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IONIC AND ELECTRONIC TRANSPORT IN ELECTROCHEMICAL
AND POLYMER BASED SYSTEMS

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Description of the cover image:

An ion exchange membrane

Ionic and electronic transport in electrochemical and polymer based systems

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To my parents, Alla and Vyacheslav.

Abstract

Electrochemical systems, which rely on coupled phenomena of the chemical change and electricity, have been utilized for development an interface between biological systems and conventional electronics. The development and detailed understanding of the operation mechanism of such interfaces have a great importance to many fields within life science and conventional electronics. Conducting polymer materials are extensively used as a building block in various applications due to their ability to transduce chemical signal to electrical one and *vice versa*. The mechanism of the coupling between the mass and charge transfer in electrochemical systems, and particularly in conductive polymer based system, is highly complex and depends on various physical and chemical properties of the materials composing the system of interest.

The aims of this thesis have been to study electrochemical systems including conductive polymer based systems and provide knowledge for future development of the devices, which can operate with both chemical and electrical signals. Within the thesis, we studied the operation mechanism of ion bipolar junction transistor (IBJT), which have been previously utilized to modulate delivery of charged molecules. We analysed the different operation modes of IBJT and transition between them on the basis of detailed concentration and potential profiles provided by the model.

We also performed investigation of capacitive charging in conductive PEDOT:PSS polymer electrode. We demonstrated that capacitive charging of PEDOT:PSS electrode at the cyclic voltammetry, can be understood within a modified Nernst-Planck-Poisson formalism for two phase system in terms of the coupled ion-electron diffusion and migration without invoking the assumption of any redox reactions.

Further, we studied electronic structure and optical properties of a self-doped p-type conducting polymer, which can polymerize itself along the stem of the plants. We performed *ab initio* calculations for this system in undoped, polaron and bipolaron electronic states. Comparison with experimental data confirmed the formation of undoped or bipolaron states in polymer film depending on applied biases.

Finally, we performed simulation of the reduction-oxidation reaction at microband array electrodes. We showed that faradaic current density at microband array electrodes increases due to non-linear mass transport on the microscale compared to the corresponding macroscale systems. The studied microband array electrode was used for developing a laccase-based microband biosensor. The biosensor revealed improved analytical performance, and was utilized for in situ phenol detection.

Populärvetenskaplig sammanfattning

Elektrokemiska systemen, som bygger på kopplingen av kemi och elektricitet, har använts för att utveckla gränssnitt mellan biologiska system och konventionell elektronik. Detaljerad förståelse av sådana gränssnitt har stor betydelse inom många olika områden inom livsvetenskaperna och konventionell elektronik. Ledande polymermaterial används i stor utsträckning som byggstenar i bioelektroniska tillämpningar på grund av sin förmåga att omvandla kemiska signaler till elektriska signaler och tvärtom. Den kopplingsmekanismen mellan massa och laddningsöverföring i elektrokemiska system, och i synnerhet i en ledande polymerbaserat system, är mycket komplex. Dessutom beror denna kopplingsmekanism på olika fysikaliska och kemiska egenskaper i materialen, vilket gör dessa system intressanta att studera.

Syftet med denna avhandling har varit att studera elektrokemiska system, inklusive ledande polymerbaserade system, för att skaffa nya kunskaper för framtida utveckling av komponenter som kan fungera med både kemiska signaler och elektriska signaler. Inom avhandlingen studerar vi funktionen av bipolära jontransistorer, som har utnyttjats tidigare för att modulera leverans av laddade biomolekyler. Vi har analyserat de olika driftlägena hos bipolära jontransistorer och övergångarna mellan dessa med hjälp av modeller som givit detaljerade koncentrations- och potentialprofiler.

Vi har också studerat kapacitiv laddning i ledande PEDOT:PSS polymerelektroder. Vi har visat att PEDOT:PSS elektrodernas kapacitiva laddning under cykliska voltammetri kan förstås med hjälp av modifierad Nernst-Planck-Poisson formalism för tvåfassystem i termer av kopplad jon-elektron diffusion och migration utan förekomsten av några redoxreaktioner.

Vidare har vi studerat elektronstruktur och optiska egenskaper för självdopad p-typ ledande polymerer. Dessa oligomerer kan självpolymerisera längs skaflet i växter, som tidigare har rapporterats. Vi har utfört *ab initio* beräkningar för molekylärsystemet i odopade, polarona och bipolarona elektroniska tillstånd. Jämförelse med experimentella data har bekräftat bildandet av odopade eller bipolarona tillstånd i polymerfilmerna beroende på applicerad spänning.

Slutligen har vi utfört simuleringar av reduktions-oxidationsreaktionen på mikrobandedelektroder. Vi har visat att faradiska strömtätheten på mikrobandedelektroden ökar på grund av icke-linjär masstransport i mikroskala i jämförelse med motsvarande makroskalesystem. Dessa mikrobandedelektroder har använts för att utveckla en laccas-baserade mikrobandsbiosensor. Biosensorn uppvisade en förbättrad analytisk förmåga och har använts för att mäta fenol in situ.

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Anton Volkov
Norrköping, March 2017

List of publications

Publications included in the thesis

1. **Anton V. Volkov**, Klas Tybrandt, Magnus Berggren, and Igor V. Zozoulenko, Modeling of Charge Transport in Ion Bipolar Junction Transistors, *Langmuir* **30** (23), 6999–7005 (2014).

Contribution: Implementation of the numerical model, performed simulation, analysis of the results, wrote large part of first draft, contributed to final editing of the manuscript.

2. **Anton V. 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, submitted.

