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Conducting Polymer Electrodes for Thermogalvanic Cells

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Description of the cover image:

The illustration of the cover represents the PEDOT-PSS electrodes thermogalvanic cell designed by Kosala Wijeratne and Udani Karunaratne.

Conducting Polymer Electrodes for Thermogalvanic Cells

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During the course of research underlying this thesis, Kosala Wijeratne was enrolled in Agora Materiae, a multidisciplinary doctoral program at Linköping University, Sweden.

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To my Loving Family!

ABSTRACT

Fossil fuels are still the dominant (ca. 80%) energy source in our society. A significant fraction is used to generate electricity with a heat engine possessing an efficiency of approximately 35%. Therefore, about 65% of fossil fuel energy is wasted in heat. Other primary heat sources include solar and geothermal energies that can heat up solid and fluids up to 150°C. The growing demand and severe environmental impact of energy systems provide an impetus for effective management and harvesting solutions dealing with waste heat. A promising way to use waste heat is to directly convert thermal energy into electrical energy by thermoelectric generators (TEGs). Solid state TEGs are electronic devices that generate electrical power due to the thermo-diffusion of electronic charge carriers in the semiconductor upon application of the thermal field. However, there is another type of thermoelectric device that has been much less investigated; this is the thermogalvanic cell (TGCs). The TGC is an electrochemical device that consists of the electrolyte solution including a reversible redox couple sandwiched between two electrodes. In our study, we focus on iron-based organometallic molecules in aqueous electrolyte. A temperature difference (ΔT) between the electrodes promotes a difference in the electrode potentials [$\Delta E(T)$]. Since the electrolyte contains a redox couple acting like electronic shuttle between the two electrodes, power can be generated when the two electrodes are submitted to a temperature difference. The focus of this thesis is (i) to investigate the possibility to use conducting polymer electrodes for thermogalvanic cells as an alternative to platinum and carbon-based electrodes, (ii) to investigate the role of viscosity of the electrolyte in order to consider polymer electrolytes, (iii) to understand the mechanisms limiting the electrical power output in TGCs; and (iv) to understand the fundamentals of the electron transfer taking place at the interface between the polymer electrode and the redox molecule in the electrolyte. These findings provide an essential toolbox for further improvement in conducting polymer thermogalvanic cells and various other emerging electrochemical technologies such as fuel cells, redox flow battery, dye-sensitized solar cells and industrial electrochemical synthesis.

Populär Sammanfattning

Fossila bränslen är fortfarande den dominanta (ca 80 %) energikällan i vårt samhälle. En betydande del av den energin används för att producera elektricitet med värmemaskiner vilka ofta har en verkningsgrad på omkring 35 %. Alltså förloras ungefär 65 % av den fossila energin i spillvärme. Andra stora värmekällor är sol- och geotermiska energier vilka kan värma upp material och vätskor upp till 150°C. Den ökande efterfrågan på energi och den betydande påverkan energisystem har på miljön skapar en drivkraft att finna lösningar där energin i spillvärme kan tas tillvara. En lovande metod är att direkt konvertera den termiska energin i spillvärmens till elektricitet med hjälp av termoelektriska generatorer (TEGs). TEGs genererar elektrisk energi från den termodiffusion av laddningsbärare som uppstår i en halvledare som utsätts för en temperaturskillnad. Det finns dock en typ av termoelektriska generatorer som inte är speciellt utforskade, nämligen termogalvaniska celler (TGCs). TGCs har elektrokemisk funktion och består av en elektrolyt, innehållande ett reversibelt redox-par, placerad emellan två elektroder. I vår studie har vi fokuserat på järnbaserade organisk-metalliska redox-par i vattenbaserad elektrolyt. En temperaturskillnad (ΔT) mellan elektroderna ger en skillnad i elektrisk potential [$\Delta E(T)$]. Eftersom elektrolyten innehåller ett redox-par som fungerar som en elektronisk förbindelse mellan de två elektroderna, kan elektricitet utvinnas då elektroderna utsätts för en temperaturskillnad. Fokus för denna avhandling är (i) att undersöka möjligheten att använda ledande polymerer som elektrodmaterial i termogalvaniska celler som ett alternativ till platina- och kolbaserade elektroder, (ii) att undersöka betydelsen av elektrolytens viskositet i syfte att utvärdera polymerbaserade elektrolyter, (iii) att förstå mekanismerna som begränsar utteffekten i TGCs; och (iv) att på djupet förstå den elektronöverföringen som sker mellan polymerelektroden och redox-paret i elektrolyten. Dessa resultat utgör grundläggande verktyg för vidare förbättring av termogalvaniska celler baserade på ledande polymerer och även en mängd andra lovande elektrokemiska tekniker så som bränsleceller, flödesbatterier; Grätzelsolceller och industriell elektrokemisk syntes.

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II Publications

LIST OF PAPERS

Paper A

Kosala Wijeratne, Mikhail Vagin, Robert Brooke, and Xavier Crispin, Poly(3,4-ethylenedioxythiophene)-tosylate (PEDOT-Tos) electrodes in thermogalvanic cells, Journal of Material Chemistry A, 2017, 5, 19619–19625

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Paper B

Kosala Wijeratne, Ujwala Ail, Robert Brooke, Mikhail Vagin, Xianjie Liu, Mats Fahlman and Xavier Crispin, Bulk electronic transport impacts on electron transfer at conducting polymer electrode-electrolyte interfaces, Proceedings of the National Academy of Sciences of the United States of America (PNAS), 2018,

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Paper D

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Papers not included in Thesis

Anton Volkov, **Kosala Wijeratne**, Evangelia Mitraka, Ujwala Ail, Dan Zhao, Klas Tybrandt, Jens Wenzel Andreasen, Magnus Berggren, Xavier Crispin, and Igor V. Zozoulenko, Understanding the Capacitance of PEDOT-PSS Advanced Functional Material, 2017, 28, 1700329

Canyan Che, Mikhail Vagin, **Kosala Wijeratne**, Dan Zhao, Magdalena Warczak, Magnus P. Jonsson and Xavier Crispin, Conducting polymer electrocatalysts for proton-coupled electron transfer reactions: towards organic fuel cells with forest fuels, Advanced Sustainable Systems, 2018, 2, 1800021

Robert Brooke, Juan Felipe Franco-Gonzalez, **Kosala Wijeratne**, Eleni Pavlopoulou, Daniela Galliani, Igor V. Zozoulenko, Xavier Crispin, Vapor phase polymerized Poly(3,4-ethylenedioxythiophene)-trifluoromethanesulfonate (PEDOT-OfT) as transparent conductor material, Journal of Material Chemistry A, 2018

Fei Jiao, Dan Zhao, **Kosala Wijeratne**, Simone Fabiano and Xavier Crispin, From Heat to Electricity: A Review of Different Thermoelectric Concepts

Manuscript

Kosala Wijeratne, Ujwala Ail, and Xavier Crispin, Electron Transfer Kinetics on Single and Multilayer Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) electrodes and application in Thermogalvanic cells

Manuscript

Part I

Background

CHAPTER

Introduction

1.1. Motivation and Research Background

The discovery of electricity has revolutionized human history; it brought the human lifestyle to a new era. From that time scientists were able to find new methods to generate electricity, but also, new ways to utilize it. Together with the world population growth, the demand for electricity increases exponentially with time. Heat engines produce electricity from fossil fuel. Hydroelectric generators produce electricity from water motion. Both fossil and water are the primary power generation sources for many years. Hydroelectric conversion is one of the cheapest and cleanest power generation methods. However, hydroelectricity cannot stand alone to deliver the current energy demand. Indeed 65 % of the electrical energy comes from thermal power plants run by fossil fuel which creates a significant impact on the environment. The conversion efficiency of fossil fuel into a useful energy form is about 35 %, therefore a substantial amount of energy, 65%

is wasted as heat (1, 2). About 50 % of the waste heat is counted as low-temperature heat (< 250 °C) coming from power plants, industries, automobiles, and household appliances. Another primary source of low-temperature heat is from nature through solar radiation and geothermal sources. Due to the growing population, economy, and climate change, considerable attention and development have been made in green energy harvesting technologies. Scientists are exploring the possibility to reduce the CO_2 emission by harvesting energy from waste heat. Solid state thermoelectric devices have been investigated for direct conversion of thermal energy to electrical energy. A thermoelectric generator (TGE) is an electronic device based on semiconductors or semimetals such as bismuth telluride (3). Their applications are limited due to low performance relative to the cost. A thermogalvanic cell (TGC) emerges as yet another class of heat to electricity conversion device. It is an electrochemical cell that consists of two conducting electrodes in contact with reversible redox electrolyte. A temperature difference across the electrolyte promotes a difference in electrical potential between the two electrodes (4). Electrical power is generated by connecting the electrodes to an external load while maintaining a temperature gradient between two electrodes. A TGC can operate in both aqueous (5) and a non-aqueous electrolyte (6) and displays Seebeck values as high as 2.9 mV/K . A high Seebeck coefficient is the advantage of TGCs over the solid state TEGs. In addition to that, the electrolyte can maintain a high-temperature difference between the electrodes due to its low thermal conductivity. However, there is no commercial application due to the low energy conversion efficiencies and low areal power out over the cost of TGCs. The cost is both related to the materials used as well as the manufacturing methods.

Platinum is the most studied electrode material for TGCs application due to its high electrocatalytic activity, high conductivity, corrosion resistivity, etc. However, the price of the platinum limits its application in TGCs. Recent studies have shown that carbon-based materials are a promising electrode material for TGCs (7). A power generation of 12 W/m^2 using activated carbon cloth as an electrode material (8).

Conducting polymers constitute another class of material that could potentially serve as an electrode in TGC, but no one has studied that possibility. The discovery of conducting polymer was made in the 1970's by Alan Heeger, Alan G. MacDiarmid, and Hideki Shirakawa by doping the polymer polyacetylene with halogens. Since then those organic synthetic metals were

considered in the different application including, energy generation, energy storage, catalyst, biosensing device, electronic devices, etc. Conducting polymers can be synthesized from solution, which is a crucial advantage over many inorganic materials since it enables the reduction of the manufacturing cost and expands the possibility of large-scale printing. In addition to this, conducting polymers combine other unique properties such as mixed ionic-electronic transport, electrochromism, transparency in its conductive state, and high abundance and low toxicity.

1.2. The goals of the Thesis

The goal of this thesis is to propose an alternative electrode material for thermogalvanic cells (TGCs). Up to now, platinum is the most common and well-studied electrode material for TGCs because of the high electrical conductivity, the absence of an insulating surface oxide, as well as a high electrocatalytic activity. However, the cost of platinum limits the potential mass implementation of TGCs as co-generators for waste heat or body heat harvesting. The researchers have been studied different materials, and currently, nanostructured carbon materials are the state-of-the-art electrode material for TGC applications. Conducting polymers constitute another promising class of material as an electrode in TGC. Indeed, they combine unique properties, such as moderately high conductivity (1000 S/cm) (9, 10), absence of insulating surface oxide layer, molecular level porosity, intrinsically transport both electronics and ionic charge carriers (11) and potential electrochemical catalytic activity (12). Moreover, they can be synthesized at low temperature by solution process (cost effective preparation) (13, 14) and they are composed of an atomic element of high abundance.

Our goal is to understand the electron transfer process between a conducting polymer or metal electrode, and a redox molecule in a liquid electrolyte. This includes varying the morphology, the thickness of the polymer electrode, as well as the viscosity of the electrolyte. We aim to correlate the bulk electronic and ionic transport within the polymer electrode and the electron transfer mechanism at the electrode-electrolyte interface. When building TGCs, we want to understand the mechanisms (charge transfer, mass transport, electrolyte resistance) that govern the performance of the generators.

1.3. Thesis Outline

The first section of the thesis presents the context and goals as well as the main results. Chapter 2 describes conducting polymers and their ability to conduct electricity. Chapter 3 is dedicated to the thermogalvanic cells (TGC) providing a state of the art and explanation of the chemical and physical mechanism governing the operation of those energy conversion devices. Chapter 4 introduces electrochemical methods and theories to explain the operation mechanism of the device. Chapter 5 is dedicated to the fabrication and characterization of materials and devices. Finally, Chapter 6 contains the conclusions and remarks.

1.4. Overview of the Publications

Paper A: Poly(3,4-ethylenedioxythiophene)-tosylate (PEDOT-Tos) electrodes in thermogalvanic cells

Summary – In this project, we demonstrate the use of a conducting polymer as electrodes in thermogalvanic cell (TGC) for the first time. We choose the conducting polymer poly(3,4-ethylenedioxythiophene)-Tosylate (PEDOT-Tos) because of its simple fabrication and high electrical conductivity (>1000 S/cm). We found that the generated power increases with the polymer electrode thickness. The power generated of thin film PEDOT-Tos TGC is the same order of magnitude as a flat platinum electrode. The novelty is that PEDOT-Tos act as both an electrochemically active electrode and the current collector.

Contribution: I contributed to the experiment design, performed most of the experimental work, wrote the first draft and contribute to the editing of the final manuscript.

Paper B: Heterogeneous electron transfer at Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) electrodes

Summary – In this project, we investigate the heterogeneous electron transfer between a conducting polymer electrode and a redox couple in an electrolyte. As a benchmark system, we use poly(3,4-

ethylenedioxythiophene) PEDOT and the ferro/ferricyanide redox couple in an aqueous electrolyte. We discovered a strong correlation between the electronic transport within the PEDOT electrode and the rate of electron transfer to the organometallic molecules in solution. We attribute this to the percolation-based charge transport within the polymer electrode directly involved in the electron transfer at the electrode-electrolyte interface. We demonstrate the impact of this finding when optimizing a thermogalvanic cell. The power generated by the cell increased by four orders of magnitude upon changing the morphology and conductivity of the polymer electrode. As all conducting polymers are recognized to have percolation transport, we believe this is a general phenomenon for this family of conductors.

Contribution: I contributed to the experiment design, performed most of the experimental work, wrote the first draft and contribute to the editing of the final manuscript.

Paper C: Effect of percolation paths in Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) on Organic Electrochemical Transistor performance

Summary – In this project, we investigate the connection between the conducting polymer morphology and the doping level on the OECT performance. We choose PEDOT-PSS as conducting polymer material and varies the morphology and the doping by introducing DMSO. The electrical conductivity measured at the dry state of PEDOT-PSS in different amount DMSO. Then the doping behavior was studied electrochemically under the wet condition for the same materials. OECTs were measured to understand the effect of the morphology. The study suggests that the PEDOT-PSS films formed with low DMSO content contains electrically isolated active material which does not take part in electrochemical doping/de-doping reactions. Further, the amount of DMSO also affects the characteristics of OECTs, with low DMSO OECTs having a stronger relative modulation than high DMSO OECTs.

Contribution: I contributed to the experiment design, performed most of the experimental work, wrote the first draft and contribute to the editing of the final manuscript.

