metals, the two bands are not separated by the band gap and electrons can easily move from one electronic band to another; making them good conductors.

Similarly to the conductors, neighboring unit cells of a semiconducting lattice may interact to form electronic bands. Unlike metal conductors, however, the two bands are separated by a band gap. Consequently, they are poor intrinsic conductors due to a hindered movement of charge carriers between the electronic bands. The conductivity of semiconductors can be improved by
minimizing the effects of the band gap. This can be achieved by introducing impurities, a process known as doping. The dopants create electron accepting or electron donating bands which are close in energy to the original valence band (for p-type semiconductor) or conduction band (for n-type semiconductor). In the sense that doping is also required to produce conduction in conjugated polymers, conducting polymers are loosely analogous to traditional inorganic semiconductors. However, doping conducting polymers seems to take a different path.

Extraction of an electron from a conjugated system, as is the case for p-type conductive polymer, creates a free radical and a positive charge. The free radical and the charge couple with each other to form a polaron which is simply a radical ion with spin $\frac{1}{2}$. The polaron is delocalized over few (3-4) monomer repeat units and is associated with chain distortion as a result of strong electron-phonon coupling. This processes creates accessible energy levels in the band gap between the valence and conduction bands which remain full and empty respectively (Figure 1.3)\textsuperscript{13-15}. Since the polaron only creates electronic states localized within the band gap, it leaves the valence and conduction bands full and empty respectively. The newly formed energy level in the forbidden band (band gap) is occupied by the unpaired single electrons.

When a second electron is ejected from the polymer system—either the unpaired single electron or an electron from elsewhere on the chain—these two scenarios both lead to the formation of a bipolaron. In the first case, the removal of free radical leaves the defect with a spinless nature (bipolaron). In the second
case, a more energetically favored bipolaron is formed by a recombination of two polarons. The chain distortion associated with formation of two polarons lead to an increase in energy greater than columbic repulsive force resulting from pairing like charges. This phenomenon favors the creation of bipolarons at higher doping levels. At sufficiently high doping levels, the bipolarons form bipolaronic electronic bands in the middle of bands gap and this gives rise to the metallic nature observed in conducting polymers (Figure 1.3).

1.3. Charge Injection and Conduction Mechanism in the Film

Discussion of charge injection and transport mechanism in conducting polymers can be roughly classified in three broad categories. The first category includes the work that focuses primarily on understanding the properties of conducting polymers on molecular level. This topic has attracted interest of physicists and physical chemists who are interested in elucidating consistent picture of molecular dynamics regulating the properties of conducting polymer films.

The second category includes the work aimed at a better understanding of microstructure and associated properties of conducting polymers. This is very important for synthetic chemists who are interested in synthesizing films with controllable properties. The ability to optimize desired properties of bulk films is the key to a wide range of potential applications.

The third category attempts to address the questions raised by macroscopic properties of the conducting polymers which may be different from their microscopic properties. This is critical for predicting how individual strands
interact with each other when they form films. While the work in the first two
categories is primarily theoretical, the experimental work in this category may
enable links to be made between theoretical predictions and experimental
results.

1.4. Charge Injection from Electrode into the Polymer Film

The charge carrier injection into the polymer film was somewhat neglected
in the early literature. While this topic is well covered in the case of traditional
semi-conductors, the mechanism of charge injection proposed in this case does
not translate to conducting polymers due to the electronic and structural
differences between these materials. Conducting polymers exhibit strong
phonon-electron coupling which may have profound effects on charge injection
efficiency. Furthermore, the conducting polymer’s structure does not offer the
simplicity of the crystalline-like semi-conductor. Consequently, the charge
injection into the polymer film is often determined by HOMOs and LUMOs of
individual strands, making the control of the process a difficult task.

A heterogeneous interface cannot be defined by the bulk properties of the
two interacting materials (Figure 1.4). The interfacial region is especially
important for modified electrodes as it defines the type of interfacial contact as
either ohmic or rectifying. The nature of the contact dramatically affects the
charge carrier flux across the interface both thermodynamically and kinetically.

A thermodynamic equilibrium between two conducting materials is
established by flow of charge carriers from one material to another in order to
equalize the Fermi levels. The flow is largely governed by the electrochemical
potential of the constituent materials. Due to the differences in electrochemical potential of the bulk phases, an interfacial energy barrier is usually established 17. The activation energy required for the charge carriers to overcome this interfacial barrier can provide important information as to whether the interface is ohmic or rectifying.

An ohmic contact displays linear $j-V$ behavior in accordance with Ohm’s law (i.e. the flow of charge carriers crossing the interface linearly depends on the applied voltage). Consequently, the net current is zero at thermodynamic equilibrium because the carrier flux across the interface in one direction is equal to that in opposite direction (not restricted in either direction). This implies a negligible (or zero) potential barrier height.

A simple model treating charge injection across a rectifying interface has been described by Conwell and Wu 18. The authors have shown that the charge carrier injection in conducting polymers cannot be described by simple Fowler-Nordheim tunneling as previously suggested by Parker 19 and Braun et al 20. This is mainly due to the fact that short conjugation and structural defects in conducting polymers (only 7-10 monomer units) prevents them from having broad bands. The model considers the charge carrier from the metal (electron/hole) tunneling into a statistical distribution of polaron energy levels. The injection energy then becomes a function of applied electric field, image force and the polaron’s binding energy described by equation (1.1).

$$W = U_x + eE_x + \frac{e^2}{4K_x}$$  \hspace{1cm} (1.1)
where $W$ is the injection energy, $e$ is the charge on charge carrier (electron) and $E$ is the electric field intensity. The last term describes the image force, where $K$ is the dielectric constant and $x$ is the distance from metal|film interface.

In a complementary treatment by Stoneham et al. $^{21}$, a new idea of the dynamic nature of the polaron creation was introduced. This approach allows the consideration of the force an electron may exert on atoms of the molecule while occupying a newly created polaron site. In this treatment, the charge injection is assumed to consist of a simple, coherent event. The energy of the charge carrier’s wave function depends on the relative position between the Fermi level of the metal (electrode) and the molecular orbital of the chain (treated as a molecular wire). This treatment offers the ability to predict charge carrier injection results of a wide range of metal substrate. Although this model adds a new dimension to the better understanding of the physics of the charge carrier injection across the interface, it ignores considerations such as the true three-dimensional nature of the interface and the structural complexity of the film.

The effects of conjugation lengths and structural disorder on the charge injection efficiency have been theoretically considered by Ramos et al. $^{22}$. This work shows that the orientation of the polymer strands relative to the electrode surface and electric field have combined effects on the charge carrier injection. The electric field increases the amount of injected charge carriers, regardless of the orientation of the stand. The injected charge carriers hop away from the interface, creating unoccupied sites for incoming charge carriers. The electric field’s effects depend also on the orientation of the polymer strands relative to the
electrode surface. For polymer strands perpendicular to the electrode surface, relatively higher electric field intensity is required to allow inter-chain hopping. For strands parallel to the electrode surface, the inter-chain hopping is favored. The mixed orientation leads to an average contribution of the two morphologies. Ramos acknowledges the extreme idealization of the model, but it does provide valuable insights into charge carrier injection.

Despite the atomistic details considered by different models, they all show an apparent agreement on the dependence of charge injection on the substrate’s work function. This makes the judicious choice of the substrate electrode a crucial step in optimization of the interface. Under specific conditions, for example, the metal|film interface can be made ohmic (i.e transparent to the flow of electrons or holes). Kinetically speaking, there are two ways that ohmic metal|polymer contact can be established. Since each charge carrier crossing the interface has to be activated to overcome the barrier height or tunnel through it, an ohmic contact can be established by either forming short barrier heights or through formation spaces charge regions with narrow widths, respectively (also mentioned in section 4.6).

In real experimental conditions, however, the energetic and electronic properties of the interface are much more complicated than the models described above. The complication often arises from the contamination of the interface which decouples or at least attenuates the direct interaction of metal and polymer species. Unlike electrodes prepared under ultra-high vacuum (UHV) conditions, this contamination is unavoidable on a practical basis for electrodes
preparated under normal conditions from solution under N\textsubscript{2} or air. Electrodes made under the solution conditions are reported to depart from the Mott-Shottky prediction (i.e. no interface states at the interface)\textsuperscript{24,25}. Surprisingly, the contaminated interface reportedly lowers the injection barrier. These observations highlight the significance of interfacial density of states.

The concept of induced density of interface states and their effects on interfacial electronic properties of traditional semiconductors has been known for decades\textsuperscript{27,28}. These interfacial states develop when a metal electron wave function penetrates into the energy states of the semiconductor. It turns out that the penetration length of this electron wave function tail has significant effects on barrier heights and on the broadening of the energy states of the semiconductor\textsuperscript{28,29}. This concept has also been applied and documented for weakly interacting metal-organic interfaces\textsuperscript{24,25,29,30}. It has been concluded that the presence of these states may facilitate the charge transfer even when the metal-organic interaction is weak.

The relative difference in position between of the metal's Fermi level (E\textsubscript{F}) and the charge neutrality level (E\textsubscript{CNL}) determines the charge injection pathway. This is primarily due to the effects of molecular energy level alignment on barrier heights. For example, if the work function of the metal is smaller than E\textsubscript{CNL}, the charge transfer processes (from metal to the interface states) establishes a dipole barrier which narrows down the energy difference between E\textsubscript{F} and E\textsubscript{CNL}. Other important considerations include the scenario in which the work function of the metal is smaller or perfectly aligns with E\textsubscript{CNL}. It is important to reemphasize
the assumption of weak interfacial interaction, which excludes important parameters such as chemical bonding that may be established between the metal and the polymer. A unified model, best known as the “pillow effect” attempts to incorporate the chemistry of the interacting materials in the theory of induced surface states. This has been explored by Vazquez $^{31}$. The pillow effect model becomes less important for weakly interacting interfacial constituents. As such, it provides a correction, without contradicting the main idea, of the theory of induced surface states in the case of strong interactions.

1.5. Charge Transfer within the Polymer Film

There are currently diverging views about the conduction mechanism in conducting polymers. Some authors propose the development, upon doping, of well-defined electronic bands like traditional doped semiconductor materials $^{13-15}$. This, in turn suggests that charge carriers move in a continuum carrier path (bands) as it would be in case of crystalline inorganic semiconductors. However, well-supported views involving hopping mechanism (based on localized redox sites) have also been suggested supporting views which rely on the concept of localized redox sites $^{32,33}$. These views advocate for charge carrier hopping between redox sites located on a given polymer chain or between neighboring chains. These mechanisms have substantial consequences for energy activation and charge recombination along the chains. These views further support the conductivity mechanism by hole/electron hopping. The hopping mechanism, which can also be envisioned as a series of redox processes taking place within the polymer film, gives rise to a charge transfer resistance and a capacitance
contribution to the predicted impedance behavior. A further consideration is the fact that ions are introduced into or expelled from the polymer film during a redox process in order to achieve electroneutrality (this aspect is discussed in details in chapter 4).

In the end, it appears that the conduction mechanism depends on the complicated morphological features of conducting polymers. Some models recognize the existence of well structured crystalline regions surrounded by amorphous regions \(^{34}\). While well structured grains are metallic in nature, amorphous domains act as insulators. The conductivity in the conducting domains (metallic) is then mediated through quantum tunneling in the amorphous domains. This observation implies that a critical issue is control of the morphology and inner texture of the film. In other words, the synthetic parameters play a central role in the optimization of conducting polymer films.

1.6. **Charge Transfer at Solution|electrolyte Interface**

The dual conductivity (both electronic and ionic) of conducting polymer films requires the exchange of ionic species with surrounding electrolyte in response the redox switching. As a result, concentration and the type of electrolyte solution with which the film is in contact have significant effects on its ionic conductivity. Studies of ionic conductivity on polypyrrole films revealed that solution ions can permeate into the film especially when it is in its oxidized state \(^{35}\). Donnan exclusion (i.e only one charge type of ionic species can enter the polymer) is usually assumed. However, Ren et al.\(^{36}\) have determined that the cation (co-ion) of the electrolyte has some effects on the ionic conductivity of
polypyrrole. Furthermore, the effects of these species are both potential- and concentration-dependent. The potential dependence was explained by the increased counterion conductivity while the concentration dependence was explained by non-exchanged ionic species. Ren’s observations support the two-carrier model for these conducting polymers. In some cases, one of the resistances (ionic or electronic) can be ignored depending on either the morphology or the oxidation state of the polymer.

In the case where the surrounding electrolyte contains electrochemically active species, the possibility of electronic charge transfer between the polymer and redox couple introduces an “interfacial” charge transfer resistance. The value of the charge resistance depends on the oxidation of the polymer film. This charge transfer resistance is slightly different in nature from that of metal|electroactive solution interface. Unlike the metal|solution interface, the charging film|solution interface can rarely be accurately defined in terms of the so-called “Gouy-Chapman-Stern model” of the double layer. This is mainly because the solution may penetrate the polymer matrix; thus making it possible for the charge transfer to take place inside the film. In general, the experimental evidences indicate that charge exchange at the film|solution go hand-in-hand with the redox switching of the polymer and the chemical nature of surrounding electrolyte.

1.7. Effects of Synthetic Parameters on Polymer Properties

Conducting polymers can be synthesized by both chemical and electrochemical methods. Each method offers unique advantages based on
targeted goals. In the early days of conducting polymer discovery, small amounts were chemically synthesized, mainly to allow their characterization. Chemical polymerization for practical application was slow to emerge. Although it is certainly of importance, chemical synthesis of conducting polymers will not further be mentioned. The rest of this section will focus on electrochemical synthesis as it is a preferred laboratory-scale method for producing conducting polymers with controlled parameters.

The electrochemical polymerization mechanism of polypyrrole deserves a special emphasis because it provides insight into that of many other heteroaromatic conjugated polymers. As the first to be successfully electrochemically synthesized, the electrosynthesis reaction mechanism of polypyrrole has been extensively studied. Anodic polymerization of pyrrole monomer is irreversible and results in a polypyrrole film which displays redox activity. The mechanism involves nucleation and growth steps. Two electrons per monomer are required for electropolymerization.

Oxidative coupling of the monomer and free radical polymerization are the most widely accepted mechanisms. Oxidative coupling mechanism (Figure 1.5) is initiated by a one electron oxidation of the monomer by electrode substrate. This reaction is followed by a rate-limiting dimerization of two monomer radicals. The newly created dimer undergoes the same mechanism until a chain composed of few monomer units forms. These insoluble oligomers precipitate on the electrode surface to form polymer films. Based on this electropolymerization mechanism, a number of synthetic parameters such as
Electropolymerization time, electropolymerization potential, solution, counterion and temperature have been proposed to affect the electrochemical properties of the film.
1.1. Structure of polyacetylene: an illustration of a conjugated backbone of a conducting polymer.
1.2. Illustration of a typical electronic band structure of: a) a conductor, b) a semiconductor c) an insulator. VB is the valance band, CB is the conduction band, \( E_G \) is the band gap energy and \( E_F \) is the Fermi Level.
1.3. Illustration of a typical electronic band structure development in doped conducting polymers: VB is the valance band, CB is the conduction band, $E_G$ is the band gap energy.
1.4. Illustration of an electronic structure of an interface (polymer|metal) where $E_A$ and $I_E$ are respective electron affinity and ionization energy of the polymer. $\Delta$ is the dipole of the interface, $E_{CNL}$ is the interface density of gap states and charge neutrality level, and $\Phi_{Bn}$ and $\Phi_{Bp}$ are the electron and hole injection barriers respectively (redrawn from\textsuperscript{23}).
1.5. A general electropolymerization mechanism: An example of pyrrole
1.8. References


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CHAPTER 2
METHODS AND MATERIALS

2.1. Cyclic Voltammetry

Cyclic voltammetry, CV, is carried out using a typical three electrode configuration. The three electrodes are the working, the auxiliary and the reference electrodes\(^1\) (Figure 2.1). These electrodes hence become components of a single circuit where they are connected by the electrolyte solution. The three electrodes are statically immersed in unstirred solution. In some cases, a supporting electrolyte may be used to ensure high conductivity of the solution. This decreases the impact of ohmic drop on the electrochemical processes being investigated. A reference electrode has an invariant potential which does not dependent on the electrolyte solution. This reference is required for controlling and measuring the potential on the working electrode. This measurement is made possible by the auxiliary electrode which completes the circuit. It is important to make sure that neither the reference electrode nor auxiliary electrode interferes with the reaction of interest occurring at the working electrode by engaging in a competitive reaction or introducing undesired contamination into the cell.

Cyclic voltammetry is probably the most versatile electrochemical technique widely used to study the kinetics of redox processes occurring at the working electrode surface. CV is one of the many potential sweep methods during which the potential is cycled between two switching potentials as a function of time \(^1\). The potential cycling follows a triangular potential waveform
Analysis of the voltammogram can provide considerable information about the kinetics and the influence of experimental conditions on the electrochemical processes at the electrode.