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5. Alina N. Sekretaryova, **Anton V. Volkov**, Igor V. Zozoulenko, Anthony P.F. Turner, Mikhail Yu. Vagin, Mats Eriksson, Total phenol analysis of weakly supported water using a laccase-based microband biosensor, *Analytica Chimica Acta* **907**, 45-53, (2016).

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2. Daniel Tordera, Dan Zhao, **Anton V. Volkov**, Xavier Crispin, Magnus P. Jonsson, Efficient Plasmonic Heating in Metal Nanohole Arrays, submitted.
3. Alina N. Sekretaryova, **Anton V. Volkov**, Igor V. Zozoulenko, Mikhail Yu. Vagin, Mats Eriksson, Evaluation of the electrochemically active surface area of microelectrodes by capacitive and faradaic currents, manuscript in preparation.

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Chapter 1

Introduction

1.1 Ion and electron transport phenomena and its applications

The effect of conductivity modulation in a semiconductor devices has attracted attention of many researchers and engineers in the beginning of 20th-century. The transistor technology established in Bell labs was the foundation for the industrial growth of the modern electronics. Walter Brattain, John Bardeen and William Shockley reported on development of the point contact transistor and bipolar junction transistor[1]. The proposed transistors have been dominant in transistor technology for more than twenty years. Due to significance of the research in semiconductor transistor effect' they were awarded the Nobel Prize in physics (1956). Based on these achievements other key blocks for conventional electronics such as a metal-oxide-semiconductor field-effect transistor (MOSFET)[1] and integrated circuits were developed[2].

Along with the development of conventional electronics, the synthesis of ion conductors was carried out in the 1960s. Nafion[3] was the first reported synthetic polymer that could conduct ions with specific charge (cations). The polymer molecules in ion conductors generally consist of repeated blocks (monomers) with covalently bonded ionic group. In Nafion, sulfonate groups attached to the polymer backbone are compensated for by cations, which can freely move in the material. The cation-selective (or cation exchange) properties of the Nafion material make it the ionic equivalent to p-doped semiconductors. This property allows a broad range of applications[4] including fuel cells, batteries, catalysis application, etc. Later anion-selective materials were also developed[4]. By combining cation-selective and anion-selective membranes the basic ionic rectifier devices called bipolar membrane have been assembled[4]. These discoveries of ion selective materials laid the foundation for future development of ion transporting devices.

The next stage in the development of electroactive materials was the invention of conducting polymers[5, 6, 7] in the 1970s. Conducting polymers can efficiently transport both electronic charge carriers and ions when sufficiently hydrated. The electrical conductivity of conducting polymers can be tuned in a wide range via chemical doping, electrochemical doping or by electric field. The physical and chemical properties of the conducting polymer material de-

depends also on the structure of monomers, monomers bound and arrangement of molecules in the polymer material. The possibility to design conducting polymer materials with required properties by varying structural and morphological parameters was played a pivotal role in the rising area of organic electronics. Conductive polymers were intensively used in the development and manufacturing of various electronic devices, such as organic light emitting diodes[8], photovoltaics[9] and field effect transistors[10]. In virtue of ability to conduct electronic and ionic charge carriers conducting polymers also becomes attractive for conversion between electronic and chemical signals in various application within life sciences.

In the 1960s, before the invention of conducting polymers, systems with biological entities that rely on coupled phenomena of chemical change and electricity had been intensively studied[11]. In these studies enzymes, cells or tissues were used as a catalytic element for specific electron transfer reaction. Such systems nowadays are used for various purposes including chemical synthesis, electricity generation and sensing of biomolecules[11].

All the above research studies contributed to the establishment of bioelectronics area. The field of bioelectronics comprise studies of biological systems in conjunction with electronic systems[12]. Biological systems use ions and molecules in addition to electrons for signaling. Thus using ion-conductive and mixed ion-electron conductive materials is desired for the development of devices for bioelectronics and other applications. A number of bioelectronic devices based on such combinations of ion-conductive and mixed ion-electron conductive materials have been reported recently, e.g. ion bipolar junction transistors[13], drug delivery devices based on ion pumps[14, 15, 16] and artificial neurons[17].

1.2 Aim and outline of the thesis

Ion and electron transport phenomena together with electron transfer phenomena enable the development of the various devices for bioelectronics, energy conversion and other applications. The mechanism of the coupling between the mass and charge transfer in these devices, and particularly in conductive polymer based devices, is highly complex and depends on various physical and chemical properties of the materials composing the system of interest. The aims of this thesis have been to study electrochemical systems including conductive polymer based systems and provide knowledge for future development of the devices, which can operate with both chemical and electrical signals.

In order to reach these aims, the properties of several electrochemical systems are studied in this thesis. The thesis starts with background information about bioelectronics and conducting polymers in Chapter 2 and 3. Chapter 4 gives an overview of methods used for modeling transport phenomena in electrochemical systems. Chapter 5 describes first principal methods utilized for study of the molecular systems. A short overview of experimental methods used in this work is given in Chapter 6. Finally, a summary of the papers included in this thesis is presented in Chapter 7.

Chapter 2

Conventional electronic components and electrochemical devices for bioelectronics applications

This chapter contains the basic information about key concepts in electronics and bioelectronics used in the work presented in the thesis. A brief overview of passive and active components is given in the beginning of this chapter. Further, two main focuses of bioelectronics are discussed. The first focus is sensing of biomolecules and biological signals and a second focus is actuation of biological systems.

2.1 Passive and active components

Electronic components incapable of introducing power into circuits are referred to as passive devices. The two-terminal electrical components such as resistors, inductors, capacitors, and diodes are all considered passive devices. In contrast, active components rely on a source of power and can amplify signals. The triode vacuum tubes and transistors are typically included in this category.