Paper D: Role of the electrolyte viscosity in iodide/tri-iodide thermogalvanic cells

Summary – In this project, we investigate the effect of the electrolyte viscosity on the performance of the thermogalvanic cell. High viscous/gel-like electrolytes provide beneficial features in the application of TGCs over the low viscous/liquid electrolytes, including avoiding possible leakage and long-term stability are essential aspects in practical applications. However, the role of chemical environment (polymer matrix/solvent) remains poorly understood. Here, we study the thermodynamic and kinetic aspects of the Iodide/tri-Iodide redox reaction in viscous electrolytes. Different volume ratios of polyethylene glycol (PEG) dissolved in diethylene glycol monoethyl ether (DE) provides a solvent of varying viscosity and high solubility for the redox couple. The similar chemical environment of those solvent mixing reveals that the viscosity plays a crucial role in the performance of the maximum power output of TGCs. For iodide/tri-iodide redox couple, both the Seebeck coefficient and power output decrease with the increase of viscosity of the electrolyte.

Contribution: Contributed to the experiment design, performed some of the experimental work, wrote the first draft and contribute to the editing of the final manuscript.

2

CHAPTER

Conducting Polymer and Electronic Conduction

In general, saturated polymers, that possess single bonds between carbon atoms, are well known as insulating materials and are used around electrical cables. However, in the 80's A. Heeger, G. MacDiarmid, and H. Shirakawa discovered that the conductivity of unsaturated conjugated polymers significantly increased by oxidative doping with halogen: electrically conducting polymers were born. For this finding, they were awarded the Nobel prize in chemistry in 2000. The discovery of electrically conducting polymers lead to the emergence of the new research field of organic electronics. This class of materials combines the electronic properties of metals or semiconductors with chemical and mechanical properties of plastics (15).

Over the past decade, organic materials have been significantly improved and displayed potential applications in electronic and electrochemical devices over the conventional inorganic materials (2). This is mainly due to a combination of unique properties, low cost and high abundance,

processability from solution, mechanical flexibility, and chemical design of the electronic structure. Solution processability is one of the critical features of organic materials, which allows to easily fabricate thin films at low temperature by coating techniques (mostly at room temperature), as well as patterns on the various (flexible) substrates by printing techniques (16). In addition to that, due to the soft nature, organic materials can not only be used on flexible substrates but eventually on stretchable substrates, which expand further their applications in areas where inorganic materials cannot be used (17). The transparency or color of organic materials (conducting polymers) is another important property, which often can be controlled by varying the oxidation state of the polymer (18, 19). This property is known as electrochromism. It is the basic principle in the smart windows and smart screen/displays (19). There are many other applications which successfully demonstrate the integration of conducting polymers such as solar cells for light energy harvesting (9), organic light emitting diodes (20), and organic field effect transistors (21).

2.1. Conducting Polymer

Polymers are composed of long chains of repeating molecule units called as monomers. Monomer units are bound to each other via covalent bonds. The name ‘polymer’ originates from the Greek language where ‘poly’ means ‘many’ and ‘mer’ means ‘parts’. There are many natural biopolymers such as protein in food or cellulose in paper (22). There are synthetic polymers, such as polyethylene terephthalate (PET) and nylon, used in items for their mechanical, thermal, or dielectric properties. For many years, polymers were known to be insulating materials. However, there is a class of polymer which conducts electricity known as conducting polymers. A conducting polymer backbone is conjugated, that is, it consists of alternating single and double bonds between adjacent atoms (e.g., carbon, sulfur, nitrogen, oxygen) in the chain. Intrinsically, these polymers display poor conductivity. However, electrical conductivity can be enhanced by many orders of magnitudes through the introduction of charge carriers (electrons/holes) in the polymer chains. This process is known as doping, however, unlike inorganic semiconductors, doping of conducting polymer is not in ppm level instead per percentage level. Moreover, doping is associated with oxidation (p-doping) or reduction (n-doping) of the polymer chains. The charges carried by the polymers are stabilized by the counterions so that the polymer system remains neutral. Upon

doping, conducting polymer can reach conductivities as high as 10^3 S/cm, i.e., similar values as the indium tin oxide (ITO) glass used as a transparent electrode in optoelectronics (19).

2.2. Electronic Structure

The electronic band structure is a crucial feature to understand the properties of conducting polymers. It describes the energy states of the electrons within the material, and they are involved in the optical properties, electrical transport as well as chemical reactivities.

2.2.1. Atomic Orbitals

An atom consists of a positively charged nucleus (positively charged protons and neutral neutrons) surrounded by negatively charged electrons. The electron is described by the quantum mechanical wave function, $\Psi(x, t)$ and $|\Psi(x, t)|^2$ represents the probability of finding the electron at location x , relative to the nucleus, at the time, t . The solutions of the Schrödinger equation for an atom gives the wave function of the electrons in the atom (15). They are called atomic orbitals. These atomic orbitals are characterized by three quantum numbers. The first “ n ” is known as the principal quantum number, which describes the energy level of the electron and it has only positive non-zero integral values, $n = 1, 2, 3, 4, \dots$. The second quantum number is “ l ”, the orbital angular momentum quantum number which describes the angular momentum of the electron around the nucleus. It can be a zero or a positive integer but not larger than the principle quantum number, $l = 0, 1, 2, 3, \dots, (n - 1)$. The third one is “ m_l ”, the magnetic quantum number, which can have a negative or positive integer including zero. The possible values of the m_l is determined by l : $m_l = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l$. According to the Pauli principle, each orbital is occupied by a maximum of two electrons, and they must have opposite spin, spin up and spin down.

Orbitals having same n values are known as a shell, where, $n = 1$, is known as the K – shell, $n = 2$, is called as L – shell, $n = 3$, is called as M – shell, etc. the K – shell is the innermost shell and it has the lowest energy. Angular momentum of the orbital denoted as follows, $l = 0$ referred to as s – orbital, $l = 1$ referred to as p – orbital, and $l = 2$ referred to as d – orbital. As shown in

figure 2.1. s – orbitals are spherical shape, and p – orbitals are having two lobes separated by a nodal plan which passes through the nucleus.

Figure 2.1. (a) The atomic orbitals (s and p) of carbon and (b) The molecular σ orbital of carbon constructed by the overlap of two p_z and π orbital constructed by the overlap of two p_x . [adapted from (15)]

The energy of an electron increases with the shell number that is principal quantum number and the orbital type. To minimize the energy of the atom, electrons fill from the innermost shell to define the ground state of the atom. The electrons in the outermost shell are called valence electrons. These valence electrons are responsible for forming chemical bonds. The allowed energy levels, E_n of an electron in an atom having an atomic number, Z are proportional to $-\frac{Z^2}{n^2}$ (23). Since n is an integer, the electron has a discrete set of allowed energy levels. The electronic configuration of a carbon atom, which has six electrons, can be written as follows $1s^2 2s^2 2p^2$. The numbers denote the principal quantum number of the orbitals, the letter represents the orbital type, and the superscript number indicates the number of electrons of the respective orbital. There are four valence orbitals for carbon ($n = 2$), one is an s –orbital with $l = 0$ and $m_l = 0$, and the other three are p – orbitals with $l = 1$ and $m_l = -1, 0, +1$, respectively. Due to their different orientation in space and these orbitals are denoted as p_x, p_y, p_z (figure 2.1).

2.2.2. Hybridization

In general, the number of bonds formed by a given atom equals the number of unpaired electrons in the valence band. However, this not right in some cases. As an example, we consider the electronic configuration of the carbon atom in its ground state; $1s^2 2s^2 2p^1_x 2p^1_y$. It has two unpaired electrons in p orbitals. Therefore, it should just be able to form two bonds with other atoms. However, a carbon atom can form bonds with three or four other atoms, as in ethane, C_2H_4 , and methane, CH_4 . This can be explained according to the valence bond theory; an electron can be promoted to a higher energy level (24). If one of the 2s electrons is promoted to a 2p orbital, the electronic configuration of carbon becomes $1s^2 2s^1 2p^1_x 2p^1_y 2p^1_z$ with four unpaired electrons in different orbitals, which allows forming four bonds. According to the electronic configuration, three of the bonds should be formed by the p-orbitals, and the fourth bond formed by the s – orbital. This would lead to 2 types of bonds of different lengths and strength. However, this is not true in the case of methane, CH_4 where four hydrogen atoms bind with one carbon atom with four equivalent bonds. To explain this, the concept of hybridization is introduced, which also known as hybrid orbitals (figure 2.2.). The interference between the 2s and 2p orbitals result in four equivalent hybrid orbitals, known as sp^3 orbitals since they are formed by one s – orbital and three p – orbitals. A tetrahedral methane CH_4 molecule possesses a sp^3 hybridized carbon atom. Another case is when one s – orbital and two p – orbitals can form three equivalent sp^2 hybrid orbitals. Such sp^2 hybridized carbon has one remaining non-hybridized 2p orbital.

Figure 2.2. Hybridized Orbitals of Carbon. The orbitals with dotted outline/blue-yellow are non – hybridized p orbitals [adapted from (25)].

As seen in the figure 2.2., the sp^2 hybrid orbitals lie in a plane with a 120° degree angle in between each orbital. The p – orbital which does not participate in the hybridization is perpendicular to the plane. The next hybridization is sp -hybridization, in which one s – orbital and one p – orbital combine to form two sp hybridized orbitals. The sp hybridized orbitals lie on the same axis across the nucleus. The two unhybridized p – orbitals are in two planes perpendicular to each other (see figure 2.2). The hybridized orbitals can form a sigma bond with other atoms, whereas the non – hybridized p – orbitals can form a π bond.

Figure 2.3. The molecule (a) ethane consists only of 3 single bonds with two sp^3 carbons, (b) ethylene consist with a double bond with two sp^2 carbons and (c) ethyne has a triple bond with two sp carbons [adapted from (25)].

Most of the time, only one bond forms between two atoms in an occupied molecular orbital. However, there is a possibility to form multiple bonds between two atoms in a molecule, a double bond can form by occupying σ and π molecular orbitals. For example, all the bonds are single in ethane, formed by σ molecular orbitals (figure 2.3.a), whereas, ethylene has an additional π molecular orbital between the carbon atom that results in a double bond (figure 2.3.b), and ethyne has two additional π molecular orbitals between the carbon atom resulting in triple bonds (figure 2.3.c).

2.2.3. Molecular Orbitals and Chemical bonds

The number of bonds that can form around a carbon atom is four, but the type of bonds determines by the number of hybrid orbitals and the remaining p – orbitals. The electrons in the hybrid orbitals and the p – orbitals (*valence electrons*) can form a bond with the neighboring atom by interacting with its valence electrons. Then, the electron no longer belongs to one atom; these electrons are shared between two atoms. Therefore, these electrons are no longer assigned to a single atomic orbital but to a *molecular orbital* (MO) (24). MO's are linear combinations of the atomic orbitals (25). When these atomic orbitals, wave functions constructively interfere, there is a higher probability of finding the electrons in between the atomic nuclei. This combination of atomic orbitals forms so-called bonding molecular orbital, which has lower energy than the original atomic orbitals (24). Whereas for the other combination, the wave functions destructively interfere, which reduces the charge density and lower the probability of finding the electrons in between the atomic nuclei. Such a MO has higher energy than the original atomic orbitals and is an *antibonding molecular orbital* (denoted with a *) (24). The electronic ground state of a molecule is achieved when the electrons fill the molecular orbitals from the lowest level. To form a stable bond, the total energy of the molecule must be lower than that of the separated atoms. The highest energy level that contains electrons is called the *highest occupied molecular orbital* (HOMO). The lowest energy level without electrons is known as *lowest unoccupied molecular orbital* (LUMO), and the gap between the HOMO level and the LUMO is the band gap (figure 2.4).

2.2.4. Electronic Structure of the conjugated polymer

A conjugated polymer is a polymer chain which consists of alternating double and single bonds. The simplest conjugated polymer is trans-polyacetylene (C_2H_4)_n that contains only sp^2 hybridized carbon atoms (figure 2.4). Each carbon atom binds to three other atoms to form three sigma bonds, two of which are formed with hydrogen and one with the neighboring carbon atom. The unhybridized p – orbitals of the carbon atoms are perpendicular to the plane of the carbon chain and bonds with the adjacent carbon atom to form a π bond. The π orbital has a high probability density above and below the plane of σ - molecular orbitals. Therefore π -electrons can move along the carbon chain (15), to give further electronic interaction (figure 2.4.), resulting in additional bonding and antibonding orbitals across the polymer. As the number of carbon atoms in the backbone of a conjugated molecule increases, the number of π -electrons increases, and the energy levels of the π and π^* orbitals split further.

Figure 2.4. The energy diagram of the formation of π orbitals of polyacetylene of different length [adapted from (24, 25)].

For a large number of carbon atoms in a polymer chain π and π^* bands are formed. The π -band is also called the valence band, and the π^* -band is called the conduction band according to the

terminology used in conventional semiconductors. As an example, C_2H_4 has only one π and one π^* level. However, two π and two π^* levels are found for C_4H_6 and $\frac{n}{2}\pi$ and $\frac{n}{2}\pi^*$ levels for a polyacetylene chain of n carbon atoms (figure 2.4). As the length of the carbon chain increase, the HOMO and LUMO levels approach each other which translates into a reduction of the band gap. In the case of polyacetylene, all the bonding orbitals are filled with electrons and the anti- orbitals remain empty. Therefore, the top energy level of π energy levels match with the HOMO and, the lowest energy level of π^* energy levels match with the LUMO (24). The filled π band and the empty π^* band considered as valance band and conduction band respectively. If the single and double bond lengths were equal in a conjugated polymer, the band gap would disappear for an infinitely long polymer chain like in metals. However, according to Peirl's theory, a polymer chain with alternating single and double bonds is more stable than a chain with equal bond length. Hence a semiconducting state is more stable than a metallic state for conjugated polymers. Conducting polymer typically has a band gap between 1 eV to 4 eV (26).

2.2.5. Charge carriers and Doping

Conjugated polymers possess a wide range of conductivities. They can be as poorly conducting as a typical insulator ($< 10^{-7}$ S/cm) or as conducting as bad metals ($< 10^4$ S/cm) (Figure 2.5). Between those two cases, the conductivity can be tuned by doping.

Figure 2.5. Conductivity state of some conducting polymer compares with metallic, semiconductor and insulators [adapted from (27, 28)].

To increase the free charge carriers (electrons or holes) of a semiconductor, a suitable impurity element, (29) known as dopants, is introduced in the lattice structure of the semiconductor. A dopant atom can act as an electron donor or acceptor which resulted in new conduction band with mobile charge carriers. Also, the doping allows adjusting the conductivity and the position of Fermi level of the semiconductor. Similar to conventional inorganic semiconductors, organic semiconductors can be doped by introducing electron donors or electron acceptors. However, doping of organic semiconductors is different from the conventional semiconductor doping; it is either partial oxidation or partial reduction of polymer with the charge transfer between the polymer and dopant (30). Electron transfer from polymer to dopant is identified as p-doping, where the polymer is oxidized due to the removal of an electron from the polymer backbone, leaving a positively charged on the conjugated system. On the other hand, electron transfer from dopant to polymer is known as n-doping, and the polymer is reduced due to the addition of an electron into the polymer backbone by creating a negative charge carrier. Doping of organic semiconductors can be achieved by two processes, chemical doping, and electrochemical doping. P-type conducting polymers are dominating in device applications due to high stability in ambient conditions whereas, n-type conducting polymers often suffer from instability due to spontaneous oxidation by dioxygen (31). As described above, doping of conducting polymer introduces charge carriers, which results in a reorganization of carbon bonds, coupled with localized lattice deformation and charge trapping entities according to the nature of conducting polymer (32). As a result of such a deformation, a quasi-particle is created, which is referred to as soliton in the case of a degenerate ground state energy and as polaron in the case of non-degenerate ground state energy (33).