The power of cyclic voltammetry lies in that it incorporates chemistry into an electric circuit. As such, it allows control of the kinetics and thermodynamics of the reaction by changing the voltage. The relationship between the thermodynamics and the chemical equilibrium of the system can be deduced from the well-known Nernst equation (2.1).

$$E = E^0 - \frac{RT}{nF} \ln Q$$  \hspace{1cm} (2.1)

where $E$ is the actual cell potential and $E^0$ is the standard electrode potential. $R$ is the universal gas constant; $T$ is the temperature given in Kelvin, $n$ is the number of electrons involved in exchange reaction and $Q$ is the reaction quotient.

The potential at the working electrode is controlled by comparing it to that of the reference. The reference electrode exhibits a stable, well-known potential that is almost independent of surrounding medium. By monitoring the potential of the working electrode versus that of the reference electrode, important parameters such as redox potential and polarization over-potential can be established for a particular system. From the redox potential, other critical information can be obtained by careful inspection and systematic manipulation of the data.

When a potential is applied on the working electrode and scanned back and forth between the switching potentials, the change in the current between the working and counter or auxiliary electrode is associated with the reduction and
oxidation processes occurring between the scan limits. During a scan toward more positive potentials the current rises sharply as the potential approaches the oxidation peak and then decreases as the concentration of reduced/neutral analyte species are depleted near the electrode surface. During the reverse scan, reduction peak which is theoretically identical (in terms of charge transferred) to the oxidation peak appears. Due to the mass transport of reduction/oxidation of analyte, the peaks may deviate from theoretical predictions. The relationship between the current and the current associated with a diffusion governed process is described by the Cottrell equation (2.3) \(^1\). It can be observed, from equation (2.3) that the current of a diffusion-governed reaction is linearly proportional to the square root of scan rate.

\[
i = \frac{nFAC^2\sqrt{D}}{\sqrt{\pi t}}
\]

(2.3)

where \(i\) is the current, \(n\) is the number of electrons involved in the reduction/oxidation of one molecule of analyte, \(A\) is the electrode surface area given in \(\text{cm}^2\) (planar), \(D\) is the diffusion constant of analyte, \(C_0\) is the initial concentration of analyte and \(t\) is time.

The separation of peaks (cathodic and anodic peaks) can be used to evaluate the reversibility of the system. The redox peaks are often separated by a hysteresis resulting from polarization overpotential. The polarization overpotential may arise from the diffusion and activation energy barrier of analyte. The dependence of electrical current on electrode’s potential during a cyclic voltammetric experiment can be conveniently expressed by the Buttler-Volmer equation (2.4) \(^1\).
In this equation, $I$ is the electrode current, $i_0$ is electrode’s current density, $\eta$ is the over-potential, $A$ is the electrode’s surface area (cm$^2$), $T$ is the absolute temperature, $n$ is the number of electrons involved in the electrochemical reaction, $\alpha$ is the symmetry factor or transfer coefficient, $R$ and $F$ have their universal meanings (also defined in 2.1).

Equation (2.4) describes the behavior of the system when the current is controlled by the charge transfer at the electrode surface. The Buttler-Volmer equation has become central to the field of electrochemistry. It can be combined with the Cottrell equation and reduced to equation (2.5), which gives a theoretical prediction of a peak-to-peak relationship of an ideal reversible system. It can be concluded, for example, that the peak separation of an ideal system in which only one electron per molecule is involved should be 57mV (at 298 K). This value assumes the ohmic compensation which is the resistance caused by the solution.

$$E_{red} - E_{ox} = \frac{57 \text{mV}}{n}$$

In this equation, $E_{ox}$ and $E_{red}$ are the peak potentials for the reduction and oxidation processes. Other variables have the same meaning as previously defined. It is important to mention that it is possible to estimate the electron transfer rate constant by analyzing the peak separation.

In general cyclic voltammetry has proved to be very useful in conducting mechanistic investigation of electrochemical systems. As is the case with many other techniques, however, it can be greatly limited when used to investigate the
system of slow electron-transfer kinetics. Its sensitivity to such a system can complicate the measurement and acquisition of quantitative data. In such cases, other techniques such as chronocoulometry \(^1\) can be used to overcome the limitation. Nonetheless, cyclic voltammetry has been successfully used to address a wide range of electrochemical challenges \(^4,5\).

### 2.1.1. Cyclic Voltammetry for Deposition of Conducting Polymer Films

Cyclic voltammetry can also be used for electrodeposition of polymer films on the electrodes \(^6\). While conducting polymer films can be prepared using various electrochemical methods including potentiostatic \(^7\), potentiodynamic \(^6,8\) and galvanostatic \(^9\) methods, the choice of polymerization technique is very important for controlling the morphology and electrochemical properties of the film. For smooth morphology, cyclic voltammetry may be the technique of choice due to its ability to periodically reduce and oxidize the polymer during electropolymerization.

When a positive potential is applied to the working electrode, the monomer is oxidized and forms oligomers as the potential approaches that of monomer oxidation. At high enough oligomer concentration, the oligomers precipitate back onto the electrode surface to form layers of the film. Although not always well resolved, the polymer and monomer oxidation peaks can be seen on the cyclic voltammogram. The current associated with polymer oxidation and charging increases with the number of cycles. This increase is a good indication of polymer film growth (increasing thickness). It is important to carefully choose the switching potential, as applying an excessively positive potential can lead to
overoxidation of the polymer. The polymer then becomes nonconductive, increasing the potential drop. In such cases, the potential at the surface may become too low to oxidize new monomer. As a result, the growth of the film may stop and it becomes difficult to synthesize thicker films. This limitation can be overcome by extending the potential window when such potential drop is suspected. This, however, can be very difficult to monitor and a better alternative may be to use potentiostatic methods.

Despite the limitations, potentiodynamic electropolymerization may be advantageous for forming smooth and compact structures. It is well known that incorporation of dopants in the polymer matrix affect the morphology \(^{10}\). Using cyclic voltammetry for electrodeposition allows incorporation of dopants followed by their expulsion during the electropolymerization on every cycle. For neutrality purposes, dopants are incorporated during oxidation of the film. When the voltage is reversed, the dopants near the surface are expelled into the solution as a result of film reduction. As a result, the pores and polymer chains relax to form a more compact structure. It is worthwhile to reemphasize that other parameters such as monomer concentration, counterion identity, and solution electrolyte will still affect the morphology and the texture of the film regardless of the method used for electrodeposition.

2.1.2. Electrode Characterization by Cyclic Voltammetry

As mentioned in chapter 1, conducting polymers are complex systems that may require a number of characterization techniques for a thorough understanding. Cyclic voltammetry is one of the many electrochemical methods
that are often used to elucidate important information about the electrochemistry of conducting polymers. The characterization can take place insitu, ex-situ or both. Charging/discharging mechanism, redox potential, electrochemical activity and charge transfer at the electrode’s interface are the most sought after information which can be obtained from a cyclic voltammetric experiment.

In addition to the relative location of the oxidation and reduction peaks, cyclic voltammetry can be used to gain insight about the film’s capacitance. A typical cyclic voltammogram of a conducting polymer is characterized by a large separation between the anodic and cathodic currents. This separation (plateau) is indicative of film capacitance which is numerically given by equation (2.6)\textsuperscript{11}.

\[ C = \frac{I}{\nu} \]

(2.6)

where \( C \) is the capacitance, \( I \) is the current and \( \nu \) is the scan rate.

The capacitance can be a combined result of redox processes within the film and interfacial double layer capacitance. The double layer is formed within a few milliseconds at an electrode surface due to adsorption of one layer of ions and then accumulation of ions of the opposite charge. In porous electrodes, the double layer capacitance extends within the pores walls inside the film. Discrepancies between the capacitance calculated from the voltammogram and from other techniques such as impedance spectroscopy have been reported and the discrepancies were explained in terms of conformational changes in conducting polymers resulting from redox processes\textsuperscript{11}. 
2.2. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy, EIS, is a powerful electrochemical technique based on the theory of a linear transfer function. The power of this technique lies in the large amount of information that can be derived from a single experiment. This is due to the ability to extend the signal perturbation over a wide range of frequency. At the same time, EIS is a very complex technique that requires a great deal of data analysis to extract that information; a drawback that has limited its use until the advent of computer algorithms for easy manipulation of the data. Furthermore, extensive development of this technique has made it possible to establish patterns that allow one to predict the mechanisms of electron transport and electrochemical processes from EIS spectra.

2.2.1. Theory of and Evolution of Impedance Spectroscopy

The theory of EIS dates back to the 1900s. The foundations of the field were established by Heaviside but continuously refined by others such as Warburg and McDonald. Due to the technical and mathematical challenge, however, the development of the technique was very slow until the invention of the potentiostat and frequency analyzer. These inventions marked the revolutionary step in the development of EIS as they stimulated the development of commercial software, allowing easy measurement and data analysis.

Impedance spectroscopy can be defined as the ratio of Laplace transforms of voltage and current as described by equation (2.7).

\[ Z(f) = \frac{V(f)}{I(f)} \quad (2.7) \]
In this equation, \( V(x) \) and \( I(x) \) are Laplace transforms of voltage and current and \( Z(s) \) is impedance. Through his remarkable work on impedance spectroscopy, Heaviside introduced his own transform \( s=j\omega \) which allows the shift from Laplace domain to Fourier domain. This transformation is crucial for the visualization of real processes and analysis of experimental data.

Having stressed the power of and emerging popularity of EIS, it is important to remind the reader that EIS is only limited to linear system where the conditions of causality, linearity, lack of memory effects and observability are fulfilled. Furthermore, it is required that a single input provides a single output. Unfortunately, electrochemical systems are often non-linear and a number of processes such as mass transport and irreversible charge transfer are always of concern. These requirements, thus, are very difficult to meet in a typical experimental setting which forces the investigator to make assumptions.

### 2.2.2. Basic Experiment and Data Acquisition Description

EIS is often conducted in a three-electrode electrochemical cell (Figure 2.1). In principle, the system is perturbed by a small sine wave signal input and the output, which is also a sine wave signal with the same frequency, is measured. The ratio output/input contains both real and imaginary components which determine the impedance at the corresponding frequency. The real and imaginary components of impedance, \( Z' \) and \( Z'' \), and the phase angle depend on the particular nature of the dominant conductive behavior (a resistor or a capacitor present within the system) at a given frequency range. For example, while resistive behavior lacks the imaginary component \( (Z'') \) and its associated
phase angle, $\phi$, is $0^\circ$, capacitive behavior lacks the real component ($Z'$) and exhibits $\phi = -90^\circ$. In the frequency domain, the impedance which is a complex quantity can be expressed by equations (8-10).

$$Z(j\omega) = Z' - jZ''$$  \hspace{1cm} (2.8)

Where $Z'$ and $Z''$ are the real and imaginary components of the impedance. $j$ is defined as $j = \sqrt{-1}$

Alternatively, the impedance can be expressed as in equation (2.9):

$$Z(j\omega) = |Z|e^{j\phi}$$  \hspace{1cm} (2.9)

In this equation, $|Z|$ and $\phi$ are the magnitude of the impedance and the phase angle as defined in equations (2.10) and (2.11) respectively.

$$|Z| = \sqrt{(Z')^2 + (Z'')^2}$$  \hspace{1cm} (2.10)

$$\phi = \tan^{-1}\left(\frac{Z'}{Z''}\right)$$  \hspace{1cm} (2.11)

Although equations (2.8) and (2.9) describe the same quantity, both are mentioned here because they present different features of the impedance data. This is illustrated by respective representation plots highlighted in the subsequent section.

2.2.3. Impedance Data Representation

Visual inspection of an impedance spectrum is very informative especially if one is familiar with impedance data representation. On the other hand, it can be misleading due to the difficulties to explicitly represent all variables on the same graph. This is, in part, due to the fact that complex impedance data inherently involved the interplay of three variables which are the imaginary
component of the impedance, $Z''$, the real component of the impedance, $Z'$ and the phase angle, $\phi$. The need to represent these variables as a function of frequency complicates the picture even more in that at least one of the variables has to be unavoidably obscured. This has lead to different approaches to representing impedance data \(^{14}\). Nevertheless, the Nyquist and Bode representations have become the most widely used graphical representation of impedance data.

In the Nyquist format, the $-Z''$ is plotted on the $+y$ axis and $Z'$ is plotted on the $x$ axis. The impedance magnitude, $|Z|$ for a circuit, like the one shown in (Figure 2.3.A), is equal to the magnitude of a vector from the origin ($0,0$) to the point of interest ($x,y$) and the phase angle $\phi$, is given by the angle between the vector and the $Z_{\text{real}}$ axis. The shortcoming of this presentation is that the frequency and phase angle corresponding to a particular data point cannot be directly determined. However, trends with frequency can be found knowing that frequency decreases from left to right of the semi-circle (or from bottom to top in case of the capacitor).

The Bode presentation may be more informative, especially because it shows more clearly the general frequency dependence of impedance and phase angle variation. The Bode format displays the phase angle $\phi$ or the impedance magnitude $Z$, ($y$-axis) as a function of log frequency ($x$-axis) (Figure 2.3.B,C). As such, the information it displays complements the information available about $Z''$ and $Z'$ from the Nyquist plot.
Graphical inspection should only be considered as the first step preceding a thorough data analysis especially in case of complex circuits. The same circuit may produce two different shapes of spectrum in the Nyquist plots due to differences in relative values of the elements and geometric connections of the circuit, and \textit{vice versa}.

\subsection*{2.2.4. Equivalent Circuits}

It is a common practice to model electrochemical behavior in terms of an equivalent circuit composed by a number of single and/or sub-circuit elements. These models are, however, only our perception of the reality. The intention of using these models is not only to elucidate the physico-electrochemical properties of the system of interest but also to understand the mechanism in which the charge transfer processes take place. For example, (Figure 2.4) shows the well known Randle’s circuit which is often used to model the interfacial electrochemical reaction combined with a semi-infinite diffusion of electroactive species. From this circuit, the numerical values of the solution resistance, $R_s$, double layer capacitance, $C_{dl}$, charge transfer resistance, $R_{ct}$, and the diffusional impedance $Z_w$ can be determined.

\subsection*{2.3. Raman Spectroscopy}

Raman spectroscopy is an analytical technique based on the theory of light scattering effects established by Raman in 1928 \textsuperscript{15}. Although Raman spectroscopy was not a very popular research tool in the early days, it is now becoming more and more popular in the research areas such as pharmaceuticals, forensic sciences, nano-materials and semiconductors. Raman
spectroscopy is specifically used in this research in order to elucidate the doping level and structural information about the polymer chains.

2.3.1. Theory of Raman Spectroscopy

When incident light strikes a sample, it can be absorbed, reflected and/or scattered by the sample. The scattered wave can have the same frequency as the incident light (Rayleigh scattering) or may have a different wavelength than the incident light (Stokes and anti-Stokes Raman scattering) (Figure 2.5). In principle, Raman spectroscopy analyses the change in frequency between the incident light and scattered light to provide information about the vibrational motions of the sample. Due to the low quantity of scattered light compared to incident light (about $10^{-7}$ to $10^{-12}$ of the incident light) the sensitivity of Raman spectroscopy can be very low. However, there exists an advanced technique called Surface Enhanced Raman Spectroscopy (SERS) which can be used to enhance the signal on a roughened gold surface $^{16}$.

2.3.2. Raman Spectroscopy and Conducting Polymers

Conducting polymers exhibit a dramatic change in their optical and structural properties as a result of redox switching. These changes produce interesting electrochromic and electrical properties. A reduced polymer has a highly conjugated π-system in its backbone. When it is oxidized, the system is disrupted by the creation of solitons, polarons or bipolarons. Additionally, counterions are introduced into the polymer matrix for the purpose of counter-balancing newly created charges. The ability of the polymer to localize the charges over a few monomer units in the chain allows the polymer to undergo
structural changes that are energetically favorable, and these changes can be detected by Raman spectroscopy.

From the Raman data, critical information regarding the film thickness and doping level can be extracted. One of the most noticeable stretching bands in the Raman spectrum is that due to C=C. The stretching frequency of C=C assignable to an oxidized portion of the polymer chain is different (usually higher) from that of C=C belonging to a reduced portion. These stretching modes give rise to two different Raman bands. The intensity ratio of these two bands is correlated with the ratio of the oxidized to the reduced (neutral) forms of the polymer film. The thickness information can be gathered based on the idea that doping level increases with film thickness. Although the C=C stretching band is by and large the easiest to detect, other bands associated with the ring deformation as a response to the incorporation of the bipolarons could be analyzed for similar information.

Raman spectroscopy does not apply to conducting polymers without limitations. First, it widely acknowledged that conducting polymers are porous and sometimes inhomogeneous. As results, the data collected may not represent the composition of the entire sample. Furthermore, the thickness and structure of the film can be either disadvantageous or advantageous. If the film is too thick compared to the depth probed by the excitation beam (a few nanometers, depending on the wavelength of the probing laser and the absorption coefficient of the polymer), the data collected will only reflect the doping level in the outer layer of the film (which may be different from the doping level in the inner layer of
the film depending on the structure). If the film is too thin, the probing laser will also collect the surface features of underlying electrode. In such cases, the roughness of the electrode and the porosity of the film may lead to an enhancement effects which are reported to selectively enhance the bands associated with oxidized moieties of the film $^{19}$. This would lead to erroneous peak’s intensity ratios and hence misleading doping level and thickness.