2.1.1 Capacitors

A capacitor is a passive two-terminal electrical component used to store charge. A typical capacitor consists of a dielectric film sandwiched between two metal electrodes (see Figure 2.1.1 a). When potential bias V applied is to the metal electrodes the dielectric develops an electric field and electrodes hold charge $+Q$ and $-Q$ on their surfaces respectively. An ideal capacitor is characterized by constant capacitance $C = Q/V$.

However, capacitors used in electrical circuits are not ideal. The metal-oxide-semiconductor capacitor (MOS capacitor) represents an example of the most wide spread device with non-linear capacitance voltage characteristics. The

Figure 2.1.1: (a) Schematics of the parallel plate capacitor. (b) Schematics of the MOS capacitor. (c) Capacitance-Voltage curves of MOS capacitor.

double layer capacitor is other example of a system with non-linear capacitance voltage dependence and its characteristics is discussed in Chapter 4.

Figure 2.1.1 b shows a schematics of a MOS capacitor [18]. It consists of an oxide layer (SiO₂) and semiconductor body (p-Si) layers sandwiched between two metal electrodes. The capacitance of a MOS capacitor varies with applied voltage and differential capacitance $C = dQ/dV = (dQ/dt)/(dV/dt)$, which used for its characterization. The typical Capacitance-Voltage (C-V) curves of MOS capacitors are shown in Figure 2.1.1 c. Because of the presence of a semiconductor body in a MOS capacitors, it reveals three different regimes of the operation: low frequency (LF), high frequency(HF) and depletion modes.

2.1.2 Transistors

Transistors are semiconductor devices that can switch and amplify electronic signals. A transistor is composed of semiconductor materials, in which current can be modulated by electric fields and usually has three-four terminals for connection to an external circuit. Field effect transistors (FETs) and bipolar junction transistors (BJTs) are two major types of transistors.

The operation of a FET is based on the modulation of resistance of the semiconductor channel by a voltage or electric field applied perpendicular to the semiconductor channel. Figure 2.1.2 a shows schematics of a metal-oxide-semiconductor field effect transistor (MOSFET)[18]. The semiconductor body of the MOSFET channel is the p-type silicon substrate. The N⁺ region is heavily doped with n-type dopants and has very high conductivity. The surface of the two N⁺ regions is contacted by a metal. These terminals are known as the source and drain electrodes. Surface oxide layer (SiO₂) is located between the source and drain electrode. The oxide layer serves as the dielectric layer and the gate (poly Si) can sustain high transverse electric field for modulation of the conductance of the channel. When a positive voltage is applied between the substrate and the gate, the electrons are attracted to the oxide layer/semiconductor interface to form the n-type conduction path which connects n-type source and drain regions. Applying a positive voltage between the source and drains leads to migration of electrons from source to drain. In the case when negative voltage is applied between the substrate and gate there is no surface conduction channel connecting source and drain regions.

The first solid state amplifier manufactured in large volumes were BJT[1]. Figure 2.1.2 b shows schematics of *nnp*-BJT [18]. In this type transistor p-Si base layer is located between N⁺ emitter and collector regions. Electrons and

Figure 2.1.2: Schematics of (a) the metal-oxide-semiconductor field effect transistor and (b) the bipolar junction transistors

holes are responsible for charge transport processes within the *npn*-BJT. The minority charge carriers in the emitter layer (electrons) are injected from the emitter into a thin p-Si base layer where they diffuse over to the collector. The electrons recombine with the holes in the base layer and the recombination rate as well as collector current can be tuned by the base voltage.

2.2 Biosensing

2.2.1 Electrodes

Implanted microelectrode arrays have been widely utilized for recording activities of neurons[19, 20]. When an electrode is placed in close proximity to a neuron, changing of the neuron action potential leads to the potential shift at the recorded electrode. Highly conductive and low impedance electrodes are required for recording high frequency signals from neurons to provide low noise levels. Gold iridium oxide and platinum are common electrode materials used in such microelectrode arrays.

Electrodes can be also used for restoring lost motor functions in paralyzed humans. For example, neuromotor prostheses based on microelectrode arrays implanted in primary motor cortex have been demonstrated[19]. The electrode array in neuromotor prostheses have been utilized for routing movement related signals from neurons to external actuators.

2.2.2 Modified electrodes

Most electrodes without modification are not suitable for distinguishing different chemical signals. However, the detection of specific chemicals can be achieved by the immobilization of enzymes on the electrode surface. This specificity based on a mediated electron transfer finds broad applications in biosensing devices nowadays. The laccase (copper-containing oxidase enzyme [21]) modified electrode system reported by Wasa[22] was the first biosensing device based on copper-containing enzymes. In Paper V we study phenol detection in water using laccase-based microband biosensor. Other enzymes such as flavoenzymes[23], dehydrogenases[24] and oxidases[25] have been utilized for sensing applications.

Figure 2.2.1 shows schemes of electron transfer for laccase modified electrode utilized for sensing phenolic compounds. If the solution does not contain any phenols a four electron oxygen reduction to water occurs at the laccase modified

Figure 2.2.1: Schemes of the (a) direct and (b) mediated electron transfer at laccase modified electrode Cat and BQ corresponds to catechol and benzoquinone, respectively.

electrode (Figure 2.2.1 a). In this case cathodic current of oxygen reduction increases due to the presence of enzymes.

The addition of an analyte such as catechol (Cat) to the electrolyte leads to the mediated electron transfer in the system. Cat first reacts with laccase and forms benzoquinone (BQ) and then BQ participate in rapid electron transfer with electrode (Figure 2.2.1 b). Thus the analyte acts as mediator in an enzymatic oxygen reduction reaction and the reduction current enhanced with increased analyte concentrations.