Trans-polyacetylene is a conducting polymer that has a degenerate ground state. It means that by changing the alternation in the bond length pattern (adjacent single and double bonds and changed to double and single bonds), the energy of the molecular system remains same. These two different structures of trans-polyacetylene have the identical energy (24), i.e., the equal probability of occurring and can thus coexist in two domains on the same chain. This creates a transition region between the two domains (with different bond length alternation), which is associated with an unpaired electron, and it is known as a soliton (25, 34). A soliton introduces a new energy level (for the unpaired electron) in the middle of the intrinsic polymer band gap. A soliton defect is neutral and present in chains of uneven numbers of carbons. The soliton can be charged negatively or positively by reduction or oxidation (figure 2.6).

Figure 2.6. Three different solitons in Trans polyacetylene[adapted from (16)].

However, most of the conducting polymers have a non-degenerate ground state, and the alternation of single and double bonds changes the polymer energy. A typical example is a polythiophene, where the two configurations are its aromatic and quinoid forms. The aromatic form (figure 2.7.a) has lower energy than the quinoid form (24) (figure 2.7.b). Introduction of a positive charge into the polymer creates a local conformational change from the lower energy aromatic structure to the higher energy quinoid structure. This structural deformation due to the auto-localization of the charge introduced is known as polaron (35) (figure 2.8.). Its energy spectrum is characterized by two new energy levels within the intrinsic band gap of the semiconducting polymer. Two polarons located close to each other can form a single bi-polaron defect, which is energetically more favorable than the two separate polarons (35). Polarons can be either positive or negative depending on the charge introduced into the conducting polymer (figure 2.8.).

Figure 2.7. (a) The aromatic form of polythiophene, where the double bonds are inside the ring, (b) the quinoid form of polythiophene [adapted from (24)].

Figure 2.8. Positive and negative polaron and bi-polaron of polythiophene [adapted from (27, 36)].

In a neutral conjugated polymer, the lowest electronic transition has the excitation energy corresponding to its band gap, typically in the UV and visible light region (UV-Vis), and it is highly involved in the definition of the color of the polymer (16). However, upon removal of electrons from the top of the valence band (or addition to the bottom of the conduction band), a polaron/bipolaron is formed. The quinoid geometrical structure of the polaron is characterized by one energy level higher than the valence band and one lower than the conduction band. New electronic transitions become possible due to these two new energy levels appear in the band gap of the doped conjugated polymer. Therefore, new absorption peaks appear at lower transition energies, in the visible and near infrared (VIS-NIR) parts of the spectrum leading to color changes (37).

Figure 2.9. Illustration of the generation of positive polaron and bipolaron of PEDOT and the energy level of the respective state of PEDOT [adapted from (16)].

The electrically conducting state of conducting polymers requires delocalized charges along the conjugated backbone(38). A peculiar case is that of polyaniline where the positive charge is introduced in the π -electronic system by a proton attached on the nitrogen. The positive charge of the proton ends up in the π -electronic system. This is the case of acid doping. In the case of PEDOT, the conductive state is achieved by redox doping. Here, the role of the PEDOT is to carry the charge of the electrically conductive state of PEDOT (oxidized PEDOT) whereas counter ion balance the charge (38). Figure 2.9 illustrates the oxidative doping of PEDOT. An electron is removed from the polymer chain which leads to a positive polaron characterized by an energy level in the band gap. To keep electroneutrality in the material, one negative counter ion balances ($A^- = Cl^-, PSS^-$), the positive charge carried by the polymer chain. The PEDOT chain can be further oxidized by removing two electrons and obtain the bi-polaron defect delocalized on few monomer units and neutralized with two anions. The chemical nature of the counterion can affect the morphology, packing, and conformation of the PEDOT chains; which leads to variation in conductivity levels (38-40). However, the conductivity of PEDOT does not only depend on the counterion, but also on the fabrication and processing conditions. The electrical conductivity of PEDOT-PSS can be tuned from 0.001 S/cm to 1000 S/cm with those various phenomena.

Figure 2.10. Optical absorption spectroscopy of PEDOT [adapted from (13)].

Three redox states of PEDOT, namely, bi-polaron, polaron and neutral can be probed by the optical absorption spectroscopy. These three different states show absorption at different wavelengths ranging from UV-Vis-NIR. Neutral PEDOT displays absorption around 600 nm, polaron state absorption around 900 nm and bi-polaron state show broad absorption in the infrared region (from 1250 nm and above) (see figure 2.10) (13).

2.2.6. Charge Transport

In general, in semiconductors, a current flow can be observed by applying an electric field or/and when there is a charge carrier concentration gradient. The total current is a combination of drift and diffusion currents (41); (see equation 2.1)

$$j = en\mu E - eD\Delta n \quad 2.1$$

Where, e is electron charge, n is charge carrier concentration, μ is mobility, E is electric field and D is diffusion coefficient.

In phenomena without light generation of carriers, the current is dominated by the drift mechanism. Therefore, the mobility is a crucial parameter for charge carrier in organic semiconductors/conducting polymers (equation 2.2 & 2.3) and the conductivity of organic semiconductors/conducting polymers can be expressed as follows including the mobility (42) (see equation 2.4);

$$j = en\mu E \quad 2.2$$

$$j = \sigma E \quad 2.3$$

$$\sigma = en\mu \quad 2.4$$

Soliton, polarons, and bi-polarons are the charge carriers in conducting polymers, and they can move both along a single polymer chain and jump between different polymers chains or polymer segments. At the macroscopic level, the transport is limited by the slowest phenomenon. In the case of organic conductors, the jump between the polymer chains/polymer segment, known as the intermolecular transfer is the limiting factor. Charge transport in disordered conducting polymers

can be described via phonon-assisted hopping between localized sites(43, 44), while for highly ordered conducting polymers band transport model applies (42). Charge transport also depends on several factors including polaron formation energy, the orbital coupling between polymers and energetic and spatial disorder (45).

The charge carriers are transported by hopping from state to state by thermal activation or tunneling, resulting in transport known as variable range hopping, with conductivity described as follows: (45, 46)

$$\sigma = \sigma_o \exp\left(\frac{E_c - E_{eq}}{k_B T}\right) \quad 2.5$$

where, E_c is the mobility edge energy, E_{eq} is the equilibrium energy and σ_o is the pre-exponential factor.

Figure 2.11. (left) Gaussian density of state. (right) Illustration of a high energy charge carrier that relaxes in the energy landscape made of localized electronic levels coming from adjacent molecular orbitals in organic material [adapted from (42)].

The probability of hopping transport is described by the Miller-Abrahams theory (47) of charge transport (equation 2.6) and depends on the distance, Δx and the energy difference, ΔE between two states and α is the inverse localization radius.

$$p \propto \exp(-2\alpha \cdot \Delta x) \cdot \exp\left(\frac{-\Delta E}{k_B T}\right) \quad 2.6$$

The transport energy level, E_T is the energy level to which the probability of charge carrier hopping is maximum (see figure 2.11). The variable range hopping transport model can be derived using the Miller-Abraham equations of transport, which can be described as follows, is the temperature and the dimensionality of the material.

$$\sigma = \sigma_o(T) \exp \left[- \left(\frac{T_o}{T} \right) \right]^{\left(\frac{1}{1+d} \right)} \quad 2.7$$

The variable range hopping model can reproduce the conductivity versus temperature of most conducting polymer samples at a low and medium temperature range (48-50). However, at high temperature (above room temperature), the transport is dominated by nearest neighbor hopping (48). In that specific case, one often finds that the conductivity is experimentally close to an Arrhenius behavior (48). The fundamental of nearest neighbor hopping transport mechanism is close in description to an electron transfer between two similar molecules. The fundamental physical ingredients that described the hopping step resemble those found in the Marcus theory of electron transfer (51, 52). The rate of hopping is related to the electron transfer rate constant, k given by an Arrhenius type function:

$$k = A \exp \left(\frac{-\Delta G^*}{k_B T} \right) \quad 2.8$$

$$\Delta G^* = \frac{\lambda}{4} \left(1 + \frac{\Delta G^o}{\lambda} \right)^2 \quad 2.9$$

Where, ΔG^o is the standard free energy of reaction, k_B is the Boltzmann constant, T is the temperature and λ is the reorganization energy term. The reorganization energy is consisting with two contributions, the inner reorganization energy, λ_{inner} and outer reorganization energy, λ_{outer} . The inner reorganization energy, λ_{inner} is associated with the intra molecular distortion occurring when the molecule becomes charged and the outer reorganization energy, λ_{outer} is associated with the change in molecular energy due to the inter molecular displacement and polarization (15). However, for organic semiconductors/conducting polymers, molecular displacement is negligible therefore the inner reorganization energy dominates (15). The polaron formation energy is considered as the charge reorganization energy, λ associated with the structural changes of the conducting polymer, hosting the charge, and the changes in the surrounding solid upon charge transfer from one molecule to another (45, 53).

2.3. Poly(3,4-ethylenedioxythiophene) – (PEDOT)

In the 1980s scientists at Bayer AG research laboratory in Germany developed a unique polythiophene derivative called poly(3,4-ethylenedioxythiophene), often abbreviated as PEDOT (54) (figure 2.12). Due to its high stability, high electrical conductivity in its oxidative state and solution processability, PEDOT is one of the most investigated conducting polymers. The poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) and poly(3,4-ethylenedioxythiophene)-tosylate are the most studied materials among the PEDOT family. Both materials contain unique properties which makes them attractive in device fabrication and fundamental studies.

Figure 2.12. The structure of poly(3,4-ethylenedioxythiophene) (PEDOT)

2.3.1. Poly(3,4-ethylenedioxythiophene) polystyrenesulfonate – (PEDOT-PSS)

The polymer blend PEDOT-PSS is the most widely used among all intrinsically conducting polymers due to its water processability, its high electrical conductivity (up to about 1000 S/cm) and good air stability (54). The chemical structures are presented in figure 2.13. The sulfonate-to-thiophene ratio is about 3 indicating an excess in PSS that is not involved in the neutralization of the positively charged PEDOT chains (55). The excess of PSS is introduced during the synthesis to provide a stable water dispersion of PEDOT-PSS negatively charged nanoparticles (56). This nano-suspension has excellent processing characteristic to fabricate thin, highly transparent and conducting films (57). However, PEDOT-PSS typically has a modest conductivity of about 1 S/cm, which limited its application though it is a water-dispersed polymer, unlike other PEDOT. Fortunately, the conductivity of PEDOT-PSS can be increased by several orders of magnitude

through a change of morphology. This morphological effect is called “secondary” doping, and it is not related to any change in oxidation level; it is thus distinguished to the “primary” doping, which is solely due to a tuning of the oxidation level of the polymer. In the secondary doping, a highly conducting state is obtained for PEDOT-PSS by adding inert high boiling solvents in the PEDOT-PSS water suspension. Examples of solvents are sorbitol, N-methylpyrrolidone (58), polyethylene glycol (PEG), dimethyl sulfoxide (DMSO) (59), and ionic liquids (50, 60). The possible simple explanation for the increase of conductivity is the phase separation of the excess PSS into nanodomains creating percolation paths of highly conducting PEDOT-PSS particles. This phase segregation occurs during drying the water solution since the high boiling point solvent remains last and reduces the Coulombic interaction between the positively charged PEDOT chains and the negative PSS counterions by a screening effect (60).

Figure 2.13. The structure of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS)

As mentioned in the above section, the electrical conductivity is due to the conjugated polythiophene backbone of PEDOT and the average mobility of the charge carrier. In the case of secondary doped PEDOT-PSS charge transport is promoted by hopping of charge along the π -

stacked PEDOT chains due to the small interchain distance (61). The morphological change in the PEDOT-PSS films due to the secondary doping is attributed to the change from the coil to the linear conformation of the chains. PEDOT is in the coil conformation in its water dispersion due to the Coulombic interaction between PEDOT and PSS. Though the coil conformation remains in the dry PEDOT-PSS layer, a post-treatment/pre-treatment with the high boiling point solvents can trigger a conformational change of linear or extended coil due to the partial removal of PSSH. The adjacent thiophene rings in the PEDOT polymer chains are oriented in the same plane for the linear conformation, which facilitates the delocalization of π – electrons over the polymer chains and improves the interchain packing due to the π - π interaction stabilization in the system (60). After the phase separation, PEDOT chains formed three-dimensional conducting network reorganize at the microscopic level by changing shape and/or improving the interchain packing due to π - π interaction stabilizing the system. Because of the π - π interaction between the chains, charge carrier mobility improves. As result of that, the linear conformation of PEDOT-PSS chains leads to high charge carrier mobility.

Besides the above mentioned method, many other approaches have been investigated for increasing the conductivity, post-treatment of PEDOT-PSS films with organic solvents (62), organic (63, 64) and inorganic acids (65) show better results than pervious method. Upon concentrated H_2SO_4 acid post-treatment, both a morphology changes and removal of excess of PSS ion take place within the PEDOT-PSS film, which leads to a conductivity reaching as high as 4400 S/cm (65). In the presence of H_2SO_4 , the negative charged PSS ion interacts with H^+ from H_2SO_4 to form a neutral species PSSH (66) due to the higher pka value (-6.4) of H_2SO_4 than the PSSH. These neutral PSSH chains are not Coulombic interacting with the positively charged PEDOT chains and thus phase separate (66). Also, the PSS that was interacting with PEDOT is replaced by negative HSO_4^- ion. This ion exchange leads to a conformational change in the PEDOT chains. Since the electrical insulator polymer PSS is removed, the energy barrier for the charge transport in the material diminishes due to an efficient interchain and inter-domain packing (66).

The conductivity of PEDOT strongly depends not only the counter ion but also the fabrication methods and the processing conditions (38-40). As an example, PEDOT-PSS has conductivities ranging from 0.001 S/cm to 1000 S/cm due to the difference in the process in conditions (10, 60, 65-69) and PEDOT-Tos can have conductivity of 100 S/cm up to 9000 S/cm due to both the

difference in counterion and processing conditions (39, 40, 70-74). This behavior can be explained by studying the crystallographic and morphological structure of the PEDOT films. Grazing incidence wide-angle X-ray scattering (GIWAXS) has been extensively used to study the crystallographic and morphological structure of conducting polymers (71, 75-78).