To make the best use of Raman spectroscopy for the analysis of conducting polymers in this study, the laser wavelength was carefully chosen with respect to the thickness of the film. Comparing the data collected from different spots (including the back and the front of the sample) ensures the validity of the data.

2.4. Scanning Electron Microscope

The scanning electron microscope $^{20}$ (SEM) is a type of microscope that uses a highly energetic beam of electrons to generate morphological and topographical information of the specimen. SEM does not directly show the magnified true image of the specimen. Instead, it qualitatively generates an electronic map of the specimen which resembles the actual picture of the specimen and can be viewed on the monitor. SEM is particularly attractive in that it is nondestructive, fast, easy to use and yet sophisticated enough to reveal the surface features of the specimen (at the resolution of nanometers). It has been widely used to examine surface details of biological samples, semiconductors and interfaces. In this study, it is used to investigate the morphological features of the polymer films.
2.4.1. Theory of Scanning electron Microscopy

SEM is an instrument which operates under high vacuum condition to allow unhindered electron movement in the chamber and to avoid the electrical discharge in the gun. To generalize, the SEM image is generated in three main events. First a beam of electron is thermionically or field emitted from the emission gun (often a Tungsten filament or Tantalum hexaboride, LaB$_6$).

The following event is the acceleration and focusing of electron beam into a narrow beam with high intensity as it travels down the electron chamber. This process is accomplished by applying an acceleration voltage (up to 30kV) to the beam through a series of condenser lenses. The accelerating voltage and the beam diameter are important parameters for the resolution of the instrument.

When the beam strikes the specimen, the electrons interacts with the specimen’s atoms either elastically or inelastically to generate a beam of secondary electrons; a process known as backscattering. Different levels of backscattered electrons add collectively carry the specimen’s image information. The backscattered secondary electrons are then sent to the detector through a photomultiplier tube which enriches the signal. The signal is finally projected to the screen of the monitor. It should be noted here that the specimen should be conductive in order to avoid charging and appearance and brightened areas. Non-conductive specimens can be coated to render their surface conductive.
2.4.2. Usage of SEM to Investigate Conducting Polymers

One of the most sought-after pieces of information about conducting polymers is their morphological features. SEM generates the most morphological information (more backscattered electrons) at the fractures of the surface. Consequently, the porosity and inhomogeneity of the film may be easy to detect with high resolution. However, the concerns for using SEM to characterize conducting polymer is the requirement to dry the film. Electrochemically grown films may shrink upon drying and show smaller pores compared to pores which exist in the solution or cracks may be introduced.

2.5. Chronocoulometry

Chronocoulometry is an electrochemical technique method based on the Faraday’s fundamental laws of electrolysis. Practically, it involves the measurement of the charge as a function of time at a constant applied potential. Chronocoulometry has a range of applications from measurement of surface area, diffusion coefficient and electrodeposition of thin layers on solid substrate. Chronocoulometry was used in this research for monitoring the deposition of polymer films on the electrode.

2.5.1. Theory of Chronocoulometry

As noted, the theory of chronocoulometry is based on Faraday’s laws of electrolysis which states that the charge transferred can be summarized by equation (2.12)\(^\text{22}\).
where $Q$ is the charge consumed during the electrochemical experiment, $I$ is the current and $t_0$ and $t_1$ are the initial and final times respectively. In practice, the electrode is instantaneously ramped from a potential $E_1$, at which there is no electrochemical reaction, to a potential $E_2$ at which the reaction takes place. The potential is then held constant for a preset time of the experiment. The potential step induces the current flow which can be integrated according to equation (2.12). The charge passed is plotted as a function of time to generate a chronocoulogram.

### 2.5.2. Use of Chronocoulometry for Electrodeposition of Films

Chronocoulometry can be used to deposit and characterized adsorbed species. In this study, it was used to deposit the gold layer on the platinum electrode and to electropolymerize the polymer film onto the gold-coated platinum electrodes. This method allows the control the potential, which leads to a continuous oxidation and deposition of monomers to the electrodes. Assuming a linear relationship between the material and the charge consumed, the film thickness can be determined.

Like the potentiodynamic method described earlier, a potentiostatic deposition may lead to a potential drop across the film producing an applied voltage which is different at the outside layer of the electrode. This may alter the deposition mechanism.
2.1. Illustration of a typical 3-electrode, one compartment electrochemical cell
2.2. Illustration of a typical triangular potential waveform scan where $V_i$ is initial voltage, $V_f$ is final potential (switching potentials), $T_i$ is initial time, $T_f$ is final time. $T_f - T_i$ indicates the duration of an experiment. Redrawn from $^2$. 
2.3. Impedance data representation: A) Nyquist plots and representative equivalent circuit, B) Bode plot displaying the phase angle as function of frequency, C) Bode plot displaying impedance magnitude as a function of frequency.
2.4. The Randles circuit where $R_s$ is solution resistance, $C_{dl}$ is double layer capacitance, $R_{ct}$ is the charge transfer and $Z_w$ is diffusion hindered impedance.
2.5. The different possibilities of light scattering: Stokes scattering (molecule absorbs energy), Rayleigh (No observable Raman effect) and anti-Stokes scattering (molecule loses energy)
2.6. References


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(22) Strong, F. C. *Journal of Chemical Education* 1961, 38, 98.

(23) Ursula Rammelt¹, S. B., Mohamed El-Dessouki¹, Renate Schulze¹, Waldfried Plieth¹ and Lother Dunsch² *Journal of Solid State Electrochemistry* 1999, 3, 6.
CHAPTER 3

INVESTIGATION OF OHMIC BEHAVIOR IN PEDOT ELECTRODES

3.1. Poly(3,4-ethylenedioxythiphene)

Poly(3,4-ethylenedioxythiphene), PEDOT (Figure 3.1) is one of the most extensively studied conducting polymers. PEDOT has emerged as the most promising conducting polymer for practical applications. Examples of current and future prospective applications include chemical sensing, photovoltaic devices, battery and capacitors, actuator, etc. The success of PEDOT as a conducting polymer results in part, from its low band gap (~1.7eV), good conductivity and electrochemical stability.\(^1\) The electrochemical properties of PEDOT and its potential applications have been the subject of excellent reviews by Groenendaal et al.\(^2\) and Kirchmeyer et al.\(^3\).

EDOT monomer was first developed as a derivative of the thiophene monomer\(^4\). It was recognized that improved electrochemical stability and a smaller bandgap resulted from the attachment of electron donating groups to the ring\(^5\). In the case of EDOT, the derivatization takes place at 3,4 positions of the heterocyclic ring. Blocking the 3- and 4-positions on the ring by substitution with an ethylenedioxy group imparts improved regioregularity and effective formation of long polymer chains due to lower incidence of defects due to α,β-coupling. Furthermore, it helps improve the mechanical stability, and increases the conductivity (up to 600 S/ cm)\(^6\).

PEDOT has emerged as one the most promising conducting polymers for practical applications. Examples of current and future prospective applications
include chemical sensing, photovoltaic devices, battery and capacitors, actuator, etc. As noted in Chapter 1, however, the wide application of conducting polymers in the design of biomedical devices is still hindered by diffusion-governed impedance and high impedance in the physiologically relevant frequency range (this limitation is also known for other electrodes (Table 3.1). From (Table 3.1), it can be observed that the impedance is high and it exhibits frequency dependent behavior. This can be problematic for sensing applications as discussed earlier.

Table 3.1: A compilation of metal, semiconductor and conducting polymer electrodes investigated for sensing/stimulation applications by other groups

<table>
<thead>
<tr>
<th>Type of electrode</th>
<th>Working potential range</th>
<th>Impedance magnitude (Ohms)</th>
<th>Impedance magnitude/phase angle (at 1kHz)</th>
<th>Frequency window (Hz)</th>
<th>Comment/Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iridium Oxide (IrOx)</td>
<td>-0.6V-0.8V (Ag/AgCl)</td>
<td>$10^4$-$10^5$</td>
<td>~6x10^3 Ω/(25°)</td>
<td>10-10^5</td>
<td>7</td>
</tr>
<tr>
<td>Titanium Nitride (TiN)</td>
<td>-0.6V-0.8V (Ag/AgCl)</td>
<td>$10^4$-$10^5$</td>
<td>~1.5x10^4 Ω/(50°)</td>
<td>10-10^5</td>
<td>Data not shown above 100Hz. 7</td>
</tr>
<tr>
<td>PEDOT</td>
<td>-0.9-0.5V (SCE)</td>
<td>$10^4$-$10^5$</td>
<td>~10^4 Ω/(15°)</td>
<td>10–10^5</td>
<td>PEDOT/DCD PGYIGSR 8</td>
</tr>
<tr>
<td>Platinum (Pt)</td>
<td>-0.6V-0.8V (Ag/AgCl)</td>
<td>5x10^3-5x10^5</td>
<td>~5x10^3 Ω/(70°)</td>
<td>1-10^5</td>
<td>9</td>
</tr>
<tr>
<td>Sputtered IrOx</td>
<td>-0.6V-0.8V (Ag/AgCl)</td>
<td>$10^4$-$10^5$</td>
<td>~10^4 Ω/(10°)</td>
<td>0.05-10^5</td>
<td>Data depends on thickness 10</td>
</tr>
<tr>
<td>Activate Iridium Oxide (AIROF)</td>
<td>-0.6V-0.8V (Ag/AgCl)</td>
<td>$10^3$-$10^6$</td>
<td>10^3 Ω/(15°)</td>
<td>0.05-10^5</td>
<td>11</td>
</tr>
<tr>
<td>Electrodeposit d Iridium Oxide (EIROF)</td>
<td>-0.6V-0.8V (Ag/AgCl)</td>
<td>$10^3$-$10^7$</td>
<td>10^3 Ω/(10°)</td>
<td>0.05-10^5</td>
<td>11</td>
</tr>
</tbody>
</table>
In 2006, we reported non-diffusion governed impedance behavior for PEDOT bioelectrodes in the frequency range of 25Hz to 806 Hz\textsuperscript{12}, a range which spans that which is important for many biological signals. The purpose of the \textit{in vitro} studies reported herein was to develop an efficient and practical method to reproducibly electrosynthesize electrodes based on PEDOT that exhibit such ohmic behavior and to find polymerization conditions that extend that behavior to lower frequencies.

It is well known that the electrochemical characteristics of conducting polymers are influenced by a number of different electropolymerization parameters\textsuperscript{13}. We focus here on systematic exploration of the influence of electropolymerization parameters on deposition kinetics and their impact on the occurrence of ohmic behavior. These studies guide development of a model for conduction in these films which provides a direct connection between structure and function. Such a clear link between morphology and EIS behavior will allow prescreening of electrodes before carrying out \textit{in vivo} characterization, thus reducing the number of animal—or human—subjects required for comprehensive evaluation.

3.2. Basic Electropolymerization Mechanism

Electropolymerization of EDOT is regarded as mirroring that of other heterocycle polymers\textsuperscript{14} (Figure 1.5). In summary, electropolymerization is initiated by the oxidation at the surface of working electrode. The radical cation produced then diffuses back into the solution where it can react with an already formed cation or an intact monomer to form a neutral dimer or dimeric cation.
This cycle of reactions (oxidation followed by oligomerization) eventually leads to the formation of polymer films.

The growth mechanism of the electropolymerized films have been shown to follow three major pathways: two-dimensional nucleation, three-dimensional instantaneous growth, and three-dimensional progressive growth. In the case of PEDOT electropolymerized in presence of polystyrene sulfonate, contributions corresponding to three-dimensional instantaneous and progressive growths have been reported. It is believed that, after an induction period, the monomer first diffuses toward the electrode surface where it is oxidized into a radical cation. It then diffuses back into the solution where oligomerization takes place. A high density oligomeric layer forms in the vicinity of the electrode’s surface. Insoluble oligomers then precipitate on the electrode surface. This step-wise growth process can be extremely sensitive to reaction conditions.

Effects of reaction parameters such as temperature, monomer concentration, counterion identity, and solvent system must be considered and optimized in order to obtain the film with desired morphological, mechanical and electrochemical properties. For example, the monomer concentration can affect the diffusion of the monomer to the electrode. Similarly, the polarity or acidity and the dielectric constant of the solution medium are likely affect the reactivity of the radical cation.

### 3.3. Materials

Platinum (Puratronic grade) and silver (99.99%) wires, as well as hydrogen tetrachloraurate(III), were purchased from Alfa-Aesar. Sulfuric acid,
potassium chloride, potassium ferrocyanide, and acetonitrile (99.9%) were purchased from Fisher Scientific. The EDOT monomer, 3,4-ethylenedioxythiophene, was obtained from Aldrich. Tetrabutylammonium tetrafluoroborate, tetrabutylammonium hexafluorophosphate, poly(sodium 4-styrenesulfonate), p-toluene sulfonate (TS) and lithium perchlorate and Tetrabutylammonium perchlorate (electrochemical grade) were obtained from Fluka Chemika or Aldrich. Acetonitrile was dried over 4Å molecular sieve (Fisher Scientific) before use. All other chemicals were used without further purification. Adhesive polymer was obtained from Stan Rubenstein Associates (Foxboro, MA) or M.E. Taylor Engineering, Inc (Brookeville, MD). Non-porous polymer (TorrSeal®) was purchased from Varian Vacuum, Inc. Aqueous solutions were prepared using 18.3 MΩ water produced with a Millipore RIOS purification system.

3.4. Methods

3.4.1. Electrochemical Cell

All electrochemical reactions were carried out in a three-electrode, one-compartment glass electrochemical cell (Figure 2.1). The reference and auxiliary electrodes were Ag/AgCl (BAS RE5) and platinum wire, respectively. All deposition and electrochemical characterization studies were performed using a Radiometer PGZ402 instrument controlled by VoltaMaster 4 software. No ohmic compensation was applied.
3.4.2. Fabrication of Working Electrodes

The working electrodes (Figure 3.2) were fabricated by attaching a 250 μm diameter x 2 cm Pt wire to a 250 μm diameter x 10 cm Ag wire via conductive silver epoxy. The Ag/Pt junction area was housed in a short glass tube (approximately 8 cm long) and a nonporous polymer was applied at the exit of the working electrode from the glass tube to avoid any liquid contact with the junction. The conductive epoxy and masking polymer were each allowed to cure for 24 hours before proceeding with the next step.

3.4.3. Electrode Cleaning

Each substrate electrode was electrochemically cleaned to assure cleanliness of the surface and adhesion of the film, using the following sequence: -0.2 V in 5M NaOH for 15 minutes; 1.4 V for 10 minutes in 1 M H₂SO₄; 0.2 V for 30 seconds; twenty cycles between -0.2V to 1.2V in 1.0M H₂SO₄ at a scan rate of 100 mV/sec. The solution was purged with N₂ prior to, and blanketed with N₂ during, each step. The acid and base solutions were changed every after every five electrodes and each electrode was rinsed with deionized H₂O between steps.

3.4.4. Electroplating of Gold and Electrodeposition of PEDOT Film

In this investigation, a polycrystalline gold layer was electrodeposited before polymer deposition to improve film adhesion.¹⁶ The plating process was allowed to run for 1 min (until approximately 100 mC had passed) using a three-electrode electrochemical cell at a constant potential of 0.3V vs Ag/AgCl in 50mM HAuCl₄ prepared in 0.1 M NaCl. The solution was changed between every five
electrodes and was deaerated with N₂ prior to, and blanketed with N₂, during the plating process.

The PEDOT film was electrodeposited potentiostatically (1300mV vs Ag/AgCl) in acetonitrile solution containing different salts as background electrolyte (the anion of which acts as dopant) (Table 3.2). Electropolymerization time was varied between 30 seconds and 120 seconds to produce films of thickness 1.1-2.4 μm (as estimated by SEM and/or charge transferred during deposition). The concentration of the monomer (EDOT) and the identity and concentration of the dopant salts were varied between 0.05M and 0.5M. The films were characterized using impedance spectroscopy, cyclic voltammetry and Raman spectroscopy. “Near ohmic” impedance behavior (defined as the maximum range of frequency over which the impedance modulus was constant and/or the phase angle from electrochemical impedance spectroscopy was <2°) was the primary optimization criterion.

3.5. Characterization of the Film

3.5.1. Morphology Studies by SEM

Samples of polymer modified wire were cut and placed onto circular adhesive carbon films for affixing to aluminium sample stubs. The electron micrographs were collected using a Zeiss Ultra Plus Field Emission scanning electron microscope with an operating voltage ranging between 1- 5 kV. The images (Figure 3.3) were captured using the software SmartSEM Ultra Plus under ultrahigh vacuum conditions.
SEM images (Figure 3.3A-G) provide concrete evidence for the proposed morphological model (discussed in details Chapter 4). The variation of the film morphology as a function of film thickness is confirmed by SEM images (Figure 3.3.A, B, and C). Figure 3.3.A and 3.3.B show the beginning of nucleation (7 seconds) and the outer surface of the film which has been electropolymerized for 30 seconds respectively. It is obvious that the initial nucleation sites start coalescing and forming compact structures. The film made for 30 seconds exhibits a more compact structure and a smoother morphology compared to that of the film electropolymerized for 90 seconds (Figure 3.3.C). The sample electrodes were either electropolymerized from the same electrochemical cell (without changing the monomer solution and background electrolyte) or from two different cells (using fresh monomer and background electrolyte for each run). It can be argued that the presence of oligomers in solution (formed during the first run) will affect the electropolymerization and the morphology of the second run. Interchanging the order of electropolymerization (longer times first and shorter times second or vice versa) showed that longer electropolymerization time produces more porous film than shorter electropolymerization time regardless of the order of electropolymerization.