2.3 Actuation of biological systems

2.3.1 Electrical stimulation

Various cell types may be stimulated by conductive electrodes. For example, neuron action potential can be modulated by varying the potential of an electrode placed in close proximity to the cell. The electrical stimulation can be achieved by charging double layers at the electrode surface or by faradaic electrochemical reactions of reactants in the electrolyte. Faradaic currents can lead to the formation of toxic compounds in the electrolyte and usually electrodes operate in the polarization regime(double layer charging) in order to avoid toxic side reactions.

2.3.2 Chemical stimulations

Controlled delivery of chemical compounds to the cells has a huge potential for biomedical applications. Various techniques have been developed for controlled release of biologically active species. The main types of devices utilized for controlled delivery are discussed in section 2.3.3

2.3.3 Devices for delivering chemical species

Micropump with convective delivery A micropump is a device with characteristic features having length scales in the order 100 μm or smaller that can moves fluids. Delivery therapeutic species into the body by micropump is an attractive topic for many researchers since the early 1980s when the first micropump was developed for controlled insulin delivery [26]. Micropumps are

Figure 2.3.1: The mechanism of the cation delivery from the polymer electrode to the target electrolyte

generally divided to two following categories: displacement pumps and dynamic pumps.

In the displacement pumps, pressure on the fluid is induced by one or more moving boundaries. Reciprocating displacement pumps in which thin, semi-rigid membrane vibrate to produce pressure are the most studied micropumps.

In the dynamic pumps, the kinetic energy of the fluid is modulated in a manner that increases either its pressure or its momentum directly. Dynamic pumps usually utilize electromagnetic field which interacts directly with the working fluid to produce pressure and flow (electroosmotic pumps, electrohydrodynamic pumps, and magnetohydrodynamic pumps).

Conducting polymer electrodes Conducting polymer electrodes were also utilized for electrically controlled release of small sized charged molecules[27, 28]. Charged molecules can be incorporated into the conductive polymer matrix during electropolymerization or by electrochemically induced ion-exchange process with electrolyte. When a positive voltage is applied to a conductive electrode, electronic charge carriers are injected to the polymer and repel charged molecules from the polymer to the electrolyte (see Figure 2.3.1). Thus, controlled release can be achieved by modulation of applied voltages. It should be noted that this technique is applicable only for delivery of charged biomolecules. Conducting polymer electrodes can be also used for mechanical actuations since applying voltages to polymer electrode leads to changing its volume.

Ion pumps The local electrically controlled delivery utilized for therapy using ion pump have been reported[15, 29]. The ion pump typically consists of the ion exchange channel connected to the the source and target reservoirs.

Figure 2.3.2: Schematics of the ion bipolar junction transistor

The source reservoir is filled with solution containing charged biomolecules to be transported and contacted with conducting polymer electrode. The target reservoir is connected to the recording electrode. A cell culture or tissue can be placed close to the target. Application of voltages between polymer and recording electrodes induce an ionic current flow through the ion exchange channel. Overoxidized PEDOT:PSS or PSS is typically used as channel material. Such polymers have dense structure and are suitable only for delivery of small molecules that can penetrate the polyanion. Delivery of metallic ions such as potassium and calcium[16], and small sized charged biomolecules such as GABA[15] and glutamate[14] have been studied.

Ion transistors Nanofluidic transistors and ion bipolar junction transistors are two major types of ion transistors that have been developed and studied previously. Nanofluidic field effect transistors[30] comprise a channel with one or two dimensions in the nanometers range. The ion current in these devices depends on the gate voltage which can modulate surface charges of the channels. Since functions of nanofluidic transistors depends on surface charges these devices are sensitive to high electrolyte concentration. The other type of ion transistors is the ion bipolar junction transistor[13] (IBJT), which is ionic equivalent to BJT discussed in Section 2.1.2. The transport processes in IBJT theoretically studied in Paper I. The *npn*-IBJT comprises a collector, an emitter, a base, and a neutral junction (see Figure 2.3.2). The emitter and collector are polycation channels, while the base is a polyanion channel. The ionic current between emitter and collector in this device can be tuned by the injection and extraction of cations into the junction region from the base. When positive voltages are applied between emitter and collector, a positive emitter base voltage injects cations into the junction from the base. Injected positive charges are compensated by anions injected from the emitter, leading to high ion conductivity in the junction region. If the collector base voltage is negative, the junction region is depleted and conductivity in this region low.

Chapter 3

Conductive polymers

3.1 Conductive polymers

A large molecule that consists of many repeated sub-units, monomers, is commonly referred to as a polymer. Properties of polymers depend on the chemical structure of monomer, nature of monomer bonding and polymer morphology. In general, an accurate description of the properties of the bulk polymer materials requires model systems including many polymer chains. This makes theoretical and computational studies of polymers a big challenge. However, some physical properties of polymers such as absorption/emission spectral properties can be obtained from single molecule calculation. On the other hand, calculation of the electrical conductivity of polymers requires the consideration of an ensemble of molecules.

Conjugated polymers with alternating single and double bonds are often referred to as conducting polymers[5, 6, 7]. Chemical structures of some conjugated polymers are shown in Figure 3.1.1. The key building block for these polymer backbones is the carbon atoms. In ground state a single carbon atom has the following electronic configuration: $1s^2 2s^2 2p^2$. For the molecule with a number of bonded carbon atoms, the electrons of carbon atoms occupy states that correspond to the set of linear combinations of atomic orbitals. Such a linear combination of atomic orbitals is called a hybrid orbital. Carbon atoms in polymers are either sp , sp^2 or sp^3 hybridized[31]. In the sp^3 hybridization the carbon electrons have four equivalent orbitals that are linear combinations of s and p electronic orbitals. In sp^2 hybridization the valence electrons on each carbon center reside in a p_z orbital, which is orthogonal to the other three orbitals that are linear combinations of s and p electronic orbitals. In the case of sp hybridization one p orbital is mixed with the $2s$ orbital and the remaining two p orbitals remain unhybridized. The backbone of conducting polymers consists of sp^2 hybridized carbon centers and all the p_z orbitals combine with each other and form a delocalized set of orbitals. The electrons in these delocalized orbitals possess high mobility when some of these delocalized electrons are removed. Removing of delocalized electrons by oxidation (chemical or electrochemical) is called "p-doping" of the material which is analogous to the doping of solid state semiconductors. For a long polymer chain the conjugated p -orbitals form a one-dimensional valence electronic band. Valence band electrons become mobile when the valence band