Most of the conducting polymers are semi-crystalline, where the crystalline phase of high conductivity coexists with an amorphous phase of lower conductivity (76). Since the conductivity is related to the direction of π orbital overlap, a crystalline sample would display an anisotropic conductivity. High conductivity is observed along crystallographic axes and lower conductivity for the other directions. Therefore, it is essential to study the crystallographic data such as the degree of crystallinity, the size of the crystals and the orientation of the crystallites to understand the charge transport properties. There are two orientation of polymer chains in the crystalline nanodomains: i) the *edge on* orientation, which refers to the backbone chain with the $\pi - \pi$ stacking parallel direction to the substrate plane, ii) the *face on* orientation, refers as the $\pi - \pi$ stacking vertically direction to the substrate plane (perpendicular direction) (75, 76) (see figure 2.14). According to the GIWAXS data, pristine PEDOT-PSS has both edge-on and face-on orientation, but the overall intensity and the crystallinity are low which featuring amorphous or weakly ordered polymer aggregates (71, 75, 79). After introducing high boiling point solvent such as DMSO into the polymer, PEDOT chains reorient towards face-on nano-crystals; also, the crystallinity increased (80).

Figure 2.14. lamella structure of PEDOT [adapted from (42, 65)]

2.3.2. Poly(3,4-ethylenedioxythiophene) tosylate – (PEDOT-Tos)

The conductivity of PEDOT-Tos (figure 2.15) varies from 500 S/cm to 4000 S/cm which depends on the preparation technique. Vacuum vapor phase polymerization (VPP) and chemical polymerization (CP) are the most widely used fabrication methods for thin films. The high electrical conductivity (≈ 4000 S/cm) PEDOT-Tos thin films are fabricated by VPP (70, 81, 82). The polymerization takes place when the EDOT vapor comes in contact with the layer of the oxidant of iron(III) tosylate $[\text{Fe}(\text{Tos})_3]$ dispersed in a copolymer matrix of PEG-PPG-PEG. Typically CP methods provide lower conductivity values about 1000 S/cm (1, 13, 83). The significantly different conductivity obtained for the same oxidant and counter ion but different methods are due to the microscopic morphology and packing of the PEDOT chains.

Figure 2.15. The structure of poly(3,4-ethylenedioxythiophene) tosylate (PEDOT-Tos)

The mechanism of chemical polymerization of EDOT to its polymer is shown in figure 2.16. First, $\text{Fe}(\text{Tos})_3$ oxidizes the EDOT monomer to generate a cation radical. Next, a pair of radical cations dimerize, and the dimer is stabilized by removing two protons. This process is assisted with a base, which can be either Tos^- ion or free amine (pyridine) (84). After that, another $\text{Fe}(\text{Tos})_3$ oxidizes the

dimers, and these processes steps are repeated continuously to form the polymer (PEDOT) (85). In this thesis, PEDOT-Tos is synthesised by using $\text{Fe}(\text{Tos})_3$ as the oxidant and pyridine as a base inhibitor (85, 86). An amine such as pyridine increases the pH in the reaction medium. Subsequently the redox activity of $\text{Fe}(\text{Tos})_3$ is reduced due to the reduction of the redox potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in the presence of pyridine (according to the Nernst Equation)(84, 86). Because of this, reduction of Fe^{3+} to Fe^{2+} becomes difficult thereby the polymerization is kinetically controlled. It is well known that the direct oxidation using $\text{Fe}(\text{Tos})_3$ resulted in a poorly conducting polymer due to the high acidity of the $\text{Fe}(\text{Tos})_3$ (87). Therefore, the acidity of the reaction medium is controlled to maximize the conductivity of PEDOT-Tos.

Figure 2.16. Chemical polymerization mechanism [adapted from (88)]

In PEDOT-Tos, the molecular anion is small compared to the poly-anion PSS in PEDOT-PSS. This difference has substantial impact on the morphology. According to the crystallographic study (GIWAXS), unlike PEDOT-PSS, PEDOT-Tos exhibits nano-crystallites separated each other by a less ordered amorphous matrix (71). The absence of the amorphous polymer ion and the small size of the Tos promote a more densely packed crystalline structures characterized by lamella structures (89). The tosylate anions are located between the lamella formed by a π - π stack of PEDOT chains resulted in high conductivity (90, 91).

3

CHAPTER

Thermogalvanic Cell (TGC)

3.1. Fundamentals on Thermogalvanic cells

A thermogalvanic cell is an electrochemical device which consists of two identical electrodes in contact with a redox electrolyte (figure 3.1). The redox electrolyte is an electrolyte including of the presence of a reductant and an oxidant belonging to the same electrochemical half-reaction; moreover, this redox couple provides a reversible reaction at the electrode. A temperature gradient across the two electrodes generates a difference in electric potential (92). Power can be extracted by connecting two electrodes to an external load. The thermogalvanic cell is continuously generating power due to the transport of redox molecules by convection, diffusion, and migration between the two electrodes (93). For instance, reduced molecules are transported to the anode, where they are oxidized; consequently, those formed oxidized species are transported back to the cathode where they are reduced. This transport loop leads to a continuous reaction and a continuous current is generated by the thermogalvanic cell.

Figure 3.1. Schematic diagram of thermogalvanic cell

3.2. Thermogalvanic voltage

The thermogalvanic cell operation principle associated with the ferro/ferricyanide redox couple in an aqueous solution is sketched in figure 3.2. Here, a thermogalvanic cell consists of two half-cells. At the initial stage, both the temperatures at the electrodes and electrolyte are identical. Then the redox process occurs dynamically and reversibly but at a similar rate at both electrodes, such that there is no electric potential difference between the two electrodes (94).

Ferro/Ferricyanide redox reaction described;

The redox reaction is characterized by a reaction free energy (ΔG) composed of an enthalpic (ΔH) and an entropic (ΔS) contributions:

$$\Delta G = \Delta H - T\Delta S \quad 3.2$$

The relationship between free energy and the electrode potential is:

$$\Delta G = -nFE \quad 3.3$$

Figure 3.2. Schematic diagram of the Thermogalvanic cell at an isothermal condition [adapted from (94)].

We can thus rewrite the electrode potential as:

$$E = \frac{-(\Delta H - T\Delta S)}{nF} \quad 3.4$$

The first derivative with respect to the temperature provides the variation of electric potential upon a temperature gradient, which is the definition of the Seebeck coefficient;

$$S_e = \frac{dE}{dT} = \frac{\Delta S}{nF} \quad 3.5$$

Hence, the Seebeck coefficient for a redox electrolyte is directly related to the entropy variation upon the electron transfer.

Figure 3.3. Schematic diagram of Thermogalvanic cell operation under a temperature gradient [adapted from (94)].

In the expression above, the Seebeck coefficient is due to the electron transfer at two electrodes set at different temperatures. In reality, another phenomenon is also taking place in a temperature gradient: the Soret effect. The Soret effect is related to the thermodiffusion of matter. When matters are ions that carry a charge, the thermodiffusion leads to a concentration gradient of the ions, which result in an thermoelectric voltage. The more general expression of the Seebeck coefficient S_e of the redox electrolyte was proposed by Agar and Breck for steady state (95). On top of the entropy change during the electron transfer for the redox couple, there are entropies of transport originating from the Soret effect (1, 96).

$$nF \left(\frac{\partial E(T)}{\partial T} \right)_{t=\infty} = (S_{Ox} + \hat{S}_{Ox}) - (S_{Re} + \hat{S}_{Re}) - n\bar{\bar{S}}_e \quad 3.6$$

where n is the number of electrons involved in the redox reaction, and F is the Faraday constant S_A , and S_B is the partial molar entropy of species A and B, $\hat{S}_A$ and $\hat{S}_B$ are their Eastman entropies of transport, and $\bar{\bar{S}}_e$ is the transported entropy from the electrons in the metallic electrodes. The thermo-diffusion of the ions (Soret effect) is a slow process, and it takes a long time to reach the electric potential difference between a hot and cold electrode at steady state ($t=\infty$) (97). Therefore, it is reasonable to neglect the Eastman entropies and consider that the practical Seebeck coefficient in a thermogalvanic cell is close to that obtained at initial time. The Seebeck coefficient appears thus as difference in partial molar entropy of the species as obtained in equation 3.5.

$$nF \left(\frac{\partial E(T)}{\partial T} \right)_{t=0} = S_{Ox} - S_{Re} = \Delta S \quad 3.7$$

A large number of entropy variation upon redox reactions in aqueous medium have been measured (98). Very little is known on the entropy effect upon redox reaction in other solvents such as those considered in this thesis (ether and polymeric of various viscosities).

3.3. Redox Couples

The open circuit voltage of a TGC is determined by the Seebeck coefficient of the redox couple. From equation 3.6, the Seebeck coefficient originates from the change in entropy when the redox species is oxidized/reduced. The change in entropy is affected by several factors including the

geometrical structure of the redox couple, nature of the solvent (aqueous and non-aqueous), the interaction between redox couple and the solvent, and the charge of the redox couple (99). The sign of the Seebeck coefficient is attributed to the difference between the absolute charge of the oxidant and reductant (100). If the charge of the oxidant is larger than the reductant, the Seebeck coefficient is positive and vice versa (98, 100). This can be related to the reaction entropy with the temperature differential of Gibbs energy based on Born equation.

$$\Delta S = \frac{e^2 N}{2\epsilon r T} \frac{d[\ln(\epsilon)]}{d[\ln(T)]} (Z_{ox}^2 - Z_{red}^2) \quad 3.8$$

Where, e is elementary charge, N is the Avogadro number, ϵ is the static dielectric constant of solvent, r is the effective radius of the species, and the absolute charges of the oxidant and reductant, Z_{ox} and Z_{red} .

The choice of redox couples in TGCs is not only guided by a high Seebeck coefficient, but also by other features such as solubility, stability, electrochemical reversibility, and chemical abundance issues. Redox couples that have been studied for application in TGCs include inorganic, organic and radioactive redox couples in aqueous or non-aqueous electrolytes, displaying positive and negative values of Seebeck coefficient. For aqueous electrolytes, the highest values of S_e reported, -1.4 – -1.5 mV/K for $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ (92, 101, 102), 0.5 - 0.7 mV/K for $\text{Fe}^{3+}/\text{Fe}^{2+}$ (97, 103), 0.55 mV/K for I_3^-/I^- (104), 1.87 mV/K for $\text{Np}^{4+}/\text{Np}^{3+}$ (97), and -1.53 mV/K for $\text{Pu}^{4+}/\text{Pu}^{3+}$ (97). The values of S_e reported for non-aqueous electrolytes, 1.64 –2.19 mV/K for $\text{Co}^{2+/3+}$ tris(bipyridyl) redox couple (96, 105), 0.97 mV/K for I_3^-/I^- in Ethylammonium nitrate (EAN) (106), 0.81 mV/K for FeI_3 redox couple (107) and thiolate/disulfide organic redox couple (- 0.6 mV/K) (6).

Aqueous ferri/ferrocyanide [$\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$] redox couples is listed as the benchmark redox couple for TGCs due to its good stability in water and high exchange current density, yielding typical Seebeck coefficients of 1.4 mV/K. Seebeck coefficient of ferro/ferricyanide is slightly dependent on the concentration of redox couple and it remains constant above 0.1 M. Its maximum value of 1.72 mV/K is reported for infinitely diluted (5 mM) solutions (92). The high exchange current, which is typical of ferro/ferricyanide, is however limited by the solubility of potassium ferrocyanide, such that only solutions with concentration up to 0.4 M could be used for stable TGC applications. A recent study has successfully demonstrated high concentration (0.9 M) ferro/ferricyanide aqueous solution (8) by replacing the conventional $\text{K}_4\text{Fe}(\text{CN})_6/\text{K}_3\text{Fe}(\text{CN})_6$ with

$(\text{NH}_4)_4\text{Fe}(\text{CN})_6/\text{K}_3\text{Fe}(\text{CN})_6$. The modified ferro/ferricyanide redox couple provided Seebeck coefficients of 1.43 mV/K. Increasing the concentration from 0.4 to 0.9 M also resulted in a 66% increase in the ionic conductivity and a 5.7% decrease in the thermal conductivity of the electrolyte. Because of this improvement, TGC power generation increased by 50% (8).

Iodide/tri-iodide is yet another redox couple that is studied a lot for TGCs, and it has been studied in both aqueous and non-aqueous electrolyte (104). The Seebeck coefficient of the iodide/triiodide redox couple significantly depends on the concentration of the electrolyte and the solvent. It has been reported that the Seebeck coefficient of iodide/triiodide varies from positive to negative when the electrolyte nature changed (108, 109) as an example by changing the counter ion of an ionic liquid. TGCs based on ionic liquid electrolytes are one of the promising ways to harvest low-grade heat in the range of 100 - 150 °C. Abraham et al. has studied the Seebeck coefficients of the iodide/triiodide redox couple with different ionic liquids, at various concentrations, and over different temperature gradients (104). It was shown that iodide/triiodide, used in combination with ionic liquids, yields a Seebeck coefficient which is lower than with the corresponding water-based electrolyte. Further study of iodide/triiodide with ionic liquids showed a power output of 29 mW/m² when the TGC is operated with the hot side at 150 °C. Zhou et al. reported the highest Seebeck coefficient (2.0 mV/K) for iodide/triiodide redox couple in aqueous electrolyte. This was based on the encapsulation of triiodide ions in α -cyclodextrin (α -CD) which controls the local concentration of electroactive species, eventually leading to the high Seebeck values (110).

3.4. Power and internal resistance

The power generated by a TGC (equation 3.9) is not only determined by the Seebeck coefficient, S_e of the redox electrolyte, but also by the current I which is limited by the internal resistance of the device. The electrical current is transported in the device through several steps: (i) an electron transfer at both electrode-electrolyte interface, i.e from the redox couple to the electrode (oxidation) and from the electrode to the redox couple (reduction), (ii) the electronic transport through the electrode and the electrical contacts, (iii) the ionic transport through the electrolyte to keep the balanced charge upon electrochemical reaction at the electrode, (iv) the mass transport of the redox molecules toward (diffusion, migration, convection) (111).

$$P = \Delta E \cdot I = S_e \cdot \Delta T \cdot I \quad 3.9$$

Hence the redox molecules can be seen as a shuttle carrying an electron from one electrode to the other electrode. The internal resistance of the device will be limited by the slowest of those phenomena; which will depend on the kinetics of electron transfer (affected by the density of state of the electrode, the solvent, temperature, energy match of the redox couple, etc.), the concentration of supporting electrolyte, the concentration of redox couple, the distance between the two electrodes, the quality of the contact and the conductivity of the electrode. After we connect to an external load, current can be extracted, and the voltage within the cell adjusts according to the current and the external load (figure 3.4).

Figure 3.4. Schematic diagram of Thermogalvanic cell operation principle [adapted from (94)].