The increase of film’s porosity as a function of thickness is also illustrated in Figure 3.3.D. The electrode was electropolymerized by partially immersing the wire in the electropolymerization solution and raising a part of it above the solution after 45 seconds. The bottom portion of the electrode is left in the solution to allow additional polymerization for 75 seconds. It can be observed
that this portion is much more porous than the top portion and the structure seems more compact near the underlying metal substrate.

The compact nature of the sample film at the metal|film interface is clearly shown (Figure 3.3.E and Figure 3.3.F). Figure 3.3.E shows the underlying metal, the film’s cross section and the outer surface. While the gradual change in the film’s morphology is not visibly clear from the cross-section, the outer surface area is clearly much more porous from than the inner layers. The two layer morphology of the film is nicely illustrated by Figure 3.3.F. The sample film was mechanically pulled off the electrode in order to look at the side of the film which is attached to the electrode. It can be observed that the metal|film surface is compact and smooth. The gaps where the film adhered to the surface of the electrode show that the film is porous towards the outside (shown by circles).

This two layer morphology, which is proposed to be the origin of the observed ohmic behavior, is further supported by the film of PEDOT/PSS⁻ (Figure 3.3.G). Zooming in on a crack and looking at the film’s surface shows that, unlike PEDOT/BF₄⁻ films, the film is homogeneously compact. Its outer surface can be described as rough instead of porous. The morphological model, as suggested by these images is in congruence with the resulting impedance data. While PEDOT/BF₄⁻ exhibit ohmic behavior, PEDOT/PSS⁻ lacks an ohmic signature in the region of interest.
3.5.2. Raman Spectroscopy

Raman measurements were carried out employing a Renishaw Ramascope instrument equipped with a 25 mW 785 nm laser (SpectraPhysics), a Rayleigh filter and a 1200 line/mm grating and interfaced to an Olympus BH-2 microscope. Data acquisition was controlled using Wire 2.0 software. Peak areas used for determination of doping level were based on the deconvoluted areas reported by the Wire 2.0 software.

Raman spectroscopy has been used to estimate the doping level achieved within the films as described elsewhere in detail \(^{17,18}\). The samples were analyzed under ambient conditions without any special pre-preparation. (Figure 3.4) presents a comparison of Raman spectra of PEDOT electrodes doped with different counterions. The peaks assignable to PEDOT for each PEDOT/X\(^-\) sample (where X\(^-\) is the counterion) given in (Table 3.2) and are compared with literature values for the peaks\(^{18}\). All electrodes investigated show structural vibration modes typical for PEDOT \(^{18}\). The maximum of the C\(_\alpha\)=C\(_\beta\) absorption band resulting from the doped, oxidized polymer is located at 1432 cm\(^{-1}\). The shoulder which appears at about 1412 cm\(^{-1}\) has been assigned to the asymmetric vibration of C\(_\alpha\)=C\(_\beta\) associated with the neutral (reduced) form \(^{18}\). The natural logarithm of the integrated intensity ratio of these peaks (\(I=I_{1412cm^{-1}}/I_{1432cm^{-1}}\)) was used to estimate the doping level (in %), \(y\), based on the equation (3.1) \(^{18}\).

\[
I = 0.087y - 2.279
\]  

(3.1)
**Table 3.2:** Doping level (%) of PEDOT polymers in this study

<table>
<thead>
<tr>
<th>Counterion</th>
<th>Estimated doping level (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrafluoroborate (BF₄⁻)</td>
<td>35.2</td>
</tr>
<tr>
<td>Hexafluorophosphate (PF₆⁻)</td>
<td>31.6</td>
</tr>
<tr>
<td>Polystyrene sulfonate (PSS⁻)</td>
<td>26.1</td>
</tr>
<tr>
<td>Perchlorate (ClO₄⁻)</td>
<td>31.3</td>
</tr>
<tr>
<td>p-toluene sulfonate (Ts⁻)</td>
<td>28.4</td>
</tr>
</tbody>
</table>

### 3.5.3. Cyclic Voltammetry

Cyclic voltammetry (CV) was performed on samples of electrode before and after EIS experiments. All experiments were conducted in the electrochemical cell described above. The potentiostat used to control the voltage was Radiometer PGZ402 instrument controlled by VoltaMaster 4 software. No ohmic compensation has been applied. The voltammograms were recorded in a solution containing 0.01 M Fe(CN)$_6^{3/-4}$ / 0.1 M KCl (Figure 3.5).

Cyclic voltammetry (CV) was used to investigate stability and to screen for the possibility of overoxidation of PEDOT films. Such overoxidation has been reported to result in production of sulfoxide moieties in the film and a decrease in conductivity and stability$^{1,19}$. If present, evidence for overoxidation would appear as large (>57 mV) peak separation in the CV of a reversible redox probe. Electrodes prepared as described above exhibited reversible electrochemical behavior for ferricyanide before and after EIS experiments. (Figure 3.5) shows a
CV of PEDOT/BF$_4^-$ in 0.01 M Fe(CN)$_6^{3-/4-}$ / 0.1 M KCl. It can be seen that the electrode has a relatively narrow (82 mV) peak separation, and the voltammograms exhibit steady state behavior beginning with the second scan. We attribute the capacitive current background to double layer charging. Stability of the film was verified by monitoring charge transferred during the anodic and cathodic processes for the electrode in background electrolyte, and no decrease was observed.

3.5.4. Impedance Spectroscopy

Impedance spectra were measured in the frequency range 100 KHz–100 mHz using a Radiometer PGZ402 instrument controlled by VoltaMaster 4 software. All experiments were carried out in a three-electrode cell described above and reference and counter electrodes were Ag/AgCl and Pt wire respectively. All of the figures (Figure 3.6-3.8) were obtained by transferring and analyzing the data using the computer program, ZView v3.1, purchased from Scribner Associates Inc.

3.6. Discussion

3.6.1. Effect of Deposition Time

It was observed that the film porosity increases with electrodeposition time. As seen in (Figure 3.3), at 0.0125M monomer concentration and potentials below the overoxidation potential for the polymer, a smooth, compact layer is formed during the initial stages of electropolymerization. This is confirmed by the compact and smooth morphology of the face of the film which is in contact with
the metal substrate (Figure 3.3A). The morphological features start to appear and the film eventually gets more porous as the electrodeposition time increases (Figure 3.3B and 3.3C). A more porous structure forms on the top of the initial compact layer after. Consequently, the film can be macroscopically envisioned as a two-layer structure. These results are in agreement with previous reports which have shown that polymers often grow into morphologically different layers.\(^2\)

In theory, the longer deposition times should result in a thicker porous layer. However, as more polymer is deposited on the outer layer, it is possible that the monomer and oligomers penetrate or get trapped within the inner layer, subsequently polymerizing to fill in the inner-most pores. In this case, a proportional growth of the compact layer and porous layer would occur, leading to the same impedance behavior.

The optimum deposition time is guided by the balance between achieving ohmic behavior within a wider frequency and achieving good mechanical properties of the film. While a shorter deposition time under 30 seconds results in a film which exhibits largely capacitive impedance, \(C=40\mu F/cm^2\) at 0.1 Hz), the deposition time over 120 seconds (ca 150 sec) results in thick, porous and brittle films. The fragility of the film may be caused by large voids (gaps between polymer strands) that may form, essentially isolating some polymer chains from the actual film. The capacitive behavior of the thinner film (electropolymerization time less than 30 seconds) is consistent with what would be expected when the porous layer is absent in which case the surface would be considered as rough
instead of porous. It is also possible that short polymerization time lead to incomplete coverage of the film, thus exposing the underlying substrate. Assuming that the compact layer exhibits good electronic conductivity and spatially limited ionic diffusion, impedance of very thin film would be mainly determined by the double layer capacitance. As it will be discussed in the next chapter, this double layer capacitance does not exist in thicker film exhibiting a two-layer morphology.

(Figure 3.6) compares the Bode plots of electrodes produced using different deposition times. It is obvious that the ohmic resistance is almost the same (see $|Z|$ values) in the high, intermediate, and moderately low frequency ranges. However, it is also observed that impedance of thinner film (short electropolymerization time) deviates from ohmic behavior before that of thicker films does. Thin films exhibit higher capacitance at low frequency than thick film as a consequence their smooth morphology. As will be discussed later, ohmic behavior can be attributed to the presence of the porous layer which allows an increased ionic penetration depth. In case of its absence (thin film), microporosity of the film leads to high double capacitance contribution at medium and low frequency range.

3.6.2. Effect of Dopant Identity

(Figure 3.9) shows the impedance magnitude, $|Z|$ of PEDOT electrodes doped with $\text{ClO}_4^-$, $\text{PSS}^-$, $\text{BF}_4^-$, $\text{Ts}^-$ and $\text{PF}_6^-$ as a function of frequency. PEDOT/PSS$^-$ electrodes clearly exhibit the highest impedance. Though the impedances of other three electrodes are more comparable in magnitude,
PEDOT/BF$_4^-$ is clearly distinguished by slightly lower impedance magnitude and frequency-independent behavior over a broader frequency range. It is observed that PEDOT prepared as described above with smaller anionic background electrolytes than PSS$^-$, or even its monomer $p$-toluene sulfonate, exhibit near ohmic behavior at frequencies as low as 10 Hz or less, which is unusual for polymer-modified electrodes. These effects can be attributed to the size of anion. Smaller counterions seem to be best for producing the desired morphology which leads to ohmic behavior. From (Figure 3.3) it can be observed that PSS$^-$ leads to a much smoother morphology which lacks the porous layer; thus explaining the absence of ohmic behavior in PEDOT/PSS$^-$ electrodes.

The range over which the impedance was frequency independent for the PEDOT/BF$_4^-$ electrodes was, as described below, a function of electrodeposition parameters. However, when fabricated using the optimal conditions, a typical batch of ten electrodes exhibited constant, almost resistive impedances (phase angle < $\pm 2^0$) over the frequency range which extended from 8-30 Hz on the lower end to an upper limit of 80-100 KHz.

### 3.6.3. Effect of Dopant Concentration

With increased solution conductivity, the rate of nucleation and growth of the film on the electrode surface is likely to be faster, leading to a less structured compact layer containing random polymer aggregates and increasing the $|Z|$ value as seen in (Figure 3.7). The anions have also been implicated in inhibition effects on the oxidation of the monomer onto the electrode surface when monomer concentration is too much lower than that of the dopants $^{22}$. Blocking
the nucleation sites could result in a less structured first layer and inhomogeneous growth leading to high impedance. An alternative interpretation of this high impedance hinges on the ionic and electronic (or $h^+$) charge carrier interaction (within the film). It is generally agreed that anions can act as binding sites which immobilize the charge carriers with opposite charge $^{23}$.

Although increasing the concentration of dopants in the solution does not translate into the incorporation of counterions in the film under normal circumstances, some counterions may be trapped in the compact layer. These would hinder the hopping of positive charge from one site to the neighboring site. This is consistent with the slightly increased electronic resistance assignable to hole/electron transport in the compact layer (see Chapter 5). Furthermore, the inclusion of more counterions would be expected to contribute to structural deformation, particularly in the t-layer (compact layer), and lead to limited inter-chain transport and observable diffusion transport. Therefore, the suggested explanation of higher impedance under higher counterion concentration is primarily based on the contributions of the counterion’s effects on the disruption of the compact layer and associated hindered electronic transport.

### 3.6.4. Effect of Monomer Concentration

Higher concentrations of the monomer should lead to faster development of the high density oligomeric region and hence a faster initial polymer deposition rates at the surface of the electrode. This faster deposition rate would be expected to result in a less ordered and less compact layer adjacent to the surface of an electrode for a given total charge passed (in other words, would
decrease the compact layer thickness). While crystalline regions are highly conductive, the disordered regions will act as insulator islands due both to absence of $\pi$ wave function overlap. Eventually, charge carriers would experience more resistance while moving from one crystalline region to another because they have to overcome the resistance caused by amorphous regions and chain imperfections. The impedance also would increase not only because this layer is no longer blocking to the electrolyte, but also this more porous layer would be characterized by smaller non-interconnected pores. Furthermore, in such a model, the influence of ionic diffusion is more pronounced.

This is supported by our experimental results shown in (Figure 3.8). It can be observed that impedance of the polymers increases as the concentration of the monomer is increased. This can be attributed to the disorder introduced during the fast polymerization. It is also important to highlight the fact that at very low frequency, all films made at different concentrations seem to exhibit the same low capacitive frequency impedance behavior. These observations suggest that the charging mechanism is the same for these films: It is largely dominated by the double layer charging which takes place inside the pores of the film.

Although the increase in impedance magnitude as a response to the an increased monomer concentration is not as significant as in the case of electrodes produced at higher counterion concentration, these conditions (low monomer concentration) slightly shorten the frequency range within which ohmic behavior is observed. Electrodes prepared using a lower monomer concentration
(0.0125 M EDOT), on the other hand, exhibit lower impedance and ohmic behavior within a larger frequency range.

3.7. Conclusion

The goal of this study was to fabricate electrodes modified with a conducting polymer (in this case PEDOT) that will behave ohmically in the range of frequencies relevant to biosensing and to do so reproducibly. The conditions have been determined for consistent production of these films employing potentiostatic deposition at 1.3 V for 60-120 s. The optimum concentration of the monomer is 0.0125 M and that of the counter ion is 0.1M. It appears that these settings produce ohmic behavior over a wider frequency range. EIS data indicate that Ohmic behavior is consistently achieved under these conditions from around 10 Hz to 100 kHz. This behavior is confirmed by a near zero phase angle for the points in this range. Results suggest that observed ohmic behavior is a result of special morphology which is discussed in details in Chapter 4.
3.1. Chemical representation of PEDOT
3.2. Illustration of the working electrode used in this study.
3.3. SEM images showing external morphology of PEDOT/BF$_4^-$ film electropolymerized for 7s (A), 30s (B), 90s (C) and 45 and 120s (D). (E) shows the cross-section of PEDOT/BF$_4^-$ and (F) shows the polymer morphology at the metal/polymer interface and (F) shows the morphology of PEDOT/PSS$^-$.
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3.9. Bode plot for electrodes prepared with varying counterions: (a) poly(styrene sulfonate), (b) p-toluene sulfonate (c) hexafluorophosphate; (d) perchlorate; (e) tetrafluoroborate.

Inset shows impedance behavior at low frequency.
3.8. References


(12) Ovadia, M.; Zavitz, D. H.; Rubinson, J. F.; Park, D.; Chou, H. A. 


CHAPTER 4

ELECTROCHEMICAL MODEL AND EQUIVALENT CIRCUIT

4.1. Introduction to Impedance Modeling

As previously stated, a conducting polymer modified electrode, CPME, can be defined as an asymmetric heterogeneous system where the polymer film intercalates between the metal electrode and electrolyte solution. As such, there exist two interfaces (solution|film and film|solution) which act as transition regions between adjacent materials. The properties of these interfaces are not defined by the bulk properties of the metal electrode or polymer (at the metal|polymer interface) or by the bulk properties of the polymer or solution (at the polymer|electrolyte interface). Consequently, the impedance behavior of a modified electrode can be treated as a complex additive function that depends not only on bulk properties of each constituent but also on interfacial properties. Analysis of impedance data should reveal critical information about the transfer function that dominates the charge transport processes occurring in CPMEs. Due to the complexity of the film, however, this is an area that is still open for discussion.

The use of electrochemical impedance spectroscopy and equivalent circuit models has been the most extensively used approach for elucidating the contribution of the different possible charge transport processes in CPMEs. Equivalent circuits are assembled by connecting theoretical electrical elements which can best fit experimental impedance data within a wide range of frequency. The accuracy of the model (goodness of fit) can be judged from the value of the
Chi-square function, $\chi^2$ (the square of the standard deviation between theoretical and experimental spectrum). Alternatively, the Weighted Sum of Squares, $\Delta^2$ can be used to provide the average percentage error between the individual experimental and theoretical data.

Development of an equivalent circuit allows the separation and discrimination between these contributions. Often, the contributions of these process changes depending on the frequency range, or ranges, studied. For example, while the total impedance is an average of ionic and electronic impedances, in the case of CPMEs, the contributions of each can be quantitatively determined from the values attributed to their circuit analogs used in the model. Assuming that each element in the circuit represents a real process, the correct model helps both to understand and to visualize how physical and electrochemical properties of CPMEs all act in concert to influence the charging and discharging behavior of electrodeposited polymer layers. Furthermore, the circuit models may allow the prediction and simulation of the system’s behavior under conditions that are not necessarily experimentally accessible.