Figure 3.1.1: Chemical structures of some conjugated polymers: (a) polyacetylene [33]; (b) polythiophene[34]; (c) polypyrrole[35]; (d) poly(p-phenylene)[36]; (e) poly{(3,4-ethylenedioxythiophene) polystyrene sulfonate} (PEDOT/PSS)[37]; (f) {sodium salt bis[3,4-ethylenedioxythiophene]3thiophene butyric acid }(ETE-S); (g) poly{[N,N-9bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]alt-5,5',9,9'-bithiophene} (P(NDI2OD-T2)[32].

is partially emptied. Most conductive polymers (see Figure 3.1.1 a-f) are p-type materials and can be doped oxidatively. However, some conductive polymer materials, such as P(NDI2OD-T2)[32] (see Figure 3.1.1 g) can be doped by reduction, which adds electrons to an unfilled conduction band.

3.2 Doping of conducting polymer and oligomers.

The electronic structures of conducting polymers can be calculated with quantum mechanical methods(see Chapter 5 for details). There are two main approaches of how geometry of polymer molecule could be considered. In the first approach the polymer chain is considered as infinite periodic structure of monomers or monomer blocks[38, 39]. In the second approach the polymer chain is treated as a molecule that consists of few linked monomer units (i.e oligomer). Electronic structure of single oligomer[40], oligomer clusters[39] and disordered ensemble of oligomers[41] have been reported.

Mechanism of *p*-doping within in conducting polymers and the subsequent changes in electronic structure can be illustrated by considering electronic structure of a single oligomer chain as shown in Figure 3.2.1. In the undoped state electrons occupy delocalized molecular orbital on the polymer backbone. The band gap of most conductive polymers in the undoped state is 2-4 eV and charge carriers cannot be thermally activated.

Figure 3.2.1: Electronic structure of an oligomer

Removal of an electron from polymer chain leads to formation of quasi particle called polaron[40]. The process of the electron removal is achieved by cation insertion and thus the polaron is compensated for by ion of the opposite charge. The induced charge causes a geometric deformation in the backbone. The combination of such localized geometric deformation and charge forms a polaron state. The polaron state has a half-integer spin $1/2$ and corresponds to a fermion. The polaron state is also characterized by the formation of an unoccupied orbital in the band gap and thus its typical absorption spectra have two peaks.

When two electrons are removed from backbone the geometrical distortions lead to attraction of polarons and two types of states can be formed. If the interaction is sufficiently large, polarons are close together sharing the same distortions then that attraction leads to the formation of a bipolaron state. In chemists' notation bipolaron generally corresponds to closed-shell singlet state[40]. Bipolaron are spinless and thus are described as boson quasiparticle. In the case when charge induced lattice interaction is low the geometric deformations do not overlap and polaron pair is formed. In chemists' terminology polaron pair corresponds to open-shell singlet or triplet states[40].

It should be noted that such an illustrative description of the electronic structure is not complete since in bulk polymer materials all described states and more complex states could contribute to the total density of states (DOS) due to the presence of disorders at the micro and nano levels in most polymers.

3.3 Polymer morphology

Dissolved polymers are composed of long molecules which form entangled and disordered coils. Upon drying some polymers retain an amorphous structure. In other polymers, the molecules form partially ordered regions of crystalline lamellae embedded to the amorphous matrix. The chain stacking in lamellae regions occurs due to the Van der Waals forces and strength of the interaction depends on the chain length and the distance between chains. The fraction of ordered chains in polymer materials typically lies in the range of 10-80%[42].

The polymers with side chain groups such as thiophene-based, poly (2,5-

bis (3-hexadecylthiophen-2-yl) thieno [3,2-b] thiophene)(PBTTT) retain highly ordered microstructure of chains stacked in parallel with dopants located in the area of side chains[43]. Nevertheless, such polymer materials have some fractions of amorphous regions. The doped PBTTT reveals coherent, band-like charge transport properties due to semicrystalline lamellar structure[43].

The morphology of polymer blends can be even more complicated because of the presence two or more types of molecules in the blend. For example, PEDOT:PSS polymer blend contains two polymers: PEDOT, which can be electrically conductive, and PSS, which conducts only ions. It has been shown that PEDOT:PSS is a two phase system consisting of PEDOT-rich and PSS-rich grains[44]. The PSS-rich grains are amorphous while PEDOT-rich grains form the crystalline lamellae regions with typical thickness on the order of 10-30 nm.

Various techniques can be used for polymer deposition including vapor-phase polymerization, chemical vapor-deposition, chemical polymerization and electrochemical polymerization. The morphology of deposited polymer films can vary depending on the polymerization method used. Scanning electron microscope (SEM), X-ray photoelectron spectroscopy(XPS), transmission electron microscopy(TEM) and grazing-incidence small-angle scattering technique are generally employed for the experimental morphology characterization[45]. Using such techniques one can estimate characteristic face-to-face distance of molecules, characteristic size of lamella regions and other geometrical and structural parameters.

The polymer films can be also organized into more complex structures using variety of nano - and macro- scale dissolvable templates including fibers, rods, particles, etc[45].