A TGC can be seen as a thermoelectric generator composed of an ideal potential source coming from the Seebeck effect (equation 3.10), that is in series with an internal resistance R_C (see figure 3.5 a). The current-voltage characteristics are thus given by (equation 3.11). Hence the slope of the $I - V$ gives the internal resistance. The power versus current is given by: (equation 3.12) and it is a parabola with a maximum. For such generator, the maximum power is when the load resistance is equal to the internal resistance and the power is then: (equation 3.13). Typical $I - V$ and $P - I$ curves are shown in figure 3.5 b. The $I - V$ curve is linear and the intercepts with the V - axis and I - axis are key parameters for the generator: The current at $V = 0$ is the short circuit current I_{SC} , while the potential at $I = 0$ is open circuit potential V_{OC} .

Figure 3.5. a) the equivalent circuit and b) $P - V$ curve of Thermogalvanic cell

$$V_{oc} = -S_e \Delta T \quad 3.10$$

$$V = V_{oc} - R_c \cdot I \quad 3.11$$

$$P = V_{oc} I - R_c I^2 \quad 3.12$$

$$P_{max} = \frac{V_{oc} I_{sc}}{4} \quad 3.13$$

There are three types of resistive phenomena that contribute to the internal resistance component, i) ohmic resistance, ii) charge transfer resistance and iii) mass transfer resistance (111-113).

The Ohmic resistance/overpotential consists with several parts, the bulk electrolyte resistance, the electrode resistance and the resistance due to the electrical connections. In most of the cases, ohmic resistance is dominated by the electrolyte ionic resistance R_I , can be expressed as follows;

$$R_I = \frac{L}{A \cdot \sigma} \quad 3.14$$

Where, L is the spacing between two electrodes, A is the cross-section area of the electrolyte volume sandwiched between the two electrodes, and σ is the ionic conductivity of the electrolyte. Electrolyte resistance can be reduced by using high concentration of redox electrolyte.

The charge transfer resistance R_{ET} at one electrode is associated with the kinetics of the electron transfer reaction at the electrode electrolyte interface (111), which is characterized by the exchange current, I_0 .

$$R_{ET} = \frac{RT}{A n F |I_0|} \quad 3.15$$

where A is the area of the electrode, I_0 is the exchange current for the electron transfer, R is the gas constant, n is the number of electrons transferred during the electrochemical reaction, F is the Faraday constant, T is the temperature. This resistive component is related to the activation energy necessary to transfer the electrons between the electrode and the redox molecules in solution. The exchange current is given by the Tafel equation coming from the Butler-Volmer expression of the electrochemical current:

$$\ln(I) = \ln(I_0) - \frac{\alpha n F \eta}{RT} \quad 3.16$$

where α is the charge transfer coefficient and η is the overpotential. For the ferri/ferrocyanide redox couple in aqueous electrolyte and a platinum electrode, R_{ET} can be smaller than 1Ω (99).

The mass transport resistance is associated with the transport of reactant from the solution to the electrode. Generally, the mass transport is governed by three different processes; diffusion, convection and migration. Mass transfer resistance is expressed as follows (111);

$$R_{mt} = \frac{RT}{n F |I_{lim}|} \quad 3.17$$

Where $|I_{lim}|$ is the limiting current obtained when the steady state current is limited by the diffusion of the reactant.

$$I_{lim} = \frac{n F A D c}{\delta} \quad 3.18$$

where A is the active electrode area, D is the diffusion coefficient of the electroactive species, c is the concentration of electroactive species and δ is the thickness of diffusion layer at the electrode (114). Theoretically, the maximum thickness of the diffusion layer is the inter electrode distance. But it is always less than that of the inter electrode distance because the convection is known to reduce the thickness of the diffusive layer (111).

The various resistive phenomena are electrically coupled in series in the TGC. The mass transport resistance is often larger than the charge transfer resistance using conventional metal electrodes and the ohmic resistance with high salt and redox couple concentration. Hence, the internal resistance of a TGC is dominated by the diffusion of the redox species at the electrode.

3.5. Figure of merit

A thermogalvanic cell is a type of thermoelectric generator. Traditional thermoelectric generators are solid state electronic devices whose efficiency is related to the so-called thermoelectric figure of merit (ZT) (2). This unitless parameter consists of electrical conductivity, thermal conductivity and Seebeck coefficient;

$$ZT = S_e^2 \frac{\sigma}{K} \quad 3.19$$

However, ZT mentioned above values couldn't directly apply to the TGC since other properties such as diffusion and concentration of the redox couple contribute to the performance of the device in addition to the electrolyte conductivity. T.J. Abraham et al. has modified the conventional ZT into a new form assuming the mass transport as the limiting phenomenon. (115)

$$ZT^* = \left(\frac{z^2 F^2}{R} \right) S_e^2 \frac{D_{Lim} c}{K} \quad 3.20$$

where, z is the charge on the ion, F is the Faraday constant, R is the gas constant, D_{Lim} is limiting the diffusion coefficient, and c is the concentration of the redox couple.

3.6. Conversion efficiency

The power conversion efficiency is another important parameter that determines the performance of a TGC and it can be expressed as the ratio between the electric power output and the thermal power input used in TGC;

$$\Phi = \frac{\text{Electrical Power Output}}{\text{Thermal Power Flowing through the cell}} \quad 3.21$$

The thermal power flowing through the TGC is largely dependent on the thermogalvanic cell design as well as the electrolyte. It can be expressed with the rate of the heat flow from the hot electrode to cold electrode induced by thermal conduction through the electrolyte and the rate of heat transfer induced by the electrochemical reaction.(116)

$$\frac{dQ}{dT} = KA \frac{\Delta T}{d} + \frac{IT \Delta S}{nF} \quad 3.22$$

where, K is the thermal conductivity of the electrolyte, A is the electrode cross-sectional area, ΔT is the thermal gradient across the distance, d between the two electrodes, I is the cell current, ΔS is the entropy of the cell reaction, n is the number of electrons transferred and, F is the Faraday constant. In practice, the second term is only few percents of the total thermal power and it can be neglected. Hence, in a first good approximation, the total efficiency is given by (102):

$$\Phi = \frac{V_{oc} I_{SC}}{4KA \frac{\Delta T}{d}} \quad 3.23$$

where K is the thermal conductivity of the electrolyte, A is the electrode cross-sectional area, ΔT is the thermal gradient across the distance d between the two electrodes, V_{oc} is the open circuit voltage and I_{SC} is short circuit current (102, 113). The short circuit current I_{SC} can be assumed to be limited by the most resistive phenomena among (i) R_{ET} , (ii) R_I and (iii) R_{mt} .

The efficiency can be expressed in terms of internal resistance R_C of the TGC and the Seebeck coefficient. If the internal resistance is limited by the conductivity σ of the redox electrolyte, it can be written:

$$\Phi = \frac{S_e^2 \Delta T}{4K} \left(\frac{d}{AR_c} \right) \quad 3.24$$

$$\Phi = \frac{S_e^2 \Delta T}{4K} \sigma \quad 3.25$$

where S_e is the Seebeck coefficient, R_c is the internal resistance and σ is the conductivity of the redox electrolyte. The above expression is obtained by considering the following relationships;

$$V_{oc} = S_e \Delta T \quad 3.26$$

$$I_{SC} = S_e \frac{\Delta T}{R_c} \quad 3.27$$

$$\sigma = \frac{d}{AR_c} \quad 3.28$$

It is difficult to compare the efficiency of TGC, when the different operating temperature used. However, this issue can be overcome by normalizing the power conversion efficiency (PCE) of a given device relative to a Carnot engine operating at the same temperature and temperature gradient.

$$\Phi_r = \frac{\text{PCE (Power conversion of TGC)}}{\text{PCE (Carnot engine operating at the same temperature)}} \quad 3.29$$

The efficiency of a TGC is expressed relative to the Carnot efficiency, where T_H is the hot electrode temperature;

$$\Phi_c = \frac{\Delta T}{T_H} \quad 3.30$$

$$\Phi = \Phi_c \frac{S_e^2 T_H}{4K} \sigma \quad 3.31$$

For flat platinum electrode, PCE relative to the Carnot efficiency, Φ_r of 0.50 % is reported (97, 117). However, different types of carbon nanostructured electrodes in TGCs enable to reach efficiencies as high as 1.4% (multiwall carbon nanotube electrodes) and 2.6 % (composite of single

wall carbon nanotubes and reduced graphene oxide electrodes) (7, 101). Carbon nanotubes and platinum nanoparticles decorated aerogel electrodes reached record high efficiency of 4.0 % relative to the carnot efficiency (118).

4

CHAPTER

Electrochemical Methods

Electrochemistry describes chemical reactions which involve an electron transfer at the interface between an electrode and reactant in an electrolyte. An electron transfer taking place through an interface is known as heterogeneous electron transfer; in contrast to redox process involving homogeneous electron transfer between species in the same phase. Electrochemical reactions are found in many applications such as energy conversion/storage, chemical/biochemical sensors, synthesizing materials, etc. (119). Electrochemistry can be divided into two distinct branches: firstly, *equilibrium electrochemistry*, is the study of electrochemical reaction with a steady state potential difference has built up between the electrode and electrolyte and no net current flows (120). It depends on many thermodynamic parameters such as reaction free energy, entropy, enthalpy, activities, and pH of the electrolyte (114, 121). The second branch is *dynamic*

electrochemistry, which study of the electron transfer reaction between an electrode and reactant, in which the current monitored as a function of applied voltage. Electron transfer process can be described by the general oxidation (right to left) and reduction (left to right) reactions as follows;

Where, *Ox.* is the oxidizing agent (oxidant, oxidizer), *Rd.* is the reducing agent (also called a reductant or reducer), and *n* is the number of electrons.

Figure 4.1. (a) A schematic diagram of electrochemical double layer, (b) the potential distribution across the electrode – electrolyte interface [adapted from (24, 45)].

Before studying the electron transfer, it is essential to understand the electrical properties of the interface between the electrode and the electrolyte since it enables and affects the electron transfer (122). Between a charged electrode and the electrolyte, an interfacial region called electric double layer (EDL) is formed (22). An EDL is formed due to a redistribution of the electrolyte ions and a reorientation of the solvent dipoles at the vicinity of the metal electrode surface to screen its charge and neutralize the interfacial region. Ions that are close to the electrode surface are attracted or repelled to the electrode to build up excess of anions or cations at the interface (see figure 4.1). An EDL is viewed as a capacitor and known as double layer capacitor, C_{dl} . The potential at which there is no double layer formed is the potential of zero charge where the electrode does not carry an excess of charges. Within the EDL, there is a large potential drop and the potential profile distinguish two regions.

The layer close to the electrode surface is known as the inner Helmholtz layer, typically inner Helmholtz layer is a monolayer where the solvent dipoles are directly in contact with the electrode surface. Then, it is Outer Helmholtz layer (OHL), which consists of ions of opposite charge compared to the charge on the metal electrode. The OHL goes through the plane formed by the attracted ions and the thickness of the OHL is limited to the ion's solvation shell and the monolayer of solvent. In some case the charge on the OHL is not enough to balance the charges on the metal, moreover there the Brownian motion in the liquid tends to disorganize the OHL (123). Hence, another layer is further formed that is called the diffuse layer, which consist with both type of ions with a high concentration close to the OHL but decreasing away towards the bulk of the solution. The potential drop across the electric double layer interface is shown in the figure 4.1.b and it is linear as in typical electrical capacitor in which two layers of charges are separated by a fixed distance. Finally, the diffuse layer potential exponentially decays with the distance.

When a reactant is coming at the proximity of the surface, its electronic energy levels are shifted by the potential drop in the electric double layer; which affects the rate of electron transfer with the metal electrode. In the case of equilibrium electrochemistry, the reduction and oxidation in the half-reaction take place at the same rate, this is characterized by the exchange current, and there is no net current. We open a small parenthesis to mention the case of dynamic electrochemistry with a

net current passing. In that case, one reaction (oxidation or reduction) is predominant at the electrode and the reactant is consumed at the vicinity of the metal surface. In that case, the current might be limited by the diffusion of the reactant towards the interface. This phenomenon is taking place in the diffusion layer; which has a thickness from 1 to 500 μm (figure 4.1).

After the equilibrium is reached, a potential difference is created at the electrode-electrolyte interface;

$$\Delta E = E_{\text{Electrode}} - E_{\text{Electrolyte}} \quad 4.2$$

Where, $E_{\text{Electrode}}$ is electrode potential and $E_{\text{Electrolyte}}$ is the electrolyte potential. It is impossible to measure the electric potential in the electrolyte without another electrode and this forms an electrochemical cell (114). However, addition of another electrode will introduce yet another potential difference. Therefore, one can use a standard electrode, known as reference electrode (RE) along with the working electrode (WE). A reference electrode is an electrode which has a stable and well-known electrode potential. Since the potential at the reference electrode is constant, the change in the potential at the WE can be monitored with respect to the RE (114):

$$E = (E_{\text{Electrode}} - E_{\text{Electrolyte}}) - \text{constant} \quad 4.3$$

The electrochemical cell potential is also known as the open-circuit voltage measured at equilibrium state; and there is no current passing through the cell. The potential only depends on the concentration of the oxidant and the reductant and it is described by the Nernst Equation (114, 121, 124);

$$E = E_o + \frac{RT}{nF} \ln \left(\frac{Ox.}{Rd.} \right) \quad 4.4$$

Where E is the equilibrium potential, E_o is the standard potential (well defined conditions P, T and measured compared to a reference electrode), R is gas constant, T is temperature, n is number of electrons involved in the reaction, F is faraday constant. $[Ox.]$ and $[Rd.]$ are the concentrations of oxidant and reductant at the electrode surface, respectively, which under equilibrium are equal to their bulk concentrations.

Figure 4.2. Pathway of a general electrode reaction and processes in an electrode reaction represent by resistances [adapted from (114)].

Figure 4.3. (a) Inner sphere electron transfer process (b) outer sphere electron transfer process [adapted from (125)].

To understand the overall reaction and the electron transfer process between the electrode and the electrolyte, the mechanism of electrochemical reaction can be considered in different steps where the conversion of an oxidized species into its reduced form. As seen in the figure 4.2, the current passing through the electrode, i.e. the overall electron transfer rate is governed by four major processes: (i) a mass transfer, i.e. the transport of the reactant towards the electrode surface, (ii) an electron transfer at the electrode surface, (iii) a chemical reaction at the vicinity of the electrode, and (iv) the adsorption/desorption or crystallization/electrodeposition processes (114). At an applied potential kept constant versus time, the magnitude of the steady state current is limited by the slowest process, called rate-determining process, since all the processes are in series. The current density is driven by the overpotential of the reaction, and it is considered as the sum of all the different reaction process overpotentials, (i) mass transfer overpotential, (ii) charge transfer overpotential, (iii) ohmic overpotential (due to bulk electrolyte resistance and other resistance) etc. All these reaction processes can be represented by a resistance which equivalent to a series of resistances, each originating from the above-mentioned processes (see figure 4.2).