4.2. Difficulties in Developing Models for Conducting Polymer

Although electrochemical impedance modeling is a generally accepted, powerful method, complexity of CPME imposes challenges and limitations on its applicability in this area. The challenge in developing models which are consistent with experimental data is complicated by several factors.
First, it is possible for two different models to produce the same impedance response. Second, the overall impedance expressions corresponding to most models give little or no direct information about the physical meaning of the elements for such models. That is, it may be possible to propose a model that includes multiple capacitors and resistors, but this does not imply that it is facile to draw a parallel to a physical or an electrochemical characteristic. This makes it imperative that one must have a clear understanding of the system’s electrochemical properties in order to critically evaluate the applicability of the circuit which best fits the data and the polymer system under investigation.

It can be argued that the morphology of the film is the corner piece in the puzzle yet to be solved in order to unambiguously understand the electrochemical nature of CPMEs, but the treatment of morphology remains a controversial area in the description of the properties of CPMEs. For example, it is becoming increasingly accepted that charge transport within the film and macroscopic properties largely depend on the film texture and morphology. However, some authors describe the morphological structure of the polymer film as rod-shaped fibrils while others describe it as a collection of solid polymer aggregates enclosing pores with poor interconnectivity between the aggregates. Consequently, starting with the right morphology is an important step in developing the correct model. The choice of morphology imposes boundary conditions which may result in a circuit model that is either too complex—containing multiple elements, often with little relevance to real processes—or overly simple—based on simplified formalisms that apply only under such very
specific, limited experimental conditions, that it overlooks plausible electrochemical processes.

Another layer of complexity arises from the inability to trace the charge carrier’s path within the film (i.e. lack of detailed understanding the order in which charge transport takes place in the film). This is demonstrated by the controversial debate about how representative circuit elements should be connected. For example, the ionic resistance in the film bulk is presented in parallel with electronic resistance by some authors\textsuperscript{8} while the series arrangement is preferred by others\textsuperscript{6}. The connectivity is particularly informative for interfacial and bulk impedance contributions from slow charge transfer processes, especially at low frequency\textsuperscript{9}. In this chapter, we report the equivalent circuit model which fits the PEDOT impedance data reported in the previous chapter (Chapter 3). The model not only explains the data over a wider range of frequency (0.1Hz-100 kHz) for PEDOT, but it also can be successfully applied to other polyheterolene systems which exhibit impedance behavior similar to that for PEDOT.

4.3. Brief Overview of Prominent Equivalent Circuit Models

The simplest electrochemical model, which has been often applied to CPMEs, is that of Ho et al.\textsuperscript{10}. Initially developed for Li intercalation in WO\textsubscript{3} electrodes, this model provides a fair interpretation of impedance behavior for a thin homogeneous polymer film within which diffusion of counterions is allowed. This model, also proposed by Glarum et al.\textsuperscript{11}, is a modification of the Randles model (Figure 2.4), which applies to most inert electrode systems. It should be
emphasized at the point that the Randles circuit can only be used to describe a non-distributed system. As such, this modified version must replace the concentration-hindered impedance by the finite diffusional Warburg impedance, $Z_w$. In this situation, $C_{dl}$ stands the double layer capacitance, $R_{ct}$ accounts for the charge transfer resistance and $Z_w$ describes diffusional impedance of the film. The total impedance function is then calculated using equation 4.1.

$$Z_{tot} = \left( \frac{1}{Z_w + R_{ct}} + i\omega C_{dl} \right)^{-1}$$

In this equation, $Z_w$ describes the Warburg impedance, $C_{dl}$ is the double layer capacitance and $R_{ct}$ is the charge transfer resistance.

Ho’s model provides the justification of frequency dependence of diffusion and the capacitive impedance behavior often observed in the intermediate and low frequency ranges respectively, but it fails to provide their microscopic origins. The diffusional behavior is modeled by the Warburg element, and it does apply to thicker and porous films in which morphological details have to be necessarily considered. For example, Popkirov shows that Ho’s model nicely fits impedance data of polybithiophene thin films. For thicker films, however, a different model that takes into account the porosity and inherent morphological complexity of the film was required.

The work of de Levie for cylindrical pores has provided the basis for a number of seminal models applicable to porous electrodes. Paasch et al. proposed a model based on the concept of a macroscopically homogeneous porous film where distributed double layer charging and diffusion kinetics throughout the film dominate impedance behavior. The model was successfully
applied for modeling the impedance of thick polybithiophene films whose impedance data could not be fit by the Ho’s model \(^{12}\). The model assumes a film matrix in which interconnected electronic (in the solid phase) and ionic (in the liquid phase) conduction rails concomitantly exist. Theoretically, this model can be envisioned as an extension of Ho’s model in that it assumes a film composed of sub-layers to which the simple model of Ho applies. Assumption of homogeneous film structure, however, may be a limiting oversimplification.

A more advanced model was proposed and continuously refined by Albery and co-workers \(^{15-19}\). This model includes several more aspects of conducting polymers (Figure 4.1). This model is based on a dual transmission line model incorporating ionic and electronic resistances rails connected in parallel with a capacitance, \(C_p\). Limiting cases of the model include treatment of cases where ionic and electronic species have different mobilities. Two fundamental assumptions raise concerns about the applicability of the model in the cases of complex morphologies: the assumption of a homogeneous film and the assumption of Donnan exclusion. This last would only be valid for a fully oxidized film. It is known that the film may simultaneously exhibit reduced and oxidized domains. Additionally the types of ions incorporated in the film will affect its morphology. As a result, attempts to remove Donnan assumption from the model forced the authors to deliberately ignore the ionic resistance for mathematical simplicity.

A more generalized model based on the concept of porous electrodes was proposed by Fletcher et al.\(^{9,20}\), (Figure 4.2). This model resembles that of Albery.
but it replaces the simple elements of the transmission line by the network of resistors and capacitors. $Z$, $Y$ and $X$ to account for the charge transport processes occurring in the solid film, in the pores at the film|liquid interface, and in the solution inside the pore channels, respectively. This circuit is highly adaptable and can exhibit a wide range of impedance behaviors depending on the substituting elements for each network, their values and their connectivity and length. The model is, however, built upon a number of, perhaps, unlikely theoretical constructs such as identical, non-interconnected pores of uniform cross section and interfacial impedance (pore|electrolyte) which is independent of distance inside the pore. The authors acknowledge the simplicity of the model, but it fit surprisingly well the impedance data of polypyrrole\textsuperscript{9}.

By far, the transmission line model and its variations have been the most used models to date for explanation of the electrochemical impedance behavior of CPMEs. Theoretically, the dual transmission model is an attractive model because it succeeds in the usage of only lumped elements (resistors and capacitors) to model complex electrochemical behavior which was ambiguously modeled by the Warburg elements in the past. However, it is worth pointing out once again that there will always be fundamental assumptions in any model leaving the room for valid arguments about whether it adequately represents the electrochemical processes occurring within a particular film, especially in the low frequency range. Although the models proposed to date add a great deal of value to the current knowledge of conducting polymer, a unified concept of the model that applied to a wide range of experimental conditions is still lacking. The
practical implication of this gap, in many cases, is the necessity to develop new, unique models applicable to the system under investigation.

The next few sections summarize a new model proposed in our laboratory and provide experimental evidence for its applicability to the conducting polymer, poly(3,4-ethylenedioxythiophene) or PEDOT. From the modeling viewpoint, this new approach extends the dual transmission model in order to capture the key features of our morphological model depicted in (Figure 4.3).

4.4. Basic Equations and Theoretical Assumptions of Proposed Model

The system considered herein is a film of thickness $d$. The solution|film interface is located at the distance $d=L$. The metal|film interface is located at $d=0$. The electrode is assumed to consist of two structurally different layers. The outer layer (of thickness $x$) is porous and has a network of interconnected pores “flooded” by electrolyte solution. Its inner layer (of thickness $t$) is compact and is assumed to be inaccessible to the electrolyte solution. The model considers the dual conductivity of the film, and the total current flowing through the external circuit is $I_{\text{total}}$ defined by equation (4.2).

$$I_{\text{total}} = i_i + i_e$$ (4.2)

where $i_i$ and $i_e$ are ionic and electronic current respectively. It is further assumed that either $i_i$ or $i_e$ can increase or decrease at any given position in the film but equation (4.2) must hold everywhere in the film (Figure 4.1).

Theoretically, the total impedance response of an ordinary CPME to the imposition of small potential perturbation, $V(i\omega)$ can be obtained from equation (4.3).
In equation (4.3), \( R_s \), \( Z_{mf} \), \( Z_f \), \( Z_{ms} \) denote solution resistance, metal|film interfacial impedance, film impedance and film|solution interfacial impedance, respectively. This expression (equation (4.3)) accounts for any possible charge transfer and charging across both interfaces (metal|film and film|solution), charge transport and charging within the film, and charge transport within the electrolyte medium. Obviously, the challenge is to define a value for each of the variables of equation (4.2). Despite the complexity of its analytical solution, some simplifications can be made by imposing boundary conditions that apply to the proposed morphology. It is advantageous, at this juncture, to treat each term in equation (4.2) separately and reduce it according to the boundary conditions imposed by the proposed morphological model.

### 4.4.1. Contribution of the Solution, \( R_\Omega \) to the Total Impedance

The solution resistance can be defined as the barrier to the flow of current in the solution medium. Suppose a pair of working and auxiliary electrodes is immersed in an electrolyte with the conductivity \( \sigma \). The two electrodes are separated by a distance \( d \) and the working electrode has a radius \( a \) and a length \( l \). The ohmic resistance between them can be calculated from equation (4.4) \(^{21}\).

\[
R_\Omega = (\pi \sigma l)^{-1} \ln \frac{d}{a} \tag{4.4}
\]

Its contribution to the total impedance of CPME is a simple ohmic resistance, \( R_\Omega \) which has a numerical value that can be experimentally determined from the impedance data as the high frequency real axis intercept in the Nyquist
representation. It is important to restate that the above expression pertains to the solution resistance in the bulk electrolyte.

4.4.2. Contribution of Metal|film Impedance, $Z_{mf}$ to the Total Impedance

The metal|film interface under zero-bias potential reaches equilibrium by way of rapid faradaic processes. At equilibrium, the magnitude of equilibrium exchange current density, $J_0$ is given by the Tafel equation equation (4.5).

$$J_0 = F k_c C_A \frac{(\alpha F \Delta E_o)}{R T}$$  \hspace{1cm} (4.5)

In this equation, $F$ is Faraday’s constant $k_c$ is exchange reaction rate constant; $C_A$ is the concentration of electron acceptor sites at the plane of the interface, $\alpha$ is the symmetry factor $\Delta E^0$ is the equilibrium potential, $R$ is the gas constant and $T$ is the temperature $^{22}$.

According to the Bulter-Volmer equation (ignoring mass-transport), the current $J$ is related to the current density by equation (4.6). $^{23}$.

$$J = J_0 \left[ e^{\frac{-\alpha F \Delta E}{R T}} - e^{\frac{(1-\alpha) F \Delta E}{R T}} \right]$$ \hspace{1cm} (4.6)

For a small applied overpotential Equation (4.6) reduces to Equation (4.7)

$$J = \frac{-J_0 F \Delta E}{R T}$$ \hspace{1cm} (4.7)

Equation (4.7) shows that the net current resulting from an applied overpotential is linearly related to the applied overpotential. As such, it can be treated in manner analogous to Ohm’s law. This equation allows us to define the charge transfer resistance characteristic of the interface, equation (4.8)
This charge transfer resistance, \( R_{ct} \), accounts for the interfacial resistance experienced by charge carriers crossing it. \( R_{ct} \) can be experimentally determined from the impedance spectrum as the diameter of the high frequency semi-circle. In many cases however, the semi-circle is not fully developed if other interfacial processes are involved.

In principle, this interface may be rectifying depending on the offset between the Fermi energy level of the underlying metal substrate and the LUMO level in the polymer. In such a case, the capacitance of the depleted region of the Schottky contact can be defined by equation (4.9).

\[
C = \left( \frac{\varepsilon \varepsilon_0}{2} \right) \frac{1}{t} \left( E - \Phi_{fb} - \frac{kT}{e} \right)^{-\frac{1}{2}} \quad (4.9)
\]

Where \( \varepsilon \) is the dielectric constant, \( \varepsilon_0 \) is the permittivity in vacuum, \( E \) is the applied voltage, \( \Phi_{fb} \) is the flat band potential, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature in Kelvin, and \( e \) is the elementary charge. It can be observed from equation (4.9) that the capacitance will display a dependence on the applied potential.

A Schottky contact results in band bending and interfacial charging which introduces a capacitive component. As a result, the metal|film interface would have to be modeled by this \( R_{ct} \) and \( C \) connected in parallel. The interfacial impedance of the \( RC \) branch is given by equation (4.10):
\[ Z_{i\omega} = \frac{R_{ct}}{1+i\omega R_{ct} C} \]  \hspace{1cm} (4.10)

where \( C \) is the interfacial capacitance, \( \omega \) is the angular frequency and \( R_{ct} \) is the parallel charge transfer resistor (equation (4.8)). In ideal conditions, three diagnostic frequency values can be deduced from equation (4.10): \( \omega = 0, \frac{1}{\omega R_{ct} C} \) and \( \omega = \infty \). In such cases, the impedance will be \( R_{ct}, \frac{R_{ct}}{2} \) and 0 respectively. This trend highlights the frequency dependence of this interfacial impedance.

Since there is no indication of Schottky contact in our system, an ohmic interfacial contact between the metal and the film is assumed. This assumption is primarily based on the usage of high work function metals (Pt or Au) compared to the lower Fermi level of the film (normally 4.7-5.4 eV)\(^{24,25}\). For an ohmic contact, the net thermodynamic equilibrium current density is expected to be zero because the carrier flux across the interface in one direction is equal to that in opposite direction.

Kinetic consideration of a small amplitude perturbation signal suggests two possibilities for charge carriers to cross the interface without hindrance of potential barrier heights: 1) If the barrier height is small, the majority charge carriers will hop over it. Alternatively, 2) if the depletion layer is highly condensed at the edge and is narrow, the majority carriers will cross the interface by tunneling through it. Furthermore, it is expected that the face of the film contacting the metal will be rich in surface states due to surface imperfections and roughness resulting from electroplating. These combined effects will enhance ohmicity at the interface. Consequently, the contribution of metal|film interfacial impedance to the overall impedance will be a simple ohmic resistance.
The current injection at the film|metal interface results in the faradaic current that can be defined based on the applied potential and equation (4.8) (assuming ohmicity conditions apply).

If this interface is treated as being transparent to the charge carriers, it can be confidently omitted from the overall circuit. It has been proposed that when the film's electronic conductivity is greater than its ionic conductivity, the exchange reaction takes place at the polymer|solution interface 26. This supports the omission of the metal|film interfacial resistance because when the film is oxidized (conducting), the carrier exchange would place at the junction of x-compact layer and t-porous layer of the film. Carriers would then propagate toward the underlying substrate. In view of our model, the outer structure which is permissible to electrolyte species suggest that the “polymer|solution” interface is distributed throughout the porous layer. As such, the exchange process and double layer charging would take place along the pores and near the x-layer|t-layer interface. This is summarized in (Figure 4.4). The subsequent section will focus on how charge carriers are transported within the film.

4.4.3. Contribution of the Film to the Total Impedance

The boundary conditions proposed herein flow from the recognition that the film contacts an electronic conductor (the metal) on one side, and an ionic conductor (the electrolyte solution) on the other. These have important implications on the equilibrium current density and the impedance of the film, especially in the case of the two-layer morphology proposed herein. It follows that only electronic charge exchange is possible at the metal|film interface while
ionic exchange takes place at the film|solution interface. We consider the
collection of electronic and ionic carrier contribution through transport and
charging (Figure 4.4c) within the film in the next two sections.

4.4.3.1. Impedance of the Porous Layer

At thermodynamic equilibrium, the pore channels of the porous layer are
“flooded” with the electrolyte solution and equilibrium current is reached. It is
assumed that this condition holds for the porous layer of the film while the
compact layer remains “solution-free”. Based on this arrangement, the ionic
contribution in the porous layer can be analyzed in view of the generic
transmission line model (Figure 4.1). The impedance of a porous film in contact
with a solution containing no electro-active species will behave like a finite-length
transmission line. It is analogous to a response of a wave diffusing within a
network of distributed RC circuitry. Specifically, the transmission line is
represented by ionic and electronic parallel rails coupled through capacitive
elements. If we ignore the capacitive charging for the moment (and come back to
it later in section 4.4.4) the impedance of parallel ionic and electronic rails per
unit of volume can be defined by equation (4.11).

\[
\frac{1}{R_{tr}} = \frac{1}{R_i} + \frac{1}{R_e}
\]  \hspace{1cm} (4.11)

where \( R_{tr} \) is the total resistance, \( R_i \) and \( R_e \) are ionic and electronic resistances.
Assuming that \( R_e >> R_i \) in the porous layer, \( R_e \) element acts as an open circuit
making its contribution to the total transport resistance negligible. As a result, the
contribution of \( R_e \) in the porous layer will be omitted for simplicity. To put the
matter into perspective, $R_i$ will be treated as the only contributor to the $R_{tr}$ in the porous layer.