3.4 Charge transport models for conductive polymers

Various models describing charge transport in conducting polymers have been developed[46, 47, 48, 49, 50, 51, 52, 53]. The hopping models based on Miller-Abrahams formula[54] or Marcus formula[55, 56, 57] are widely used for the conductivity calculations. In disordered molecular system the distances between the molecules vary across the material. Rudolph Marcus proposed [57] that the movement of the charge carriers between molecular sites in such systems occurs as a combination of thermal activation to hop in the energy and tunneling to overcome the distance. In the Marcus approach a hopping rate v_{ij} (jumps per second) from molecular site i to site j is used for the description of the charge transport and is defined as follows

$$v_{ij} = \frac{|I_{ij}|^2}{h} \sqrt{\frac{\pi}{4\lambda kT}} e^{-(\Delta G_{ij} + \lambda)^2 / 4\lambda kT}, \quad (3.4.1)$$

here I_{ij} is the transfer integral, which characterizes the overlap between wave functions on given sites and responsible for charge carrier tunneling between the sites. kT is the thermal energy, ΔG_{ij} is the Gibbs energy difference between the sites and λ is the reorganisation energy related to electron-nuclei interaction of the molecules due to geometry modifications to switch from a neutral to a charged state and vice versa. Marcus approach is widely used for calculations

transport properties of disordered system of small organic molecules[48, 49, 50, 51, 52]. The molecular arrangement in such system can be calculated with molecular dynamics methods. Once the molecular arrangement is obtained all parameters can be calculated. Transfer integrals and reorganization energy is calculated by quantum mechanical methods while the Gibbs energy difference is approximated as the product of the electric field and displacement between molecules.

In Miller-Abrahams approach[54], the molecular arrangement is not explicitly taken into account. Thus, this method can be used for general discription of the systems with localized states. The Miller-Abrahams hopping rate is given by

$$v_{ij} = v_0 e^{-2r_{ij}/\alpha} e^{-\Delta E_{ij}/kT}, \quad (3.4.2)$$

where v_0 is the hopping rate constant, r_{ij} is the distance between sites, α is the localization length and ΔE_{ij} is the energy difference between the sites. If the energy of the initial state i is lower than the energy of the final state j (i.e $\Delta E_{ij} > 0$) the hopping rate exponentially decreases. However, in this case if the absolute value of the energy difference lower than thermal energy, the hopping event occurs quite likely and, thus, the charge transport is thermally activated under this condition. In the case when $\Delta E_{ij} < 0$ the hopping of charge carriers occurs downwards in energy. Such a downwards in energy hopping could be approximated to be always similarly easy regardless of absolute value ΔE_{ij} , by replacing $e^{-\Delta E_{ij}/kT}$ to 1 in Equation 3.4.2. The transport calculations within the Miller-Abrahams model requires knowlege of the space and energy distribution of localized sites[53]. The cubic lattice or random lattices with some characteristic scales have been used for space distribution of sites and gaussian distribution commonly used to describe the sites energy distribution.

The knowlege of hopping rates and site distributions in the space allows to calculate the transport properties of the system such as mobility μ dependence on concentration, temperature or electric field F . Monte Carlo technique or its modification have been widely utilized for modeling transport properties within both models[48, 49, 50, 51, 52, 53]. It should be noted that, Marcus and Miller-Abrahams models for hopping rate, are quite different, but often yields to similar results.

The basic continuous model for description hopping transport in conductive polymer [58] can be derived from Miller-Abrahams model for cubic lattice. This model yields to diffusion-migration like expression for the flux density

$$\vec{j}_h = -D_h^P \left[\vec{\nabla} c_h + f c_h \left(1 - \frac{c_h}{c_h^o} \right) \vec{\nabla} \varphi \right], \quad (3.4.3)$$

here D_h^P is the diffusion coefficient, c_h is the molar concentration of charge carriers (holes), c_h^o is the maximum accessible concentration of holes states, $f \equiv F/RT$ (F is the Faraday constant, R is the molar constant and T is the temperature) and φ is the electric potential. The factor $(1 - c_h/c_h^o)$ in the second is term responsible for the effective finite size effect for holes, and state that hole concentration could not exceed the concentration of the accessible states for hopping.

Conducting polymers can also efficiently transport ions when sufficiently hydrated. Mechanisms of electron-ion coupling in conductive polymers are ex-

Figure 3.4.1: A typical cyclic voltammogram of a conducting polymer

perimentally studied in cyclic voltammetry experiments[59]. A typical cyclic voltammogram of a conducting polymer reveals an oxidation peak followed by a current plateau (see Figure 3.4.1). The plateau is usually associated with a capacitive charging process in a polymer electrode. A variety of theoretical models have been proposed in attempt to explain the charging mechanism in conducting polymers.[60, 59, 61, 62, 63]. However, the standard electrochemical models considering only the faradaic current result in cyclic voltammograms exhibiting the peaks but failing to reproduce the plateaus[60, 59, 61]. With the goal to reproduce the plateaus, the model have been proposed by Feldberg [60] in which the total current is a sum of the faradaic current associated with electrochemical reactions and a phenomenological capacitive current which is proportional to the amount of charges in oxidized polymer [59, 61]. Otero *et. al.*[62] suggested the model for voltammetry of conducting polymers where effect of conformational movements of polymeric segments was taken into account within the phase transitions model [64]. It should be noted however that effects of conformational movements could be important under some experimental condition but this model could not fully explain a nature of the ion exchange between a polymer electrode and a solution observed in an experiment[65]. Another approach was proposed by Warren and Madden [63]. They showed that the cyclic voltammetry of conducting polymer could be modeled as an RC transmission line where the oxidation state dependence of the polymer’s electronic conductivity was taken into account.