All the studies in the thesis are related to the heterogenous electron transfer (HET) with a platinum electrode as benchmark that we compare with a conducting polymer electrode. HET can be divided in two different types. (i) An inner-sphere electron transfer occurs when there is a strong electronic coupling between the electrode and the reactant, e.g. in the case of a chemisorbed molecule on the electrode or through a chemisorbed anions (see figure 4.2.a), which provides a high rate constant (125). (ii) An outer sphere takes place when the electronic coupling is weak; which resulted in a slow kinetics of electron transfer. This is the case when the redox center of the reactant molecules is kept far from the electrode, e.g. when the redox center is separated from the electrode surface by a solvent layer (outer Helmholtz layer) (figure 4.2.b).

4.1. Dynamic Electrochemistry

In this thesis, dynamic electrochemistry is used to study the electrochemical processes involved in electrochemical devices that involves an electron transfer reaction between a conducting polymer electrode and a redox couple (e.g. ferro/ferricyanide or iodide/tri-Iodide).

4.2. Electrochemical Cell

An electrochemical cell is a device that consists of two half-cells in contact electrically. The energy devices are often grouped in two main families: energy generation/conversion, and energy storage. Fuel cells (126), dye sensitize solar cells, thermogalvanic cells (1, 8, 127), redox flow cells (128, 129) are examples for energy generation/conversion electrochemical devices. Supercapacitors(130, 131), pseudo capacitors (132), batteries (133-135) are examples of energy storage electrochemical devices. To understand the processes at the electrodes in those devices, it is desired to find a way to study the one electrode at a time. In dynamic electrochemistry we are interested in the faradic process that takes place only at one electrode, i.e., one half-cell reaction. We called the electrode under study, the working electrode – WE and a second electrode called counter electrode (CE) is introduced to the cell to complete the electrochemical cell. The CE is chosen such that the redox processes at that electrode does not interfere with the electrochemical mechanism at the WE. Therefore, usually an inert material such as platinum chose as CE. In addition to that, the CE should have larger surface area than the WE, to avoid limiting the overall current (114). Indeed, the current recorded or applied must be limited by the mechanism at the studied electrode. An ideal WE do not typically have a constant potential and cannot be considered as reference electrode. Hence, a practical electrochemical cell consists of three electrodes, WE with CE and a third electrode acting as reference electrode (RE) (figure 4.4.). A reference electrode is a non-polarizable electrode, i.e. it has no polarization (114). Its potential does not change from its equilibrium potential upon application of current. The reason for this behavior is that the electrode reaction is extremely fast (high exchange current). The electrode-electrolyte interface behaves like a resistor.

In a three-electrode system, the voltage of the WE is measured relative to the RE and the current is measured relative to the CE. The RE's are designed to deliver a constant voltage throughout the experiment, therefore, any changes in the applied voltage related to the WE, is read as follows:

$$E_{APP} = E_{WE} - E_{RE} - iR_S \quad 4.5$$

where, E_{APP} is the applied voltage, E_{WE} is the potential difference at the WE and solution, E_{RE} is the potential difference at the RE and the solution, i is the current and the R_S is the uncompensated resistance of the electrolyte. R_S can be minimized by increasing the ionic concentration of the

electrolyte, reducing the distance between reference electrode and the working electrode or chose smaller size (micro dimension) working electrode.

Figure 4.4. A schematic diagram of a typical electrochemical setup, reference electrode (RE), a counter electrode (CE) and the working electrode (WE).

Figure 4.5. The energy diagrams are showing charge transfer reactions between an electrode and a reactant molecule [adapted from (45)].

After introducing an electrode to a redox electrolyte, the electrode potential (related to the Fermi Level) equilibrates with the chemical potential (in between HOMO and LUMO level) of the redox couple as shown in the figure 4.5.a. At this point, there is no electron transfer, however, by applying sufficiently enough negative potential Φ , the electrochemical potential of electrode, ($\mu = E_F + \Phi$) becomes above the LUMO level of redox molecule. An electron transfer is thus possible from the electrode to the redox electrolyte (Figure 4.5.b). In this case, the redox molecule is reduced and repelled from the surface due to electrostatic repulsion. Similarly, a redox molecule can be oxidized by applying sufficiently enough positive potential. This reaction occurs when the electrochemical potential of the electrode is below the HOMO level. Then electron transfer takes place from the molecule to the electrode (Figure 4.5.c).

4.3. Faradic and Non-faradic Process

The current measured through the electrode in dynamic electrochemistry consists of two types of processes: faradic and non-faradic process. The faradic process contributes to an electron transfer between the electrode and the electroactive molecules in the electrolyte (114). The electroactive molecule can be either oxidized or reduced depending on the flow direction of the electrons. Non-faradic processes originate from absorption/desorption processes and changes in the interfacial structure/double layer as the potential varied. This is equivalent to charging/discharging current of the electric double layer, thus called capacitive current I_c :

$$I_c = AC_{dl} \frac{dE}{dt} = AC_{dl}v \quad 4.6$$

A is the area of the electrode, C_{dl} is the double layer capacitance, $\frac{dE}{dt}$ is the rate of potential variation also called the “scan rate” v . Both the faradic and non-faradic currents contribute to the overall current. Non-faradic/capacitive current contribution is significant for conducting polymer electrode due to their unique properties: they are mixed ionic-electronic conductor (136). Electrons and ions can completely reorganize in the bulk of the polymer electrode to provide a high capacitance. This introduces a complexity in dynamic electrochemical methods such as cyclic voltammetry; therefore, for some study we turn to steady state measurements. In those measurements, a constant

potential is applied, and the current is followed versus time until stabilization. At the early time, the capacitive current is present but after stabilization, it is only the faradic current that remains. The faradic contribution is determined by the following factors: (i) the rate of mass transport of the electroactive molecules to and from the electrode surface, (ii) the rate of the heterogeneous electron transfer between the electrode surface and the electrolyte, (iii) the rate of any homogeneous chemical reactions before and after the electron transfer. These essential topics will be discussing in coming sections.

4.4. Mass Transport

Upon electron transfer, the reactant is consumed at the vicinity of the metal surface and the electrolyte is thus locally depleted. As a result, the electroactive molecules must be transported from the bulk solution to the electrode surface. There are three types of transport processes, diffusion, convection, and migration. Diffusion is a process driven by Brownian motion with a force equivalent to the concentration gradient. This is the spontaneous movement of an electroactive molecule in the electrolyte from high concentration to the low concentration area (figure 4.6.a), which described by the Fick's first law (121):

$$J_D = -D \frac{dc}{dx} \quad 4.7$$

where, J_D is the flux due to the diffusion of the electroactive molecule with a concentration c in direction x . $\frac{dc}{dx}$ is the concentration gradient and D is the diffusion coefficient.

Figure 4.6. a) Diffusion, b) Convection and c) Migration process [adapted from (24)].

Convection involves mechanical force represented as the molecular motion of solvent molecules moving in a defined direction, that can transport along with the other minority species such as ions and electroactive molecules (137). There is two classes of convection, natural convection, governed by the variation in density of the fluids with temperature and gravitational convection triggered by a gradient of concentration.

Migration is described as the motion of a charged molecule/species due to the presence of an electric field (137). Upon applied a voltage to an electrochemical cell, an electric field is generated in the interfacial region between the electrode and the electrolyte; which triggers the migration of charged molecules towards the electrode.

The diffusion coefficient is a key parameter, which determines the transport properties of a species in an electrolyte system. It is defined as the rate at which redox molecule/ion moves down a concentration gradient (137). In the hydrodynamic theory, the diffusion coefficient is inversely proportional to the viscosity of electrolyte according to the Stokes-Einstein relation(138).

$$D = \frac{k_B T}{6\eta\pi r_H} \quad 4.8$$

Where, k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the medium, and r_H is the hydrodynamic radius of the species considered. For a charged atom or molecule, the hydrodynamic radius is often larger than the size of the charged species because solvent molecules form a solvation shell that follows the transported species.

4.5. Electrode Kinetics

We here introduce the basics of electrochemical kinetics using the approach proposed by Butler and Volmer (114). We consider the reaction:

The rate constant of the forward and backward (reduction and oxidation) reactions are k_{red} and k_{ox} and the respective currents can be expressed as follows (114);

$$i_{ox} = F A k_{ox} C_{ox} \quad 4.9$$

$$i_{red} = F A k_{red} C_{red} \quad 4.10$$

The total current flow for the reaction is;

$$i = i_{red} + i_{ox} \quad 4.11$$

$$i = F A (k_{red} C_{red} - k_{ox} C_{ox}) \quad 4.12$$

To complete the reaction, reactant (oxidant or reductant) should overcome an energy barrier, known as a transition state. According to the transition state theory, the rate of the reaction can be expressed as follows (114);

$$k_{red}^0 = A \exp \left[\frac{-\Delta G_{red}^*}{RT} \right] \quad \text{and} \quad k_{ox}^0 = A \exp \left[\frac{-\Delta G_{ox}^*}{RT} \right] \quad 4.13$$

where ΔG_{red}^* (ΔG_{ox}^*) is the free energy of activation for the reduction (oxidation) and A is the rate of collision of the electroactive species with the electrode surface. But this general expression used in chemical kinetics is lacking a feature. Indeed, the kinetic constant should also depend on the applied potential E . Hence, we should distinguish between the rate constant without applied potential (k_{red}^0) and with potential k_{red}^o . We will now describe the rate of electron transfer as a function of the electrode potential.

There is no current passing through the cell when the applied potential E is equal to the equilibrium potential E_o . However, if E becomes larger than E_o , electrolysis will become thermodynamically viable. The deviation from equilibrium potential is known as “overpotential”:

$$\eta = E - E_o \quad 4.14$$

Figure 4.7. Reaction coordinate diagram of the energy profiles for a heterogeneous electron transfer [adapted from (114)].

Figure 4.7. displays the evolution of the free energy versus the reaction coordinates. The reaction coordinate indicates the degree of evolution of a reaction from reactants to products. The energy profile (full line) indicates the evolution of the free energy when no external potential is applied. The plateau on the left-hand side corresponds to the free energy of the oxidant ($O + e^-$) without applied potential ($E = E_f^0$), and the plateau on the right-hand side corresponds to the reductant (R) (114). In this equilibrium potential the reduction and oxidation activation energies are ΔG_{red}^* and ΔG_{ox}^* , respectively. The energy profile in dashed line (bottom curve) is that of the reaction when the potential is applied E . The figure illustrates the effect of the applied potential E on the free energies of activation for oxidation (ΔG_{ox}^* becomes $\Delta G_{ox}^*(2)$) and reduction (ΔG_{red}^* becomes $\Delta G_{red}^*(2)$) for the electrochemical process.

When the potential is changed by ΔE to a new value E , the relative energy of the electron on the electrode changes as follows:

$$F\Delta E = -F(E - E_o) \quad 4.15$$

The applied potential affects the barrier for oxidation and reduction ($\Delta G_{ox}^*(2) < \Delta G_{ox}^*$) by a fraction of free energy given by $(1 - \alpha)$; where α is known as the charge transfer coefficient. When the oxidant comes at the vicinity of the electrode, it penetrates in the electric double layer and undergoes a shift in energy due to the electric potential in the double layer. Depending on the position of the oxidant in the double layer, it will undergo different potentials. The charge transfer coefficient is related to the fraction of the electric potential drop in the double layer that helps in lowering the free energy barrier for the electrochemical reaction.

Hence, the free energy for the activation barrier at the potential E is expressed as:

$$\Delta G_{ox}^*(2) = \Delta G_{ox}^* - (1 - \alpha)(E - E_o) \quad 4.16$$

$$\Delta G_{red}^*(2) = \Delta G_{red}^* + \alpha F(E - E_o) \quad 4.17$$

The rate constant at the potential E becomes;

$$k_{red} = A_{red} \exp \left[\frac{-\Delta G_{red}^*(2)}{RT} \right] \quad 4.18$$

$$k_{ox} = A_{ox} \exp \left[\frac{-\Delta G_{ox}^*(2)}{RT} \right] \quad 4.19$$

Combining equations 4.16 and 4.19 gives:

$$k_{red} = A_{red} \exp \left(-\frac{\Delta G_{red}^*}{RT} \right) \exp \left(-\frac{\alpha F(E - E_o)}{RT} \right) \quad 4.20$$

Combining equations 4.17 and 4.18 gives:

$$k_{ox} = A_{ox} \exp \left(-\frac{\Delta G_{ox}^*}{RT} \right) \exp \left(\frac{(1-\alpha)F(E - E_o)}{RT} \right) \quad 4.21$$

With equation 4.13, the above equations can be re-written as follows;

$$k_{red} = k_{red}^o \exp \left(- \frac{\alpha F (E - E_o)}{RT} \right) \quad 4.22$$

$$k_{ox} = k_{ox}^o \exp \left(\frac{(1-\alpha)F(E-E_o)}{RT} \right) \quad 4.23$$

Without applied potential, the barrier for oxidation and reduction is equal since the system is at equilibrium. Oxidation and reduction reactions take place simultaneously in a dynamic equilibrium. This means that the activation barriers are similar, and the rate of oxidation and reduction are equal since there is no net current. At the potential of zero charges, $k_{ox}^o = k_{red}^o = k_o$ is the rate of the exchange current, called standard rate constant.

Then the overall current equation 4.12 can thus be rewritten by including the equation (4.22) and (4.23), which leads to the Butler-Volmer equation (114, 139):

$$i = nFAk_o \left\{ C_o \exp \left[\frac{-\alpha nF(E - E_o)}{RT} \right] - C_R \exp \left[\frac{-(1 - \alpha)nF(E - E_o)}{RT} \right] \right\} \quad 4.24$$

The Butler-Volmer equation describes the current potential relationship for the reaction controlled by the rate of electron transfer. Importantly, the net current depends on the operating potential and the surface concentration of the redox couple. α is equal to 0.5 when both the oxidant and reductant concentration are equal at the surface of the electrode. There is no net current flowing, when $E = E_o$, at this moment the absolute magnitude at E_o is the exchange current (i_o), which is directly proportional to the standard rate constant.

$$i_o = nFAk_o C \quad 4.25$$

Then the Butler-Volmer equation can be written as follows;

$$i = i_o \left\{ \exp \left[\frac{-\alpha n F \eta}{RT} \right] - \exp \left[\frac{-(1 - \alpha) n F \eta}{RT} \right] \right\} \quad 4.26$$

Where η is the overpotential that is the extra potential beyond the equilibrium potential leading to the net current. For sufficiently large overpotential, one of the exponential terms will be negligible with compared to the other. As an example, at large negative overpotential the equation 4.26 becomes:

$$i = i_o \left[\exp \left[\frac{-\alpha n F \eta}{RT} \right] \right] \quad 4.27$$

Then;

$$\ln (i) = \ln (i_o) - \frac{\alpha n F \eta}{RT} \quad 4.28$$

Equation 4.27 is known as the Tafel equation. The Tafel plot is a $\log I$ Vs. η . It is linear only at high overpotential and by extrapolation of the linear portion of the Tafel plot to the zero overpotential gives the $\log i_o$ (137). Then by the equation 4.28, the standard rate constant can be calculated.

4.6. Voltammetry Methods

In voltammetry methods, a current response is investigated upon a varying voltage applied to an electrode. In this section, two different voltammetry methods are introduced.