$R_i$ can be alternatively regarded as the equivalent ohmic resistance of microhomogeneously distributed $r_i$ (resistance per unit length in $\Omega \cdot m^{-1}$) along the ionic rail spanning throughout the porous layer thickness $t$. Under this consideration, $R_i$ can be re-written as equation (4.12).

$$R_i = t \cdot r_i$$  \hspace{1cm} (4.12)

$R_i$ can also be expressed in terms of the concentration and diffusion coefficient of diffusing ionic species by equation (4.13) as a function of penetration length $27$

$$R_i(x) = \frac{RT}{F^2 z_i^2 D_i c_i(x)}$$  \hspace{1cm} (4.13)

It can be anticipated from equation (4.13) that $R_i$ is a position-dependent ohmic resistance which dominates the impedance behavior of the porous layer. Theoretically, the electrical modeling of the porous layer should include a capacitive component (to reflect the electrical properties of interface where ionic conductor (solution) meets electronic/mixed conductor (polymer). However, this capacitance will be treated as part of the interfacial impedance (Section 4.4.4).

4.4.3.2. Impedance of the Compact Layer

As previously argued, it is assumed that the compact layer (Figure 4.4) is macroscopically homogeneous and compact. As such, the layer is not penetrated by the solution and exhibits an appreciable electronic conductivity. Being adjacent to an electronic injector (metal substrate), the layer transports injected charge carriers towards the porous layer where the electronic current starts to
vanish. The layer’s compactness suggests that ionic species (counter ions) are spatially trapped in the polymer matrix. Under these assumptions, the impedance contribution of this layer can be analyzed in view of the transmission line with spatially restricted diffusion \(^{28}\) with some modification. The general assumptions maintained herein are the spatial restriction of the counterion’s diffusion and good electronic conductivity. From a practical point of view, these assumptions are valid if the film is oxidized and if the counterions are trapped in deep potential energy wells (large energy barriers) which are homogeneously distributed throughout the layer thickness. However, it can be reasonably argued that counterions residing in the region near the interfacial edges of the compact layer (the transition region between compact and porous layers) exhibit a faster diffusion rate or that they may be easily transferred to the surrounding electrolyte/porous layer. While this is true, the thickness of this transition region is small and the ions may be assumed to result in a negligible deviation from the general formalism.

As has been demonstrated by Bisquert et al. for the case of intercalation electrodes \(^{29}\), small ions occupying deep and shallow energy wells (slow and fast states) contribute three elements to the film’s impedance: \(C_{\text{trap}}\), \(C_0\), and \(R_{\text{trap}}\) (trap resistance) which have expressions: equations (4.14-4.16).

\[
C_{\text{trap}} = \frac{dQ_{\text{trap}}}{dV} \tag{4.14}
\]

\[
C_0 = \frac{dQ_{\text{fast}}}{dV} \tag{4.15}
\]

\[
R_{\text{trap}} = \frac{1}{\omega C_{\text{trap}}} \tag{4.16}
\]
In these equations, $Q_{trap}$ is the equilibrium charge arising from trapped ions, $Q_{fast}$ is the equilibrium charge resulting from ions occupying fast states, $\omega_t$ is the characteristic frequency and $V$ is the external applied potential. The total capacitance, $C_{total}$ of the film will be a function of the contributions of $C_{trap}$ and $C_o$ equation (4.17).

$$C_{total} = C_o + C_{trap} \quad (4.17)$$

In our modification of this model, we will replace the $R_{trap}$ by a resistive impedance $R_r$ which takes into account the resistance resulting from both electronic and ionic species. It was initially assumed that electronic diffusion transport was fast and ions experience only a low energy barrier as they move from site to site (low resistance). This assumption, however, may not be always true in our model especially at the interfacial edge of the compact layer due to an increased level of disorder. In this region, the diffusion of electronic species will likely decrease (giving a vanishing electronic current) while that of counterions will increase, making the two processes observable on the time scale of impedance spectroscopy and within our experimental frequency range. To account for these transport processes, the parallel resistive impedance, $R_r$ mentioned above is thus introduced in the circuit (in addition to $C_{total}$).

A general expression for the resistive impedance of the film, $R_r$, has been derived based on the theory of homogeneous dual conductive film by Vorotyntsev et al. equation (4.18) \(^{30}\). Although $R_r$ technically concerns the electronic species, equation (4.18) shows that its value will somehow be affected by the diffusion of ionic species.
where $D_e$ and $D_i$ are the diffusion coefficients of holes/electrons and counterions respectively. $R_p$ is the bulk resistance of the film and $\nu$ is the dimensionless frequency defined in equation (4.19) \(^{31}\):

$$\nu^2 = d^2 j\omega \frac{(D_e^{-1} + D_i^{-1})}{8}$$

\(^{(4.19)}\)

It has been shown that equation (4.18) can be simplified in the case of significantly different electronic and ionic diffusion parameters. In particular, if $D_e >> D_i$ (a situation that applies for our model) equation (4.18) reduces to equation (4.20) \(^{30}\).

$$R_p = R_p + R_p \left( \frac{D_e}{4D_i} \right) \nu^{-1} \tanh \nu$$

\(^{(4.20)}\)

The above expressions suggest that the total impedance of the compact layer electrically corresponds to the parallel combination of $C_{total}$ and $R_p$. These elements are to be added to the impedance of the porous layer to reflect the overall impedance contribution of the film (compact and porous layers). Specifically, the compact layer is electrically modeled by a parallel RC component electrically connected in series to a transmission line composed by a network of resistors, $r_i$ and capacitances $c_i$. As it will be argued, this transmission line can be simplified to a series $R_p$-CPE circuit.

4.4.4. Impedance of the Film|solution Interface

Based on the proposed morphological model, there is not a well defined “film|solution” interface. Within our boundary conditions and morphological model, the electrolyte and polymer film (porous layer) can be regarded as a
macrohomogeneously mixed liquid and a solid phase. As such, the interfacial impedance can be assessed in terms of ionic resistance and capacitances (comprising the double layer and the Poisson capacitances) as given by equations (4.13) and (4.21-4.22)\(^2\)

\[
C_i(x) = \frac{z^2 e^2 C_i(x)}{RT}
\]

(4.21)

\[C_p = \varepsilon \varepsilon_0\]

(4.22)

\[
C_{dl} = \sqrt{2C_i C_p}
\]

(4.23)

The \(C_{dl}\) is electrically connected in series with \(R_i\). These parameters can be converted to normal dimensions by multiplying them by the thickness of the porous layer, \(x\).

### 4.4.5. The Total Impedance Expression and Features

As previously pointed out, the total impedance expression can be generated from equation (4.3). If each electrical parameter in equation (4.3) is replaced by its respective expression, a general impedance expression for the model can be obtained equation (4.24).

\[
Z_{CPME} = R_n + \left(\frac{R_{ct}}{1 + i \omega R_{ct} C}\right) + \left(\frac{R_p}{1 + i \omega R_p C_{total}}\right) \left(R_i + \frac{1}{Q(i \omega)^2}\right)
\]

(4.25)

In equation (4.25), \(Q\) is the constant capacitance and \(n\) is related to the phase angle as \(90^\circ n\). Equation (4.25) represents the simplified equivalent circuit of the CPME and comprises the solution resistance, metal|film interfacial impedance, the bulk film impedance and the film|solution impedance. It would be appropriate, at this point to look at the frequency behavior of this circuit.
In response to an applied bias voltage, the equilibrium concentrations of carriers are perturbed. At perturbation frequencies $\omega$ greater than the characteristic frequency $\omega_0$ (i.e., $\omega \gg \omega_0$ or $\omega >> D/L^2$) the total impedance response will be primarily the ohmic resistance and that of the film $R_p$. At the opposite limits ($\omega << \omega_0$) the capacitive charging of the film will dominate the impedance. From the proposed morphological model and the resulting impedance expression, two main modes of charging can be anticipated.

The first mode of charging is the double layer charging. At equilibrium, electronic and ionic charges align against each other to form a double layer structure at the junction of layers. The double layer results in a capacitance which can be best described by a constant phase element as mentioned earlier. This capacitance is characterized by its own time constant which depends on the thickness of the porous layer.

The second mode of charging results from spatially trapped counterions or their interaction with the holes in the compact layer. This phenomenon has been described above as the trapped and fast state charging which result into $C_{total}$. As described for the case of the charging in the porous layer, this capacitance which is associated with the charging of the compact layer is also characterized by its own specific characteristic frequency. This characteristic frequency is most likely to be different from that of the double layer due to the differences in the layer thicknesses and/or diffusion coefficients.

The model proposed here is unique in that it attempts to more completely address the morphological features of the film. Unlike the traditional transmission
line model, which assumes a one dimensional macrohomogeneous matrix, this model introduces sub-circuits for each layer, which we propose are morphologically different. This constitutes an important step in explaining the frequency independence and deviations from ideal situation observed in our experimental data. The next chapter will be devoted to the model verification through simulation and calculation of impedance spectra using different parameter values.

4.5. Conclusion

Results discussed in Chapter 3 suggest that the electrodes exhibit “near ohmic” behavior. Attempts to explain/interpret the impedance data using prominent models such the transmission line model suggested that a more appropriate model was required. The model proposed here takes into account two morphologically different layers, each of which exhibits a different conductivity. Whereas the innermost layer is dense and compact, the outer layer is homogeneously porous to the electrolyte species, allowing ions to move through interconnected channels. It follows that in or near the channels, the ionic ohmic low resistance ($r_i$) path is preferred. Nonetheless, charging and discharging of the film may take place, particularly at pore walls which are in contact with solution species. This phenomenon is capacitive rather than faradaic. Although the film charging in the porous layer could be modeled by a transmission line, the proposed morphology allows simplification to a series lumped $R_i$-CPE branch for frequencies $\omega >> \omega_o$, where the time scale for charging is large compared the characteristic frequency $\omega_o$ ($\omega_o$ is the characteristic
frequency that depends on diffusion coefficient and film thickness). In this case, the total impedance will be dominated by ohmic ionic resistance in the pores. The CPE capacitive behavior will be observed at low frequency where $\omega \ll \omega_o$. While the model assumes negligible diffusion of the counterions which are spatially trapped in the compact layer, it incorporates their possible capacitive effects through charging. The electronic transport in the compact layer is also incorporated in the model but its effect is negligible, as discussed more fully in the next chapter.
4.1. Transmission line circuit where $R_e$ and $R_i$ are the electronic and ionic resistances, while $C_p$ is the redox capacitance. (Redrawn from\textsuperscript{19})
4.2. Generalized model of CPME where \( x, y, z \) represent sub-circuits

(Redrawn from\(^{20}\))
4.3. Morphological model of PEDOT film. \( t \) compact layer, \( x \) porous layer and \( d \) film thickness
4.4. Illustration of charge transport in CPMEs considering the differences in its ionic and electronic conductivities: A) a case of electronic conductivity of the film $\gg$ its ionic conductivity, B) a case of ionic conductivity of the film $\ll$ its electronic conductivity, C) a case where two scenarios are concomitantly probable (two layer film morphology).
4.5. Proposed equivalent circuit for a two-layer film morphology.
4.6. References


(26) Malev, V. V.; Kondratiev, V. V. *Russian Chemical Reviews* 2006, 75, 147.


CHAPTER 5
MODEL VERIFICATION

5.1. Introduction

The model proposed in chapter 4 fits the impedance data of PEDOT electrodes fabricated under the optimum conditions. The model suggests that, the ohmic behavior observed at high and medium frequency range is primarily governed by the ionic conduction in the interconnected pores channels of the film. In this chapter, we will discuss the phenomenological features of the model in its general form. Additionally, we will use the theoretical simulation approach to validate the physical meaning of electrical elements and to explain the origin of deviations from theoretical predictions. The impedance behavior of the model in response to an independent variation of electrical parameters will provide the basis of theoretical arguments regarding the window of experimental conditions under which the model is valid. This exercise, which can be regarded as a necessary step in the process of electrical modeling (Figure 5.1) will help generalize the model and assess its applicability to other systems which exhibit similar impedance as that of PEDOT electrodes.

In summary, the simulations generated by varying an individual parameter will be compared to with experimental impedance behavior where the same parameter is intentionally varied. Congruence between the theoretical predictions and experimental results will prove the validity of the element and its physical meaning. For example, it would be anticipated that increasing the value of $R$, equation (4.20) would have an obvious effect on the appearance of the high
frequency semi-circle associated with the compact layer. Increasing $R_r$ will increase the radius of the high frequency semi-circle and it will be more visible. Experimentally, this variation corresponds to reducing the film. As such, similar impedance response should be expected. It can be argued that it is practically unrealistic to assume that reducing the film will only affect the compact layer, but it is can be assumed that this layer will be the most affected. It is the only layer in which electronic conductivity is considered.

5.2. Comparison of Simulations and Experimental Data

In this section, the model is applied to fit the impedance data of PEDOT (Figure 5.2). In the proposed equivalent circuit model (Figure 4.5), $R_{ct}$ was assigned to the heterogeneous charge transfer resistance across the metal|film interface. As previously argued, it is not surprising that the value of $R_{ct}$ is small (~6 ohms) based on the fact that Pt was used as the substrate. Due to the gold electroplation, the underlying substrate would have no significant effects on the $R_{ct}$. Consequently, ohmic behavior should still be observed at high frequency. This is supported by our experimental data in which the Pt, Au, and glassy carbon electrodes were used as substrates. (Figure 5.3). The low value of $R_{ct}$ may be a combined result of high surface area of the substrate (due to the roughness resulting from electroplaton) and the electrochemical properties of the interacting materials (in this case, Au which is a good hole injector and the polymer being a good hole acceptor).

Another interfacial parameter is the capacitor $C$. In ideal conditions, the metal|film interface would predictably be ohmic (no capacitance) but result reveal
that the capacitance may exist. However, its small value ($\sim 10^{-8}$ F) indicates that its contribution to the interfacial resistive impedance is very negligible. This is supported by the lack of fully developed semicircle which is predicted by the parallel combination of $R_{ct}$ and $C$ (Figure 5.4).

The impedance behavior of $R_{ct}C$ reveals important information regarding the interfacial properties. The partially developed semi-circle indicates that the $R_{ct}$ is low and the process is fast (compared to the scanned frequency). In order to observe a well developed semi-circle, either the frequency range should be increased or the value of $C$ should be increased (Figure 5.5). The simulation results imply that the charge transfer process is fast and can only be fully observed at high frequency. Alternatively, the high frequency semi-circle can be observed if the value of $C$ is increased by a factor of 10 (Figure 5.5). These observations support the assumptions made regarding ohmic metal|film interface. As a result, it can be omitted from the circuit especially if the medium and low frequency range are of interest.

A second resistor, $R_r$, is used in the circuit to represent the resistance encountered by the electronic charge carriers in the compact layer. On electrochemical basis, $R_r$ can be regarded as a series of redox reactions occurring within the film (compact layer). Assuming that the film is oxidized and is structurally ordered, the value of $R_r$ is expected to be very small. As previously pointed out in Chapter 3, this charge transfer process may be too fast to significantly influence the impedance behavior of the film (at least in the frequency window covered in this investigation). Nonetheless, the effects of
structural disorders increase as you move toward the more porous layer (t). Consequently, its contribution to the total impedance may not be negligible but a small value is expected (~6 ohms in this case).

Another electrical element related to the electrochemical properties of the compact layer is the capacitor, $C_{total}$. $C_{total}$ is the total capacitance which results from the contribution of two different charging modes: fast and trapping sites. As previously argued, it would be reasonable to assume that the trapping sites are located deep in the innermost regions of the compact layer (closest to the underlying substrate) while the fast sites are located towards the outer boundary of the porous layer (near the edges of the compact layer and porous layer where the film structure starts loosening).

$C_{total}$ and $R_r$ are electrically connected in parallel. Theoretically, they produce a semicircle in the middle frequency range. Our experimental results, however, show that this middle frequency semicircle is, in most cases not fully developed because of relatively high capacitance (comparable to the double layer capacitance). The simulation results demonstrate that the semi-circle clearly develop when the value of $C_{total}$ is decreased by a factor of 10 (Figure 5.6). Comparing these observations and our experimental data, it can be concluded that the compact layer is charged. This suggests the presence of static charge carriers (counterions) which contribute a capacitive current to the total impedance. In theory, all counterions should be “counter-balanced” by holes. In case of fast electronic conductivity, however, the holes move to the neighboring sites along the chain and the counterions may appear to be
temporarily “necked” or unbalanced. This may cause the capacitance to increase.

The third branch of the circuit (Figure 4.5), $R_i$-CPE represents the electrochemical processes occurring in the porous layer. As previously discussed, $R_i$ represent the ionic (electrolyte) resistance within the pore channels and CPE represents the double later charging. This assignment is confirmed by experimental (Figure 5.7) and simulation results (Figure 5.8). It can be observed that increasing electrolyte concentration (low $R_i$) lowers the impedance magnitude (Figure 5.7). Above 0.5M KCl, no impedance dependence on electrolyte concentration is observed. This supports that ohmic behavior is primarily defined by the ionic conductivity in the pores and that it can be considered as a direct consequence of the two-layer morphology.