Besides cyclic voltammetry, other techniques have been also employed for studying the capacitive behaviour and the ionic-electronic transport interplay in conductive polymers. In “moving front” experiments the motion of the boundary between doped and undoped regions is monitored by dynamic color changes.[66] Three-terminal electrochemical transistors based on conducting polymers have been used to the study conductivity modulation and gate effect due to an ionic inflow from the electrolyte to the polymer channel[67]. Despite the difference in architecture of those devices, the underlying physics is identical and common with cyclic voltammetry analysis. In particular, models utilized for explaining experimental results do not typically assume any redox reactions and are solely based on the coupling between electronic and ionic motion as described by the Nernst-Planck-Poisson equations (drift-diffusion equations)[68, 69, 70].

Hence, even after decades of polymer research the most fundamental questions concerning the nature of capacitive behaviour and the electron-ion cou-

pling in these materials still remain unsolved and are highly controversial. In Paper II we propose a model that describes cyclic voltammograms of PE-DOT:PSS polymer material using equation 3.4.3 and modified Nernst-Planck-Poisson equations (discussed in detail in Chapter 4) for two phase system. This model successfully describes the main features of the capacitive charging due to the formation of double layers.

Chapter 4

Electrolytes, electrode interfaces and ion exchange membranes

4.1 Ion transport processes

Transport phenomena in the electrolytes, membranes and polymers may be described phenomenologically by the thermodynamics of irreversible processes [71]. Two fundamental hypothesis are assumed: “continuum hypothesis” and “local equilibrium hypothesis”. State variables in this approach such as energy, electric potential, pressure are functions of position r and time t . According to the “continuum hypothesis”, volume elements dV of described system with position $\mathbf{r}$ in the space assumed to be small enough that infinitesimal calculus can be applied. Note that volume is still macroscopic in the sense that it contains a large number of the molecules. The observed changes in state variables mostly take place over time scale larger than motions of the molecules. Thus, it can be assumed that internal equilibrium established within volume element dV (“local equilibrium hypothesis”).

Since molar electrochemical potentials $\tilde{\mu}_i$, number of moles n_i and pressure p may vary with position, the common thermodynamic equation for the Gibbs potential of homogeneous system

$$G = \sum_i \tilde{\mu}_i n_i = U - TS + pV \quad (4.1.1)$$

is not applicable (here U is internal energy, T is temperature and S is entropy, V is a volume of the system). Instead, equations that relate thermodynamic properties and variables in local form, i.e at every point within continuum, should be used.

However, if we divide the system volume in small volume elements dV which can be considered as homogeneous subsystems, the Gibbs potential of the volume elements can be written as

$$dG = \sum_i \tilde{\mu}_i dn_i = dU - TdS + pdV. \quad (4.1.2)$$

Dividing equation 4.1.2 by the volume dV we arrive to the fundamental thermodynamic equation that applies at the position of the volume element

$$g = \sum_i \tilde{\mu}_i c_i = u - Ts + p, \quad (4.1.3)$$

where $g \equiv dG/dV$ is Gibbs potential density, $c_i \equiv dn_i/dV$ is molar concentration of component i , $u \equiv dU/dV$ is internal energy density and $s \equiv dS/dV$ is entropy density.

Transport in a binary electrolyte Consider binary a electrolyte dissociating completely into positively charged ions or cations (+) and negatively charged ions or anions (-) whose charge numbers $z_+ = 1$ and $z_- = -1$ satisfy stoichiometric relation $z_+ c_+ + z_- c_- = 0$ in the bulk. For binary electrolyte solutions Gibbs potential density [72, 73] can be written in terms of ion molar concentration $c_{\pm}$ and electrostatic potential φ

$$g = u - Ts = -\epsilon |\nabla \varphi|^2 + c_+ F \varphi - c_- F \varphi + RT \left\{ c_+ \ln \left(\frac{c_+}{c_{max}} \right) + c_- \ln \left(\frac{c_-}{c_{max}} \right) + [1 - (c_+ + c_-)/c_{max}] \ln [1 - (c_+ + c_-)/c_{max}] \right\}. \quad (4.1.4)$$

The first three terms on the right side of equation 4.1.4 are electrostatic energy contribution u and the last two terms are entropic contribution Ts , where finite size of solvent molecules is taken into account (here $c_{max} = 1/(N_A a^3)$ is maximum possible ion molar concentration, a is solvent molecule size and N_A is Avogadro constant).

The molar electrochemical potentials of the ions are obtained as

$$\tilde{\mu}_{\pm} = \frac{\delta g}{\delta c_{\pm}} = \pm F \varphi + \mu_{\pm} = \pm F \varphi + RT \left[\ln \left(\frac{c_{\pm}}{c_{max} - (c_+ + c_-)} \right) \right] \quad (4.1.5)$$

Thus, molar electrochemical potential is the sum of two terms: molar chemical potential $\mu_{\pm}$ and electrical potential contribution $\pm F \varphi$.

In the linear approximation, ionic fluxes can be evaluated as

$$\vec{j}_i = \frac{D_i c_i}{RT} \vec{\nabla} \tilde{\mu}_i, \quad (4.1.6)$$

where D_i is the ionic diffusion coefficient. Combining equation 4.1.5 and 4.1.6 we arrive to the modified Nernst-Planck equation for the binary electrolyte

$$\vec{j}_{\pm} = -D_{\pm} \left[\vec{\nabla} c_{\pm} \pm f c_{\pm} \vec{\nabla} \varphi + \frac{c_{\pm} \vec{\nabla} (c_+ + c_-)}{c_{max} - (c_+ + c_-)} \right] \quad (4.1.7)$$

The first term in equation 4.1.7 describes the ion diffusion, the second term is related to the migration in electric field (here $f \equiv F/RT$) and the last term is a correction due to finite size of solvent molecules. Assuming $c_{max} \rightarrow \infty$ equation yields to Nernst-Planck equation for diluted electrolytes

$$\vec{j}_{\pm} = -D_{\pm}(\mathbf{r}) \left[\vec{\nabla} c_{\pm} \pm f c_{\pm} \vec{\nabla} \varphi \right]. \quad (4.1.8)$$

Transport equations 4.1.7, 4.1.8 have been used for modeling ion transport in various systems such as electrolyte/electrode interfaces, nanoporous system, ion exchange membranes, nanofluidic transistors and ion bipolar junction transistors.