4.6.1. Linear Sweep Voltammetry and Cyclic voltammetry

Linear Sweep Voltammetry (LSV) described as the measurement of current upon variation of the voltage at a fix scan rate from one voltage (E_1) to another voltage (E_2) for one direction, i.e., one sweep (figure 4.8). LSV mainly depends on electron transfer rate, chemical reactivity of electroactive species and the voltage scan rate (119).

Figure 4.8. a) a triangular potential waveform b) cyclic voltammetry of a capacitor/pseudo-capacitor and c) characteristic cyclic voltammetry for a typical redox reaction [adapted from (119)].

If the current is recorded additionally by scanning back the voltage from E_2 to E_1 , it is known as cyclic voltammetry (CV) (119). Cyclic voltammetry technique is extensively used in electrochemistry. It offers information on the kinetics of heterogeneous electron transfer reactions, on the thermodynamic properties of the electrode process; as well as the properties of the chemical reactions (119). In general, cyclic voltammetry is the first experiment to perform in an electrochemical analysis due to its capability to offer the location of the redox potential of a redox molecule. In CV, a triangular potential waveform (Figure 4.9.a) scans linearly (single or multiple cycles) the potential of a stationary electrode which is immersed in an electrolyte. The potentiostat measures the current resulting from the applied potential and the obtained current-voltage plot is known as cyclic voltammogram (Figures 4.9.b and 4.9.c).

Figure 4.9. a) A triangular potential wave form b) cyclic voltammetry of a capacitor/pseudocapacitor and c) characteristic cyclic voltammetry for a typical redox reaction [adapted from (45)].

This technique is popular because the peak shape and the peak position provide information about the electrochemical processes. Note that the ohmic drop (iR) (equation 4.5) presents in the solution can significantly distort the shape. There are two approaches to minimize the iR drop, (i) the working electrode is placed near the reference electrode; and, (ii) the concentration of the salt in the electrolyte is increased. Similar to other voltammetry techniques, CV enables the analysis of phenomena such as electron transfer, chemical reactivity of electroactive species, mass transport/diffusion process (122).

Figure 4.10. Cyclic voltammogram a) reversible waveform b) Quasi - reversible waveform and c) Irreversible waveform for a typical redox reaction [adapted from (120)].

The shape of the cyclic voltammogram help to classify if an electrochemical reaction is reversible, quasi-reversible or irreversible (figure 4.10). For a reversible process, the cyclic voltammogram shows an oxidation and a reduction peak potential close to each other and the redox potential (E_f^o) of the redox molecule is at or close to the halfway between the oxidation and reduction peak potentials (E_P^{Ox}, E_P^{Red}) (140). The shape of the reversible CV can be understood as follows: At first, the applied voltage is not enough to drive the electron transfer, therefore, there is no current measured. However, as the voltage swept to a positive direction, the current increases slowly, and then increased steadily and reached to maximum values due to the electron transfer to the reactant at the vicinity of the electrode surface. The reactant *Ox.* is consumed by the reduction, and its concentration decreases locally close to the electrode. This results in a decrease of current leading to a maximum. If the diffusion of reactant from the solution towards the electrode is slow compared to the scan rate, there is a total depletion of reactant and the current becomes zero. On the way back, the same behavior is observed but this time, it is the *Red.* form that is oxidized (figure 4.10.a).

An analysis of the peak shape and peak position enable to classify if an electrochemical reaction is fully reversible. Indeed, here are the features of such a reaction (141): (i) the separation between the oxidation and reduction peaks is given by $\frac{58 \text{ mV}}{n}$ (n is the number of electrons) at 298 K, (ii) the peak separation is independent on the scan rate; (iii) the oxidation and reduction peak current increases with scan rate and is linearly proportional to the square root of scan rate for diffusion limited process; (iv) the oxidation and reduction peak current ratio equals to one and it is independent on the scan rate. Note that as the scan rate increases, the depletion of redox species at the electrode surface becomes dominant (120). This results in a small diffusion layer and thus a high concentration gradient is created thus promoting an efficient diffusion transport (equation 4.7) (119). Therefore, the flux of redox species increases towards the electrode which increases the peak/faradic current.

In the case of a quasi-reversible process, CV shows (figure 4.10.b) oxidation and reduction peaks away from each other, and the formal potential (E_f^o) of the redox molecule is not close to the halfway between the oxidation and reduction peak potentials (E_P^{Ox}, E_P^{Red}). The shape of the CV for a quasi-reversible process can be understood the same way as reversible case, but the electron transfer rate is not fast enough to maintain the Nernstian equilibrium. Other features are that (i) the peak current is smaller compared to the fully reversible reaction, (ii) the peak separation varies

with the scan rate, and (iii) the peak current is not linearly proportional to the square root of the scan rate.

For an irreversible reaction, a broad CV shape and a small peak current are observed (Figure 4.10.c). Though the formal potential (E_f°) is same, a large overpotential is required to drive the electron transfer. As a result, a broad oxidation peak appears at a more positive voltage, which reveals a rather poor kinetic of the electron transfer (141).

The electrochemical reversibility of a redox couple is one of the crucial properties to be considered for choosing a redox couple in a thermogalvanic cell. The reversibility provides insight into the electron transfer rate of the redox couple. It occurs when the electron is transferred sufficiently fast to achieve equilibrium at the time scale of the potential variation in the CV. In that case, the electron transfer rate (kinetics) can be obtained by measuring the peak separation at high scan rates (142). The potential difference between the oxidation and reduction peaks provide a qualitative analysis of standard rate constant for an electron transfer process. The electron transfer rate (k°) determined using the analysis developed by Nicholson (142) is connected to ψ , which is the dimensionless kinetic parameter determined from peak separation (ΔE):

$$\psi = k_o \left(\frac{D_o}{D_R} \right)^{\frac{\alpha}{2}} \sqrt{\frac{RT}{\pi n F D_o v}} \quad 4.29$$

D_o , and D_R are the diffusion coefficients, α is the transfer coefficient, R is the gas constant, T is the absolute temperature, F is the Faraday constant and v is the scan rate. In general, it can be assumed that the diffusion coefficients of the oxidized and reduced form are approximately equal and kinetics are fairly symmetrical ($\alpha \approx 0.5$) (143). Then for one electron transfer process, the equation 4.29 can be simplified to:

$$\psi = k_o \sqrt{\frac{RT}{\pi F D v}} \quad 4.30$$

The Nicholson method is limited to a specific narrow range of peak-to-peak potential difference. Klingler and Kochi developed a method which allows large ΔE values for k_o calculations. This method is derived under the assumption of irreversible electrode reaction (144).

$$k_o = 2.18 \left(\frac{\alpha n F D v}{RT} \right)^{\frac{1}{2}} e^{-\left[\left(\frac{\alpha^2 F}{RT} \right) n \Delta E_p \right]} \quad 4.31$$

Besides the current peak position in the CV, the current peak value enables to extract the diffusion coefficient of the reactant. The diffusion coefficient is determined from the Randels – Sevcik equation by measuring the peak current versus the scan rate in the case of the limited diffusion process (144).

$$I_p = 0.446 n F A C \sqrt{\frac{n F v D}{RT}} \quad 4.32$$

Where I_p is the peak current, n is the number of electrons, F is Faraday's constant, A is the effective surface area, C is the electrolyte concentration, v is the scan rate, D is the diffusion coefficient, R is the universal gas constant and T is the temperature.

4.7. Electrochemical Impedance Spectroscopy

Impedance spectroscopy is a powerful technique to investigate the electrical properties of materials and interfaces (122, 145-147). The applications cover the study of electric double layer formations, electron transfer at electrode-electrolyte interface, kinetics of charge transport in electronic or ionic or mixed conductors (148, 149) as well as in semiconducting electrode materials (150), corrosion study (151), investigation of coating on metals, dielectric properties of materials and solutions/electrolyte (152), electron injection at electrode-semiconductor interface (146, 153).

4.11. A graphical representation of the complex impedance in complex space [adapted from (45)].

The impedance is a complex number with a real and imaginary part. The real part is known as the electrical resistance ($Z_{re} = R$) and the imaginary part (Z_{im}) is the reactance. The reactance can be defined as the change of voltage or current due to a capacitance (Z_C) or an inductance (Z_L) (equation 4.36). A graphical representation of the impedance in complex space is illustrated in figure 4.11.a.

$$V(t) = V_0 \sin(\omega t) \quad 4.33$$

$$I(t) = I_0 \sin(\omega t - \vartheta) \quad 4.34$$

$$Z = \frac{V(t)}{I(t)} = |Z|e^{j\vartheta} = Z_{re} + jZ_{im} \quad 4.35$$

$$Z_C = -j \frac{1}{\omega C}; Z_L = j\omega L \quad 4.36$$

Where, V_0 and I_0 are the amplitudes of the alternating voltage and current, ω is the angular frequency $\omega = 2\pi f$, where f is the frequency. ϑ is the phase difference between the voltage and the current, Z_{re} and Z_{im} are the real and imaginary parts and $j = (-1)^{\frac{1}{2}}$.

The impedance is frequency dependent unless the studied systems are purely resistive. Therefore, the method is called impedance spectroscopy since it measures the impedance over a frequency range. The impedance is determined by applying a monochromatic alternating voltage (equation 4.33) to an electrode with a wide range of frequencies while analyzing the resulting current (122). The resulting current is an alternative current (equation 4.34) if the $I - V$ characteristic of the system is linear. Then the impedance can be defined by equation 4.35. However, most of the systems do not have a linear $I - V$ characteristic over the all frequency range (figure 4.11.b). However, a system can be approximated as being linear over a small voltage range, dE , at some voltage. Therefore, it is important to apply a small alternative perturbation (≈ 10 mV) around this voltage, to obtain an alternative current response, which is a good approximation (154). The impedance data are typically presented in two different ways, a Bode plot with $\log |Z|$ and $-\delta$ over the frequency range, or a Nyquist plot with the imaginary component of the impedance over the real component of the impedance (figure 4.12.).

4.12. Impedance spectra a) bode plot and b) Nyquist plot [adapted from (45)].

Impedance spectroscopy performed on an electrochemical cell is known as electrochemical impedance spectroscopy. It can be done with a three-electrode system or a two-electrode system such as an electrochemical device. Impedance spectroscopy enables to distinguish between physical and chemical processes in the time domain due to their different kinetics. All the process can be decoupled by fitting to an equivalent circuit model, where, each of the circuit element corresponds to a certain physical meaning. Trace of those circuit elements can be easily extracted by a Nyquist plot if the processes are not too complicated. In addition to the impedance data, the phase angle also provides useful information since it tells what type of process is dominant at a certain frequency. A phase angle close to zero (0°) corresponds to a resistive behavior (155). A phase angle close to -90° corresponds to a capacitive behavior.

The Nyquist plot shown in figure 4.12.b has been simulated by an equivalent circuit called the generalized Randles circuit (inset of Figure 4.12.b). This circuit is one of the simplest and common circuit models used to analyze electrochemical processes. This circuit model consists of two resistor components (R_S and R_{ET}), a constant phase element (Z_{CPE}) and a Warburg impedance (Z_W). R_S represents the electrolyte resistance and the charge transfer resistance (which is due to the overpotential of the electrochemical reaction). The circuit also includes constant phase element (Z_{CPE}) which models a capacitance dispersion. This is introduced because of the frequency dispersion of impedance data can't be explained by simple circuit element such as resistor and capacitance (156). Equation 4.37 defines the constant phase element with Q as a constant and α

taking value from 0 to 1. When $\alpha = 0$, the *CPE* is a resistor with the value of $R = \frac{1}{Q}$ and when the $\alpha = 1$, it is equal to the impedance of a capacitor with capacitance Q .

$$Z_{CPE} = \frac{1}{Q(j\omega)^\alpha} \quad 4.37$$

The Warburg impedance (Z_W) is a *CPE* with $\alpha = 0.5$. It is specific to the phenomenon of mass transport limitation of the impedance. In the Nyquist plot (figure 4.13), it is displayed by a line at low frequency region that possesses a slope of 45° angle. While it is tempting to add more component to get a better fit to the experimental data when proposing an equivalent circuit, it is important to keep the equivalent circuit as simple as possible to avoid any misinterpretation of the physical process representing each circuit elements.

Figure 4.13. Chirea's circuit model [adapted from (157)].

In this thesis, electrochemical processes involving a conducting polymer electrode are more complex than with a flat metal electrode due to the possibility for ions, electrons and reactant transport in the bulk of the polymer electrode. Nyquist plots obtained with conducting polymer electrodes deviate from the simple Randle's circuit model. A different circuit model proposed by Chirea et al. (157) (figure 4.13) has been used in our work. The elements of the circuit are assigned to the series resistance (R_s) (which includes the resistance of the electrolyte solution (R_L), the electrode contact resistance at the electrode material and at the current collector interface), the charge transfer resistance (R_{ET}), the bulk electrode resistance (R_F), the double layer capacitance (C_{dl}), the Warburg Impedance (Z_d), and the bulk redox capacitance (C_F).

5

CHAPTER

Fabrication and Characterization

5.1. Fabrication

There are many fabrication techniques available for polymer film preparation from solutions such as spin coating, drop casting, dip coating, solvent casting, and printing. Spin coating is one of the leading techniques, and it has been used for polymer film preparation for all the papers in this thesis. The solution can be a suspension of polymer particles or a mixture of monomer and the oxidant in the case of chemical polymerization. First, a clean glass substrate or Si wafer is placed on a spinner by vacuum suction. Then the polymer solution added into the substrate, followed by spinning the substrate at high rotation speed, typically at 600 – 3000 rpm to remove the excess solution. This results in a uniform polymer solvent layer on the substrate/wafer; the thickness of the layer depends on the spin speed, the viscosity of the solution, the concentration of the solution, and the surface energy between the substrate and the solution.

5.1.1. PEDOT-Tos film fabrication by Spin coating

PEDOT-Tos coated electrodes were prepared by chemical polymerization of EDOT monomer on an electrically insulated silicon wafer (p-type, 1000 nm thermal oxide layer). An oxidant solution composed of 1 ml of iron (III) *p*-toluenesulfonate (40% solution in n-butanol) and 0.04 ml of pyridine was stirred for 1 hour. Next, 0.05 ml of EDOT monomer added into the oxidant solution, mixed well, and spin-coated onto the silicon wafer. Then the modified wafer was heated at 100 °C for 10 minutes, washed with an excess of ethanol and blow-dried with nitrogen (Figure 5.1.a). Films with various thicknesses were achieved by repeating the spin-coating process of PEDOT-Tos as needed. Subsequent polymerizations of EDOT on existing PEDOT-Tos films led to a multilayer structure of PEDOT-Tos which could be used to control the thickness (Figure 5.1.b).