Experimental data (Figure 5.7) show that the low frequency capacitance is independent of concentration. This suggests that at low frequency, the charge saturation occurs in the film. Although the double layer charging (charge saturation) takes place throughout the porous film, the high value of $C_{total}$ (comparable to that of CPE) suggests that the double layer charging is more significant at the boundary of the compact and porous layers. The proposed morphological model suggests that there no clear, well-defined boundary between the compact and the porous layers. The values of each capacitance ($C_{total}$ or CPE) are calculated by drawing an imaginary boundary line to the right or left from where the layer is clearly compact or porous. This view is supported by the simulation data which demonstrate that the same impedance behavior can
be obtained by simultaneously adjusting the values of $C_{total}$ and CPE. Increasing the value of $C_{total}$ and decreasing that of CPE (or vice versa) produces the similar impedance behavior.

5.3. Frequency-dependence of the Model

In its generality, the proposed model can produce three distinct impedance loci: two semi-circles at high and medium frequency range and low frequency capacitive vertical line. The capacitive behavior is observed at low frequencies lower than the characteristic frequency $\omega_0$ ($\omega << \omega_0$). The capacitive behavior of CPE is supported by its exponent $n$, which is close to the unity ($n>0.98$). The deviation from a perfect capacitor ($n=1$) is explained by the fact that CPE represents a distributed capacitance. Additionally, the possibility of minimal interfacial charge leakage cannot be excluded. It would be reasonable to assume that small portion of ions located at the polymer|solution interface (within the pore walls) can be exchanged between the two media. In this case, the deviation from a perfect capacitance could also be attributed to the existence of this charge leakage since this interface cannot be treated as being fully polarizable as proposed by Fletcher\(^1\). Nevertheless, there exist a strong agreement between theoretical prediction of the model and experimental data in the frequency range between $<5$Hz and $0.1$Hz ($\chi^2=9.6*10^{-5}$).

The semi-circle assignable to the impedance response of the compact layer is expected to appear in the mid-range and high frequency. As pointed out earlier, our experimental data does not exhibit a fully-developed semi-circle. In fact, it is not observed at all in some samples. The absence or presence of this
frequency range can be correlated to the values of $C_{\text{total}}$ and $R_r$ as discussed above. The comparison of experimental data and simulated data requires considering the aforementioned semi-circle in conjunction with that assigned to the metal|film charge transport. While he simulated data show a clear intersection between the two semi-circles (Figure 5.4), experimental data does not exhibit similar behavior. Instead, a randomly distributed data points are observed in the region where the two semi-circles should theoretically intersect.

The experimental deviations from predicted impedance behavior can be attributed to the morphological features of the film. Although our proposed model attempts to address the morphological aspects, it does not incorporate the three dimension aspects of the electrode. In other words, the proposed model provides the impedance of a circuit which extends throughout the film. On a practical basis, however, the impedance response at a given frequency can be envisioned as the average value of multiple geometrically parallel circuits spanning throughout the film. This is expected to have significant effects in the frequency range where the electrical elements representing the compact and the porous layers are active (high and mid-range frequency). The conduction in the portion of the film where the compact and porous layers meet may be inhomogeneously random due to structural aspects which cannot be classified as being neither porous nor compact. Such a structure has been modeled with a network of resistors by Baughman and Shacklette\textsuperscript{2}. The calculations involve the geometric factor which accounts for different orientation of the polymers chains.
It is worth pointing out that the fitting quality of high frequency data is not as perfect as that of low frequency data. This imperfection may be attributed to the limitations of the current algorism used for modeling. Like the proposed model, the theoretical basis of the equations used by the program to fit the data provides the impedance response of a single circuit rather than multiple, similar but not perfectly identical circuits. For example, theoretical ohmic impedance response should be visually a point located on the real axis ($Z'$). Under our experimental considerations, ohmic impedance response will visually appear as a cluster of points randomly distributed around the mean value which is the theoretical ohmic impedance.

5.4. Other Related Models

As previously pointed out, the proposed model is unique in that it consolidates the impedance behavior and the morphological model. To accomplish this, the model combines the transmission line and the intercalation electrode models. Combining the two models seems to address the morphological aspects of an electrochemically synthesized film. Another related model which attempts to address morphological issues was proposed by Paasch.\textsuperscript{3} The model is built on the theory of Barker/Brumleve/Buck\textsuperscript{4} transmission theory\textsuperscript{5}. It however, extends the theory to consider a porous film which exhibits two homogeneous, but different conductivities as a response of inhomogeneously oxidized film. That is, the film exhibits oxidized and reduced layers. While the model seems to propose a two-layer system, it differs from the model proposed herein. The basis of the two-layer morphology is physical rather
than electrochemical. In the model proposed by Paasch, the author evaluates the low frequency impedance and reports the similarity between the impedance response of a two-phase model and that of a homogeneous model; thus making the results of the model inconclusive.

5.5. Conclusion

In contrast to previous models, our model offers the methodology for taking into account the influence of structural variation of the film on the charge transport and electrochemical properties. The physical meaning of electrical elements used in the model is supported by the comparison of simulated data and experimental results. The slight deviation of experimental data from theoretical prediction is explained by the complexity of the morphological features of the film. As such, the ohmic behavior achieved our CPMEs can be classified as “Near Ohmic” behavior since it departs from perfect ohmic behavior. At low frequency range, the total impedance is primarily determined by the double layer charging. Electronic and diffusional processes (which are morphologically sensitive) are too fast to influence the total impedance in the frequency range. Consequently, the impedance response of the model resembles that of a homogeneous model. The low frequency data can be fitted by commercially available software and a good agreement between theoretical prediction and experimental data is reached.
1.1. Illustration of steps involved in the electrochemical modeling process.
5.2. Impedance spectrum of PEDOT electrode made from 0.0125 M EDOT and 0.1M BF$_4^-$ in acetonitrile for 90 seconds. Impedance was measured in 0.1M BF$_4^-$.
5.3. Impedance of PEDOT film electropolymerized on different substrates (Au, Pt and C. The films were polymerized from 0.0125M EDOT and in 1M BF$_4^-$ in acetonitrile for 90 seconds. Impedance was measured in 0.1M BF$_4^-$
5.4. A: Nyquist plot of impedance based on proposed equivalent circuit. B: Experimental impedance of data (a) and simulated impedance fit (b) based on proposed equivalent circuit (Figure 4.5) within 0.1Hz-100kHz. $R_{ct}= 6.026\,\Omega$, $C = 1.624\times10^{-8}F$, $C_{total} = 0.0028561F$, $R_i = 4.6\,\Omega$, $R_f = 48.319\,\Omega$, $CPE = 0.0046005F$, $n=0.989$. $X^2 = 9 \times 10^{-4}$
5.5. Simulations: A) using same parameters values as in (Figure 5.4) within 0.1Hz-10^7 Hz. B) increasing $C$ by a factor of 10 (other parameters kept same as in Figure 5.4.)
5.6. Simulation based on the proposed circuit. The parameters values are kept the same as in (Figure 5.4) except $C_{\text{total}}$ which is decreased by a factor of 10.
5.7. Dependence of ohmic behavior on electrolyte concentration ($R_i$): Electrode made from 0.0125 M EDOT and 0.1M BF$_4^-$ in acetonitrile. Impedance was measured at varying BF$_4^-$ concentrations: 0.05M, 0.1M, 0.5M and 1 M.
5.8. Simulation data varying $R$: A) 10Ω, B) 20 Ω, C) 50 Ω and D) 70 Ω. Other parameter values are kept the same as in (Figure 5.4).
5.6. References


CHAPTER 6

COMPARATIVE STUDY OF IMPEDANCE BEHAVIOR OF PEDOT, PEDOP AND PCz

6.1. Introduction

There is currently compelling evidence for the suitability of conducting polymer modified electrodes (CPMEs) for biomedical applications. A closer reflection on this topic is provided in the literature by Guimard et al. However, the development of successful biomedical devices is still a challenging task due to the difficulties in gaining the reproducibility of desired properties in a given conducting polymer and the extension of what learned from one polymer to another. The application on which we have focused is sensing of bio-electrical signals. In addition to the questions of tissue response, frequency-dependent impedance behavior has been proven to be problematic for biosensing using the conventional electrodes such as platinum, gold and Ag/AgCl. Conducting polymers offers the possibility of being ideal candidates for biosensing applications due to their biocompatibility and dual conductivity. However, up to this point, the slow ionic motion in the film has usually resulted in frequency-reactive impedance due to diffusion-governed charge transport.

As discussed in Chapter 3 and 4 we have been able to circumvent this behavior by achieving frequency-independent behavior in vivo for electrodes based on poly(3,4-ethylenedioxythiophene), PEDOT, and we have successfully extended this behavior in vitro over the frequency range extending from less than 10 Hz to around 100 kHz by systematically manipulating the synthetic conditions that affect the morphological properties. Achievement of this uniquely broad
range of frequency-independent impedance behavior for PEDOT-based electrodes provides the incentive to determine if the same behavior can be achieved in other polymers. Although there are numerous reports on various aspects of effects of synthetic parameters on CPME’s properties, a unified concept that allows discrimination between the effects of preparation approaches and chemical identity on their electrochemical properties is not yet established.

We have suggested that the frequency-independent behavior for PEDOT originates in the special morphological features (Figure 4.3). The film is postulated to consist of two homogeneous but different layers – a compact, non-porous layer adjacent to the substrate electrode and an outer layer that is characterized by microscopic pores. As such, this frequency independent feature could be used to probe how a given set of electropolymerization conditions affect impedance behavior of these conducting polymers.

Parameters such as monomer concentration, electropolymerization potential, dopant identity and film thickness have been reported to affect the morphological features and/or electrochemical properties of specific conducting polymers. These findings are often generalized to roughly apply to other polymer systems but whether a given parameter quantitatively affects different polymers to the same extent or even in the same manner remains uncertain. This provides the rationale for comparative studies of effects of specific synthetic parameters on a range of polymers in order to be able to develop predictive capability in the future design of conducting polymer-based sensing electrodes.
In this chapter, we present the comparison of impedance of poly(3,4-ethylenedioxyppyrrrole) or PEDOP, polycarbazole or PCz, and poly(3,4-ethylenedioxythiophene) or PEDOT prepared using the same optimization criteria. While the impedance behavior of conducting polymers has been extensively studied, most of the studies explore one type of polymer, with few direct comparisons to other polymer/dopant combinations. The data presented here provides further support for the general paradigm offered in our proposed model, linking deposition conditions, chemical identity of the monomer and dopant, and the resulting impedance behavior. The structural differences of these polymers highlight the importance of inter-relationship and the effects of the heteroatom and polymer backbone of the polymers on their impedance behavior.

With respect to the heteroatom identity, theoretical studies have suggested that the heteroatoms of conducting polymers have significant effects on their band gap⁵. While the origin of these effects is not clear, some studies propose that the heteroatom may affect the polymers properties through the distortion of the chains and molecular packing⁵. Based on these theoretical predictions, it is informative to determine whether these effects are experimentally significant enough to be reflected in the impedance spectra of the polymers of interest.

The second aspect of investigation on which we have focused is the polymer backbone. The backbone of the monomer is a very critical component of polymer. In fact, systematic alteration and modification of the polymer backbone has been utilized to improve their electronic properties⁶. It has been
demonstrated that the same monomer modified by attaching electron donating substituents leads to a polymer with a lower switching potential and better electrochemical properties \(^7,^8\). As will be shown, our results suggests synthetic approach and resulting morphological features can play a significant role in efforts to tune conducting polymers to exhibit the desired behavior irrespective of monomer identity.

6.2. Methods and Materials

6.2.1. Materials

Platinum (Puratronic grade) and silver (99.99\%) wires, as well as hydrogen tetrachloraurate(III), were purchased from Alfa-Aesar. Sulfuric acid and acetonitrile (99.9\%) were purchased from Fisher Scientific. The EDOP, 3,4-ethylenedioxyppyrrole, and carbazole monomers were obtained from Aldrich. Tetrabutylammonium tetrafluoroborate, tetrabutylammonium hexafluorophosphate, poly(sodium-4-styrenesulfonate), tetrabutylammonium tosylate and tetrabutylammonium perchlorate (electrochemical grade) were obtained from Fluka Chemika or Aldrich. Acetonitrile was dried over 3Å molecular sieve (Fisher Scientific) before use. All other chemicals were used without further purification. Adhesive polymer was obtained from Stan Rubenstein or ME Taylor Engineering, Inc. Non-porous polymer (TorrSeal) was purchased from Varian Vacuum, Inc. Aqueous solutions were prepared using 18.3 MΩ water produced with a Millipore RIO5 purification system.
6.2.2. Electrochemical Cell

All electrochemical reactions were carried out in a one-compartment three-electrode glass cell. The reference and auxiliary electrodes were Ag/AgCl (BAS RE5) and platinum wire respectively. All deposition and electrochemical characterization studies were performed using a Radiometer PGZ402 instrument controlled by VoltaMaster 4. No ohmic compensation has been applied.

6.2.3. Fabrication of Electrodes

Each substrate electrode was fabricated, electrochemically cleaned, and coated with a layer of gold as previously described in Chapter 3. Films which displayed the desired behavior were obtained by potentiostatic electrodeposition in acetonitrile containing salts from which the anions act as dopant. The concentration of the monomer and dopant were 0.01M and 0.1M respectively. The electropolymerization time was varied between 60 and 120 seconds to produce films with various thicknesses. The electropolymerization conditions, except the electropolymerization potential were chosen based on optimum conditions previously determined for PEDOT electrodes (Chapter 3). The appropriate electropolymerization potential of each polymer was determined based on cyclic voltammetric measurement of the peak potential for the monomer (optimum potentials chosen for the monomers were 1200 mV for PEDOP and 1300 mV Vs Ag/AgCl for PCz).
6.3. Electrode Characterization

Raman measurements were carried out employing a Renishaw Ramascope microspectroscopy instrument equipped with 25 mW 785 nm laser (SpectraPhysics), a Rayleigh filter and a 2400 line/mm grating. Instrument setup and data acquisition are controlled with Wire 2.0 software.

Electrochemical impedance measurements were carried out in a one-compartment three-electrode glass cell. The reference and auxiliary electrodes were Ag/AgCl (BAS RE5) and platinum wire, respectively. All deposition and electrochemical characterization studies were performed using a Radiometer PGZ402 instrument controlled by VoltaMaster 4.

6.4. Results and Discussion

6.4.1. Raman Spectroscopy

The Raman spectra of PEDOP doped with various dopants is shown in (Figure 6.1). Despite differences in maximum intensity related to laser focusing, these films exhibit the same vibrational modes. The C=C stretching modes which appear at around 1600 cm\(^{-1}\) are an indication of formation of polymeric backbone\(^9\). As it can be observed from (Figure 6.1), there is no significant deviation in frequency position of the peaks which suggests that the conjugation lengths of the polymer chains are relatively independent of counterion identity. The position of peaks can be correlated to the conjugation length of the polymer chains \(^{10,11}\). The differences in impedance behavior can therefore be attributed to the film’s structural disorder as discussed in the subsequent section.
6.4.2. Effects of Dopant on Impedance Behavior

It is widely accepted that the identity of the dopant, depending on its electronic properties and size, affect the properties of conducting polymers\textsuperscript{12,13}. (Figure 6.2) and (Figure 6.3) display the Bode plots of the impedance spectra of PEDOP and polycarbazole (PCz) electrodes doped with various counterions, respectively. Two points are immediately discernible. First, it is obvious that regardless of assessed counterion, PEDOP exhibit a slightly wider frequency window where ohmic behavior is observed. Second, it is observed that in both cases, PSS\textsuperscript{-} exhibits the highest impedance. This behavior has also been previously observed in PEDOT electrodes and it has been attributed to the lower doping level and/or morphological effects the counterion on the polymer alignment compared to other counterions as described in Chapter 3 of this manuscript. What might be considered the PSS\textsuperscript{-} monomer, toluene sulfonate, leads to a smaller impedance, but the onset of the frequency dependent region occurs at higher frequency. Based on the results reported by Tekemura et al\textsuperscript{13} predicting specific interaction of the counterion's and the heteroatoms \(\pi\)-electrons, one would expect similar impedance behavior of PEDOP and PCz doped with either PSS\textsuperscript{-} or Ts\textsuperscript{-}. Using the same logic, similar impedance behavior would be expected from either polymer doped with the same counterion (PSS\textsuperscript{-} or Ts\textsuperscript{-}) based on these specific electronic interactions predicted by Tekemura.

PEDOP and PCz doped with PSS\textsuperscript{-} exhibit some similarities (Figure 6.2) and (Figure 6.3) in their impedance behavior. It is observed that in both cases that the PSS\textsuperscript{-} doped polymers exhibit higher impedance compared to those
doped with other anions. However, it is also observed that the impedance magnitude in the case of PEDOP is less dependent on frequency (in the high and medium frequency ranges). In the case of Pcz, a much narrower frequency-independent impedance region is observed. This divergent behavior suggest that these two polymers have different morphologies. When these two polymers are doped with Ts⁻, comparison reveals a pattern both in terms of ohmicity and impedance magnitude. What is interesting, however, is that the impedance magnitude for polymers doped with Ts⁻ is very similar to that of the polymers doped with small inorganic counterions. In fact, comparison of impedance behavior of the polymers based on the basis of counterion reveal similar patterns with small deviations in terms of the frequency range over which the frequency-independent impedance behavior exists. Assuming that this frequency-independent behavior is governed by the same morphological model briefly discussed in Chapter 3, these results imply a rather stronger dependence of impedance on the size of the counterion than on its electronic properties.

The obvious differences between the impedance of PEDOP doped with PSS⁻ and that of PEDOP doped with Ts⁻ suggest π-π interactions between the polymer and the counterion may not be the determining characteristic that imparts the observed impedance behavior. Prior studies have shown that large organic counterions such as PSS⁻ result in lower doping level and smoother morphology (Chapter 3) compared to small inorganic counterions. The low doping level can be attributed to its bulkiness while it’s a more compact morphology can be attributed to the ability to form a micellar solution during
electropolymerization. The micellar solution allows a better alignment of the oligomers being deposited.

Although a comparison across smaller inorganic counterions show a great deal of similarity, it can be seen that the range over which ohmic behavior is observed slightly depends on the type of counterion-polymer combination. For example, BF$_4^-$ is a better choice for PEDOT electrodes while ClO$_4^-$ is better for PEDOP (Figure 6.4). If, as postulated, this frequency independent behavior arises from a two layer morphology as previously suggested (Chapter 3) it would follow that different anions lead to different layer growth proportionality.

The differences between PEDOP and PCz’s ohmic range suggests that the monomer’s identity may have tunable effects on the morphological structure of the film. This is also illustrated by the comparison of impedance behavior of PEDOT, PEDOP and PCz. It is clear that when all parameters (except optimum deposition potential) are kept the same for PEDOT, PEDOP and PCz electrodes fabrication, PEDOP exhibits a much more similar impedance behavior with PEDOT than to PCz (Figure 6.5).

6.4.3. Effects of Film Thickness on Impedance Behavior

Based on the proposed morphology, it can be argued that the films in which shorter ohmic range is observed have a thinner porous layer. This would results in an impedance dominated by capacitive behavior starting at relatively high frequency. The ohmic behavior frequency range of any polymer can be slightly extendend by adjusting the thickness of the film and it should be possible to optimize the relative thickness of the two layers to achieve ohmic range for
PCz. (Figure 6.6) shows the results for different deposition times for PEDOP and PEDOT films doped with two different dopant anions, BF$_4^-$ and ClO$_4^-$. These films were produced for 60 seconds and 120 seconds, leading to thickness of approximately 1.2 and 2.5 μm, based on both total current passed and on thickness measurements carried out by scanning electron microscopy. From (Figure 6.6), it can be seen that the frequency range where ohmic behavior is observed slightly increased by increasing the film thickness. This can be attributed to the increase of the porous layer which extends the penetration length of anions in the porous layer. The thickness of films which exhibit the desired behavior appears to be limited by the range over which homogeneity can be achieved.

An interesting observation is how the ohmic impedance magnitude is more dependent on counterion than on film thickness at higher frequency range (eg: PEDOP/BF$_4^-$ and PEDOP/ClO$_4^-$). Yet at lower frequency range where capacitive behavior dominates the impedance magnitude, the impedance becomes more dependent on film thickness than it depends on counterion (eg. PEDOP/ClO$_4^-$ (60 seconds) and PEDOP/BF$_4^-$(120 seconds)). This behavior seems to support the postulated morphological model which suggests that the ohmic range is dominated by the ionic path in the porous model. The differences would then be a result of ionic size (as they exist in the solution) and its effects on their conductivities. At low frequency where capacitive behavior dominates the impedance behavior of the films, ions reach the end of the rail where they
participate in the double layer capacitance. This behavior enforce the proposed existence of an x-layer which minimally penetrable by ions.

6.5. Comparison of PCz, PEDOT and PEDOP Doped with BF$_4^-$

Tetrafluoroborate, BF$_4^-$ as indicated in chapter 3, is the best counterion for achieving ohmic bahavior in PEDOT-based electrodes. It would therefore be insightful to compare the same counterion in the other polymers investigated. In (Figure 6.4), the impedance of PEDOT, carbazole and PEDOP electrode samples doped with BF$_4^-$ are contrasted. All electrodes exhibit frequency independent behavior over a large range of frequency (Table 6.1). With the exception of polycarbazole, this range extends down to almost 1 Hz and, even below 1 Hz the magnitude of the impedance remains well below 1 kΩ. PEDOP exhibits higher capacitance (2.63 μF/cm$^2$) compared to PEDOT at low frequency, as shown by the |Z|-intercept of the data in (Figure 6.7). This plot of Log |Z| vs log($\omega$) is based on equation (6.1) describing the impedance of a capacitor. This likely caused by the differences in the penetration length of ions. The slope which is closely equal to -1 implies capacitive behavior is dominating the entire impedance locus at frequencies less than 10Hz. Under this conditions, the limiting capacitance can be estimated by the log|Z| intercept at log($\omega$) = 0.

\[
Z_c = \frac{-J}{\omega C}
\]

where $Z_c$ is impedance, $j=\sqrt{-1}$, $\omega$ is angular frequency and $C$ is the capacitance (Figure 6.7) also confirms that PEDOT maintains non-capacitive behavior (identified as ohmic) over a slightly wider frequency range compared PEDOP, as
evidenced by its deviation of capacitance plot from the slope of -1 in the frequency range where that of PEDOP remains close to -1. Again, the most likely explanation is that this is a result of deeper ionic penetration length for PEDOT compared to the that of PEDOP with comparable overall film thickness.

Table 6.1: Comparison of ohmic impedance for PEDOT, PEDOP and PCz on the basis of dopant identity: X) No ohmic-behavior observed, ✓) Ohmic behavior observed.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Counterion (Dopant)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PSS(^{-})</td>
</tr>
<tr>
<td>PEDOT</td>
<td>X</td>
</tr>
<tr>
<td>PEDOP</td>
<td>X</td>
</tr>
<tr>
<td>PCz</td>
<td>X</td>
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6.6. Conclusions

The impedance behavior of PEDOP and polycarbazole electrodes was investigated and compared with that of PEDOT electrodes. All electrodes studied exhibit ohmic behavior within wide frequency range. PEDOT and PEDOP electrodes exhibit frequency independent impedance behavior over the range between a lower limit of 5-10Hz and the upper limit of the instrumentation
employed (100 kHz). However, polycarbazole does not show ohmic over a frequency range as broad as the other polymers.

Various dopants were studied and showed similar trends for the three polymers. The largest anion PSS⁻ showed the highest impedance magnitude and no appreciable improvement in the ohmic range was observed for the polymers investigated. The comparison of impedance behavior of PSS⁻-doped electrodes and that of Ts⁻-doped electrodes (an electronically similar dopant) suggests negligible effects of the dopant’s π-electrons through specific interaction with the polymer’s heteroatom. For the counterions considered, it appears that the counterion’s size plays the most significant effect on the impedance behavior.

Investigation of the film thicknesses and impedance behavior support the previously proposed model. It is shown that that ohmic behavior greatly depends on the ionic species (counterion) while the capacitive impedance is independent of counterion. These observations demonstrate that there exist a certain distance within the film past which the moving ions cannot travel. As such, they form a double layer as they come in close proximity with holes which are similarly slowed down by structural disorder in this region. Nevertheless, the frequency range for ohmic behavior can be slightly shortened or extended by adjusting the film thickness or more precisely the thickness of the porous layer.

In general, our results reinforce our earlier conclusion that the frequency independent impedance behavior is, indeed, sensitive to the morphological features but it can now be added that it ohmic behavior is also loosely influenced
by the heteroatom and the type of conjugated backbone of the polymer. It also can be concluded that ohmic behavior can be achieved in a number of conducting polymers. In theory, the two layer morphology can be achieved in various polymers by choosing the right counterion and electropolymerization conditions. These results suggest that an appropriate choice of monomer and monomer/dopant combination can be used to tune the impedance properties of conducting polymer films for use in applications which rely on capacitive vs faradaic charge injection or some combination of the two. The variability of frequency range for ohmic behavior across different polymer electrodes can be beneficial on a practical basis as a given polymer can be targeted for specific applications based on the desired charge transport properties.
6.1. Raman spectra of PEDOP doped with various anions (BF$_4^-$, ClO$_4^-$, PSS$^-$)
6.2. Effects of counterion identity on the impedance of PEDOP
6.3. Effects of counterion identity on the impedance of PCz
6.4. Comparison of ohmic impedance of PEDOT and PEDOP doped with BF$_4$
6.5. Comparison of ohmic impedance behavior of PEDOT, PEDOP and PCz
6.6. Impedance of PEDOT and PEDOT doped with BF\textsubscript{4}\textsuperscript{-} and ClO\textsubscript{4}\textsuperscript{-} measured at two different thicknesses (~1.2 and 2.5μm).
6.7. Plot of $\log |Z|$ vs $\log (\omega)$: a) PEDOP and b) PEDOT electrode
6.7. References


CHAPTER 7

CONCLUDING REMARKS AND FUTURE INVESTIGATIONS

7.1. Concluding Remarks

As already mentioned, conducting polymers offer many advantages over other materials, with electrical properties and biocompatibility being the most attractive. However, these interesting materials often need further optimization for specific applications. The work reported herein exemplifies how CPMEs can be tuned and optimized to exhibit interesting, rare, electrical properties suitable for specific application. For biosignal sensing in particular, it is important to tune the conductivity of CPMEs in order to successfully suppress or completely eliminate their frequency-reactive impedance behavior.

In Chapter 1, the history and development of the conducting polymer field is highlighted. A brief review on the discovery and the major progress made in the field over the past four decades is put forward. The discovery of new polymers and functionalization of existing ones, innovative approaches for making more robust films with optimized properties, and elucidation of information regarding charge processes in the film are just few examples of commendable progress that has taken place. However, there still exists room for further investigation, especially in terms of thoroughly understanding the charge propagation mechanism in conducting polymer films and electrodes.

Researchers have made usage of different electrochemical and spectroscopic techniques to investigate different aspects of the conducting polymer. Among others, cyclic voltammetry, chronocoulometry,
chronoamperometry, scanning electron microscopy, Raman spectroscopy, electrochemical impedance spectroscopy are widely used in the field. Chapter 3 introduces and highlights these techniques as they are used in this work. Although results from different techniques are complimentary, it turns out that impedance spectroscopy serves as our primary investigation tool. Impedance spectroscopy allows the determination of the dominating processes in different frequency ranges. This is particularly advantageous in our studies as we are interested in optimizing our electrodes to make their impedance behavior frequency-independent since it offers a direct assessment of impedance variation as a function of the frequency. Through the process of modeling, impedance data can be interpreted in terms of an equivalent circuit, with the assumption that each circuit element represents a real processes taking place in the system. Modeling attempts to establish a link between experimental data and theoretical prediction. Unfortunately, a thorough understanding of the electrochemical system under investigation is a prerequisite in order to discriminate between possible theoretical models that can match experimental data.

In Chapter 3, we report the optimization and investigation of impedance behavior of PEDOT-based electrodes. Consistent frequency-independent behavior in all the electrodes made under our optimum conditions is reported. Frequency-independent impedance can be consistently achieved over a range of frequency ranging from about 10 Hz to the upper limit of instrument employers (i.e 100 kHz). The type of counterion employed appears to play an important role in imparting frequency-independent behavior as well as lowering the impedance
magnitude. Among the counterions investigated, tetrafluoroborate, BF$_4^-$ is found to be the most suitable counterion for PEDOT based electrodes. Unlike a large, organic counterion such as polystyrene sulfonate, PSS$^-$, BF$_4^-$ leads to the lowest frequency independent over a wider frequency range. While the frequency-independent impedance behavior of BF$_4^-$-doped electrodes can be attributed to the ion’s smaller size (compared to that of PSS$^-$), the lower impedance magnitude can be attributed to higher doping level (compared to all dopants investigated).

The implication of film thickness in imparting frequency-independent impedance was also investigated in this chapter. It appears that the outer layer of the film (porous layer) is the most important part of the film as far as ohmic behavior is concerned. The most significant morphological feature of the outer layer is its porosity, which allows the penetration of ionic species from the solution into the film.

The underlying substrate material does not seem to affect the ohmic impedance behavior. This is a further proof that the ohmic behavior is indeed an ultimate result of polymer film’s electrochemical properties. Nevertheless, it must be emphasized that all the substrates investigated in this study are good hole injectors. This broadens the versatility of the electrode materials that can be employed to produce CPMEs which exhibit frequency-independent behavior. A combination of simulation and experimental results that highlight the above points are reported in Chapter 5.
Chapter 4 discusses the proposed morphological model that seems to produce frequency-independent behavior. Results suggest that the “near ohmic” behavior is a result of the two layer morphology. Whereas the innermost layer is dense and compact, the outer layer is homogeneously porous to the electrolyte species, allowing ions to move through interconnected channels. It follows that in or near the channels the ionic ohmic low resistance \((r_i)\) path is preferred. Nonetheless, charging and discharging of the film may take place particularly inside the film and along the pore walls which are in contact with solution species. This phenomenon is capacitive rather than faradaic. Although the film charging in the porous layer could be modeled by a transmission line, the proposed morphology allows simplification to a lumped \(R_i\)\(CPE\) branch for frequencies \(\omega>>\omega_o\), where the time scale for charging is large compared the frequency of the excitation signal (\(\omega_o\) is the characteristic frequency that depends on diffusion coefficient and film thickness). In this case, the total impedance will be dominated by ohmic ionic resistance in the pores. The \(CPE\) capacitive behavior will be observed at low frequency where \(\omega<<\omega_o\). It is important to mention that this simplified model ignores counterion diffusion within the compact film layer based on its extremely slow rate, and that high frequency arcs may not be observed depending on the degree of polymer oxidation.

These studies constitute a significant step in providing insight that can be extended to other conducting polymers systems. Chapter 6 focuses on the comparative study of impedance behavior of PEDOT, PEDOP, and PCz. Based on the chemical similarities and differences between these polymers, impedance
results suggested that ohmic behavior stemmed from macroscopic properties which may more strongly depend on synthetic approaches than monomer identity. This was demonstrated by the fact that ohmic behavior could be achieved in all the polymers we investigated. These results suggest that, for the polymers tested, the effects of monomer’s backbone or heteroatom’s identity on the ohmic impedance behavior are less important than those of the synthetic method and resulting microscopic morphology.

The effects of counterion on PEDOT impedance behavior, as discussed in Chapter 3, affect the morphology and the frequency impedance. Although this trend is observed in all polymers investigated, it also clear that the extent to which each polymer is affected is not the same. For example, a wider frequency range for ohmic behavior in PEDOT-based electrodes is achieved when BF$_4$\textsuperscript{−} is used. For PEDOP-based electrodes, perchlorate appears to result in more optimal behavior. These observations suggest a specific interaction between a given counterion and a given monomer to influence the morphology of the film. This makes a counterion’s identity an important parameter for achieving ohmic behavior in a given polymer. The choice must consider both the size and electronic properties/charge distribution density. Comparison of two comparable thicknesses of the film doped with two different dopants provides further support for a two-layer morphology.

7.2. Recommendations for Future Research and Preliminary in-vivo Results

As previously stated, achievement of ohmic behavior is a major step in extending the potential applications of conducting polymers. However, further
experiments are still needed in order to assess the correlation of the *in vitro* and *in vivo* impedance results. Preliminary results performed on perfused rodent heart were very promising. Since these experiments, our group has also begun to test these electrodes in a rat epilepsy model. A comparison of the response at a polycarbazole (on stainless steel) electrode vs that at a conventional bare stainless steel electrode resulted in both higher signal amplitude and a faster response time (Figure 7.1)\(^1\).

In addition to assessing the range over which ohmic behavior can be achieved *in vivo*, further *in vivo* experiments will address the concerns regarding the biocompatibility and long-term performance of the device. The long-term performance can be assessed by the change (most likely an increase) of impedance magnitude and loss of frequency-independent behavior over a prolonged trial period. Tissue biocompatibility should be assessed by the survival of cells and/or gliosis around the insertion point of the electrode. Preliminary results suggested that PEDOP exhibits a statistically significant decrease in gliosis (Figure 7.2)\(^1\).

More conducting polymers should be investigated in order to broaden the potential application prospects and to further investigate the chemical basis of ohmic behavior. One of the polymers being currently investigated is poly(dibenzothiophene). This polymer is chemically related to polycarbazole as PEDOT is to PEDOP. The comparison should reveal insights into the role played by the chemical nature of the monomer in imparting ohmic behavior. Various
Electropolymerization approaches are currently being investigated in order to effectively produce adherent poly(dibenzothiophene) films.
7.1. Ictal activity as measured at PEDOP electrode after injection of PTZ.
7.2. Astrocyte reaction to various polymers implanted in striatum. GFAP stain as described above. Magnification: 20X
7.3. References

(1) C. Sweeney, unpublished results