Figure 5.1. Schematic diagram of Spin Coating of (a) single layer and (b) multi-layer PEDOT-Tos

5.1.2. PEDOT-PSS film fabrication by Spin coating

The PEDOT-PSS films were deposited on the electrode Si substrates (p-type, 1000 nm thermal oxide layer). The cleaned substrates were treated with UV-O₃ for 30 min before the film deposition to make the surface hydrophilic. The commercial aqueous dispersion of PEDOT-PSS (Clevios PH1000) and 0.1 wt% of silane crosslinker, 3- glycidoxypolytrimethoxysilane (GOPS) were mixed using ultrasonicator for 5 min. The solution was spin-coated, followed by heating at 140 °C for 10 min on a hot plate (figure 5.2.a). Silane modification enhances the adhesion thus avoids the film dissolving in an aqueous solution. To boost the electrical conductivity high boiling solvent, dimethylsulfoxide (DMSO) was added to the PEDOT-PSS and GOPS mixture in various wt% amounts, 0.2 %, 0.4%, 0.45%, 0.55%, 0.6%, 0.75%, 1.0%, 1.5%, 2.0%, 3.0%, 5.0% and 6.0%. The thicknesses were increased by the addition of more than one PEDOT-PSS layer (figure 5.2.b).

Figure 5.2. Schematic diagram of Spin Coating of (a) single layer and (b) multi-layer PEDOT-PSS

5.2. Electrical conductivity measurement

Electrical conductivity (σ) measured in siemens per meter (S/m), is a material property that related to the current density (j) passed through the material to the electric field (E) created when a voltage bias is applied. The conductivity of conducting polymer is calculated by using measured resistance, R across the cuboid with a length L , width w , and thickness t , (figure 5.3) according to the following equation

$$\sigma = \frac{1}{R} \left(\frac{L}{w.t} \right) \quad 5.1$$

The conductivity measured by the two-terminal setup is affected due to the weak contact, or injection barriers which leads a voltage drop across the interface between the probe and the material. This resulted in a contact resistance which added to the final measured resistance, leads to lower conductivity than the actual conductivity of the material.

Figure 5.3. Four-terminal resistance measurement for electrical conductivity.

Contact resistance can be avoided by the four-terminal resistance measurement, this technique used to measure the conductivity of conducting polymer materials studied in this thesis. The four terminal measurement involves applying a current between two terminals, outer terminals as shown in figure 5.3., and, measure the voltage drop in between the inner two terminals. Only a minimal current will pass through the contact used to measure the voltage due to the high impedance of the measurement device. Therefore, the resulting voltage drop is negligible at the contacts. The resistance of the material can be calculated using:

$$R = \frac{V}{I} \quad 5.2$$

where V is the measured voltage and the I is the applied current, and then the conductivity is calculated using the equation 5.2.

5.4. Organic Electrochemical Transistor (OECT)

A transistor is a three-terminal device consist of a metallic source, drain and gate electrode (158) that is used in electronics to amplify or switch electronic signals. OECT's belong to the transistor family; however, unlike other transistors, it consists of a conducting polymer film directly in contact with the electrolyte, in which an Ag/AgCl gate electrode immersed (159, 160). The conducting polymer film is deposited between the source and drain as shown in figure 5.4. Source and drain have defined the channel in which electrons or holes flow from the source to the drain. The operation of OECT described by both electrochemistry and solid-state physics. OECT's operate under two types of regime: i) non-faradic, where the application of V_{GS} determines a capacitive current at the gate electrode, ii) faradic, where the application of V_{GS} determines steady state current at the gate electrode due to the reduction/oxidation of conducting polymer (161).

Figure 5.4. Schematic diagram of an Organic electrochemical transistor [adapted from (162)].

The function of OECT's are based on ions which are injected from the electrolyte to conducting polymer channel; thereby it induces the doping state which resulted in a change in conductivity. The gate voltage governs the ion injection into the channel and the doping state/redox state of the conducting polymer film.

In the standard operation mode of OECT, the source contact/electrode is grounded, and a constant voltage is applied to the drain contact/electrode (V_D) relative to ground (figure 5.4), a current flow through the conducting polymer (channel of OECT) and collect at the drain electrode, current is known as the output current/drain current, I_D . Here, the electronic charge carries(electron/hole) govern the channel/output current, and ionic charge carriers facilitate the charge balance for the electronic charge thereby modulate the charge carrier or the electrical conductivity of conducting polymer. The OECT current in the saturation regime as follows:

$$I_D = \beta(V_S + V_P - V_G)^2 \quad 5.3$$

where $\beta = \frac{W\mu C_V t}{2L}$ & $V_P = \frac{qP_0}{C_V}$, μ is the charge carrier mobility, C_V is the volumetric capacitance, V_S is the source voltage, V_P is the pinch off voltage, q is the elementary charge and P_0 is initial charge carrier density in the conductive polymer before the application of the gate voltage.

Transconductance is the most crucial parameter in transistors which used for sensor applications, defined as the derivative of channel current with respect to the gate voltage as seen in the following equation:

$$g_m = -\mu C_v \frac{Wd}{L} V_D, \quad \text{for } V_D > V_G - V_T; \quad 5.4$$

$$g_m = \mu C_v \frac{Wd}{L} (V_G - V_T), \quad \text{for } V_D < V_G - V_T. \quad 5.5$$

5.5. Absorbance spectroscopy

Upon interaction of electromagnetic radiation with a matter, it can be absorbed either by promoting an electron to an excited state with higher energy or inducing molecular vibration or rotation. Absorption spectroscopy is one of the common and simple methods which used to study the electronic structure of materials (13, 163). Not only that, it can be used to study the composition of a compound in which absorption spectra are known. Furthermore, it is used to characterize optical devices such as electrochromic devices (164-166). In this method, determine the intensity of light (I) passing through a material and then compare it to the intensity of the light (I_o) before it passes through the material at a different wavelength. The ratio between these two light intensity ($\frac{I}{I_o}$) is called as transmittance (% T), which is express in percentage (%). The absorbance can be obtained as equation 5.6.

$$A = -\log \left(\frac{\%T}{100\%} \right) \quad 5.6$$

Absorbance measurements in this thesis were conducted using a UV-Vis-NIR Spectrometer (PerkinElmer Lambda 900) in the range of 2500-300 nm. The samples were prepared on glass substrates via spin coating followed by heating at 140 °C for 10 min. Baseline correction was carried out using a glass substrate. Obtained spectra were normalized based on the thickness of each film.

5.6. Ultraviolet photoemission spectroscopy (UPS)

Ultraviolet photoemission spectroscopy (UPS) belongs to the family of photoemission spectroscopy (PES), which based on the photoelectric effect, where detect electron to study the electronic structure of materials. The basic principle of UPS is; the measurement of kinetic energy spectra of photoelectrons that emitted from the materials, that excited by the low energy ultraviolet light source. The valence electronic states of materials can be mapped out in the form of the spectrum with the intensity as the function of the binding energy. In addition, the work function,

the change/shift in work function and the vertical ionization potential can be obtained by UPS. The kinetic energy, E_k of photoelectron is given by the Einstein relation as follows (167):

$$E_k = h\nu - E_b \quad 5.7$$

where E_b is the binding of the electron before excitation relative to the vacume level, h is the plank constant and ν is the wave number. The work function, Φ of the metal/conducting polymer can then be derived from the directly measured energy of the secondary electron cutoff, E_{cutoff} , where it is the position of zero kinetic energy.

$$\Phi = h\nu - E_{cutoff} \quad 5.8$$

Photoemission experiments were carried out in this thesis using a Scienta ESCA 200 spectrometer in ultrahigh vacuum (base pressure of 1×10^{-10} mbar) with a standard He-discharge lamp ($h\nu = 21.22$ eV) for UPS. The total energy resolution in UPS measurement is about 80 meV as extracted from the width of the Fermi level (at the binding energy of 0.00 eV) of clean gold foil. All spectra were collected under a photoelectron take-off angle of 0° (normal emission). The work function of the film was extracted from the edge of the secondary electron cutoff of the UPS spectrum by applying a bias of -3 V to the sample.

5.7. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) belongs to the family of scanning probe microscopy (SPM) in which scan the surface of samples with a solid probe tip. The principle is the near-field forces between atoms of the probe tip and the surface to generate signals of surface topography. Short range forces such as Van der Waals forces, electrostatic forces, and capillary forces are the key for mapping of the sample surface. AFM can examine the surface features in the range of atomic scale up to a tenth of a millimeter. Surface topography of the sample is mapped by a microscopic force sensor known as a cantilever; a probe tip is mounted at the end of the cantilever as shown in figure 6.9. The forces generated between the probe tip and the sample surface results in the elastic bending

of the cantilever, which is detected by the laser beam deflection method. A laser beam monitors the bending/deflection of the cantilever by reflecting the beam from the back of the cantilever according to its movement, and it is recorded by a position sensitive photoanode. The photoanode consists of four quadrants and monitors the cantilever bending; the deflection is recorded by the difference between two photoanode signals. Observed deflection converted to the force that acts on the tip due to the nature of the sample (22).

Figure 5.7. Schematic presentation of AFM: the beam deflection reflects the bending of the cantilever and thus the morphology of the sample surface. Position sensitive photodiodes detect the beam deflection [adapted from (22)].

There are three basic modes of operation of AFM, which are contact mode, non-contact mode, and tapping mode. Out of these three modes, the tapping mode (also known as intermittent contact mode) is the widely used mode especially for soft materials such as biological and polymer samples. As there is no dragging of the probe tip on the sample when operating in this mode, possible chances of damaging the surface during the scans are minimal. AFM phase imaging is one of the important advantages of operating in tapping mode. In this imaging technique, the phase shift between free oscillations of the cantilever and the oscillation of it on the sample surface is detected. This phase shift is sensitive to variations properties of the sample surface such as chemical composition, adhesion, friction, etc.

For this thesis, the topography images and thickness measurement were obtained using a Veeco Dimension 3100 AFM operated in tapping mode. Si probes with tip size 20 nm were used for all the samples imaged. The morphological images were analyzed, and thickness measurements were extracted using Gwyddion software.

6

CHAPTER

Conclusions and Outlook

The primary goal was to develop TGC with only plastic electrode/conducting polymer electrodes. Two different PEDOT electrodes were tested for thermogalvanic cells applications. Unlike most of the other electrode materials tested in TGCs, here the PEDOT electrode is acting as both electrode and the current collector. The fundamentals associated with the electrochemistry at PEDOT electrodes with the redox electrolyte Ferro/ferricyanide in water were studied. Chemically polymerized PEDOT-Tos electrodes were successfully demonstrated in TGCs with a power generation increasing with the thickness of the polymer electrode to reach power value obtained with the flat platinum electrode. Two phenomena can explain the thickness dependence: the conductivity increase versus thickness and the partial penetration of the redox couple in the polymer electrode. Because the increase in thickness leads to an enhancement in the electrical conductivity of the PEDOT-Tos electrode, it was not crystal clear how to fully disentangle the effect of thickness from the effect of conductivity. Therefore, the next goal was to study the effect

of electrical conductivity. For that purpose, we changed the polymer electrode and moved to the polymer blend PEDOT-PSS composed of PEDOT with a polyelectrolyte PSS. It is possible to control the morphology and phase separation of PSS to tune the electrical conductivity by four orders of magnitude for the same thickness. The modification of the morphology is realized by introducing the high boiling point solvent DMSO. The dependence of the heterogeneous charge transfer rate on the conductivity of the polymer was investigated by various electrochemical and spectroscopy techniques. It turned out that the conducting percolation network in the bulk of the PEDOT-PSS electrode is directly governing the rate of electron transfer at the PEDOT-PSS electrode-electrolyte interface. The surface density of percolation paths is a key parameter for characterizing the overall rate of electron transfer at a polymer electrode. The power of a TGC could also be tuned by 3-4 orders of magnitude by the morphology of the polymer electrode. To expand the understanding of the fundamental properties of PEDOT-PSS electrodes, we used that polymer as the channel in an electrochemical transistor (OECT). We studied the insulator-to-conductor transition and discovered that the threshold voltage of that transition is affected by the morphology of the polymer.

Gel electrolyte offer attractive features to TGCs, such as simple manufacturing, preventing possible leakage and long-term stability. Gel electrolytes could be printed to create microfabricated TGC modules made of p- and n-type redox gel electrolytes. This motivated us to explore the impact of the viscosity of the electrolyte on the performance of the TGCs. We choose organic solvents of the family of ether and consider polymer liquids. Iodide/tri-Iodide redox couple is readily soluble in that family of solvent. Besides the transport of the redox couple in the electrolyte, we also found out that the rate of electron transfer, as well as the Seebeck coefficient of the redox couple change with the viscosity. As a result, the power of TGC is worse with gel electrolytes than with liquid electrolytes.

Future Work

A phenomenon that has not been deeply studied in this thesis is the role of the ion-exchange between negatively charged redox molecules and anions balancing the positive charge of the PEDOT chains. A TGC with PEDOT-Tos electrodes displayed decent stability, however, both the current and open circuit voltage decrease in the first few hours. A possible mechanism is that the

negatively charged redox couple ferricyanide/ferrocyanide is exchanged with the tosylate and leads to a degradation in performance. This might be simply a change in the electrical conductivity of the electrode or the prevention of redox to come close to the polymer surface. In that respect, the polymer electrode PEDOT-PSS should be more stable since the excess of immobile PSS ions in the polymer electrode should prevent the negatively charged redox molecule to penetrate the polymer electrode, thereby improving the lifetime of the TGC.

Beside stability issues, the performance of polymer TGC could be further improved by choosing other redox electrolytes. The thesis focused only on negatively charged Ferro/ferricyanide redox couple with PEDOT electrodes. However, the effect of the size and the charge of the redox species is obviously of importance. Hence, it could be interesting to investigate smaller redox molecules (e.g., Iodide/Tri-Iodide redox couple), positively charged redox couples (Cobalt redox couple) and organic redox couple (thiolate/disulfide). Another aspect is to further understand the role of the chemical environment (solvent) on the sign and magnitude of the Seebeck coefficient. To enhance the voltage of a TGC, we could build modules of thermogalvanic cells based on redox electrolyte-legs of negative Seebeck coefficient and positive Seebeck coefficient that are coupled electrically in series and thermally in parallel. This is the classical strategy used for solid-state thermoelectric generators.

Since the aqueous redox electrolyte Ferro/ferricyanide is cheap and of good performance, we could envisage other strategies to improve the polymer electrode further. We have observed that this redox couple does not penetrate in the PEDOT-PSS layer, therefore only the surface of the PEDOT electrode is used. A potential way to improve the electrode is to introduce porosity in order to increase the surface area and the exchange current density with the redox couple. Porous PEDOT electrodes can be fabricated in the micro to nanoscale by various growth techniques (e.g., by electrodeposition with and without template), by creating aerogels or by mixing PEDOT with micro or nano-structured conducting materials. Another aspect of interest is to study how the heat transfer/convection effect in the redox electrolyte is affected by the porosity and if this could be a strategy to increase the overall heat resistance of the TGC to enable large temperature gradient (and voltage). Since porous electrodes are less conducting, it is likely that a current collector strategy must be developed for porous electrodes. The challenge is to fabricate PEDOT for TGC application while keeping the high conductivity and current collecting ability.

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Part II

Papers

Papers

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