4.2 Poisson equation

In order to describe the potential distribution in a system with distributed charges, an equation that relates charge density ρ to the electric potential φ are required.

A solution of Poisson's equation for the linear, isotropic and homogeneous medium with permittivity ϵ is a common approach for finding potential distribution in systems with mobile charge carriers

$$-\nabla \cdot (\epsilon \epsilon_0 \nabla \varphi) = \rho \quad (4.2.1)$$

The local charge density in equation 4.2.1 is the sum over all charged compounds

$$\rho = F \sum_i z_i c_i \quad (4.2.2)$$

In the case when the variation of an electric field can be neglected the electroneutrality assumption may be used

$$F \sum_i z_i c_i = 0, \quad (4.2.3)$$

This assumption is common for solving ion transport equations in bulk electrolytes.

However, the description of the metal/electrolyte or membrane/solution interfaces requires a solution of Poisson's equation to represent properly the accumulated charges at these regions.

4.3 Mass balance equation

In the system with N component mass balance equation relates time change in molar concentration, ion flux and molar production rate π_i related to homogeneous reactions can be written in the form

$$\frac{\partial c_i}{\partial t} + \vec{\nabla} \cdot \vec{j}_i = \pi_i, \quad (4.3.1)$$

Generally, heterogeneous chemical reaction occurs at the interfaces between different phases and they are usually introduced as a boundary condition of the transport equation.

In absence of homogeneous chemical reactions the molar concentration is conserved and equation 4.3.1 yields to continuity equation

$$\frac{\partial c_i}{\partial t} + \vec{\nabla} \cdot \vec{j}_i = 0. \quad (4.3.2)$$

This equation under steady state condition reduces to

Figure 4.4.1: (a) Schematic structure of the double layer region. (b) A typical capacitance-voltage characteristic obtained from the Gouy-Chapman-Stern model.

$$\vec{\nabla} \cdot \vec{j}_i = 0, \quad (4.3.3)$$

which states that the total molar concentration of component i in the system is constant.

4.4 Electrode interfaces

There are two main processes observed at the metal electrode immersed to the electrolyte. Capacitive process is accomplished with formation of charged electrical double layers, and Faradaic process is related to electron charge transfer between dissolved molecules and metal due to electrochemical reactions. The mechanism of these processes are discussed in the following subsections.

4.4.1 Capacitive charging

When a potential is applied to the metal electrode an excess or deficiency of electrons with charge q^M is created at the metal surface. These electronic charges attract mobile ions with opposite charges from solution and repel ions with the same charge. As result, the region with distributed ionic charges $q^S = -q^M$ is created in the solution. This region is called an electric double layer. One of the simplest models that describes the charge distribution in double layers is the Gouy-Chapman-Stern (GCS) model[74]. In this model the ion concentrations follow Boltzmann's distribution and can be found as a solution of Nernst-Planck 4.1.8 and steady state equations 4.3.3, together with Poisson equation 4.2.1 for the charge density and electric potential. According to this model ions can approach the electrode only to a specific distance ($\lambda_s = x_2 - x_1$) due to the finite size of the solvent molecules and ions. The region with immobile molecules is called the Stern layer, compact layer or Helmholtz layer. The electric field and dielectric function ϵ_w in the Stern layer are assumed to be constant. The structure of a double layer and potential profile are schematically shown in Figure 4.4.1 a.

Figure 4.4.2: Scheme of (a) oxidation and (b) reduction reactions at the electrode. O and R is the oxidized and reduced species, respectively, while n is the number of transferred electrons.

Despite the simplicity of the GCS model, the results are not trivial. In particular this model predicts non linear dependence of specific double layer capacitance, defined as $C = d\sigma^S/d\varphi$ from applied potential φ (here $\sigma^S = q^S/A$, A is the area of electrode). Figure 4.4.1 b shows the typical capacitance voltage characteristic obtained within the GCS model.

It should be noted that, the GCS model fails to predict a capacitance at the high ion concentrations and the large applied voltages. Various approaches that take into account finite size of ions and solvent molecules have been proposed for describing double layer charging under these conditions. Modified Poisson-Nernst-Planck[72, 73], molecular dynamic[75, 76] , and density functional theory[77, 78, 76] are examples of the most accurate approaches that have been employed for modeling double layers.

4.4.2 Electrochemical reactions (Butler-Volmer model for one step electrode process)

We consider the mechanism of the simplest faradaic one step electrode process[74] shown in Figure 4.4.2. Consider two chemical species dissolved in an electrolyte and involved in a redox reaction at an electrode surface. The oxidation reaction occurs when n electrons is transferred from a reduced species to the electrode. The reduced species is said to be oxidized. In the reduction reaction, the oxidized species accepts n electrons from the electrode and is said to be reduced. Thus, the redox reaction (combination of reduction and oxidation reactions) at the electrode surface can be written in the form

Here O is the oxidized species, n is the number of transferred electrons and R is the reduced species. The reaction rates for both electrode processes are assumed to be proportional to the corresponding surface concentrations. Thus, the reaction rate of the forward reaction is $v_f = k_{O \rightarrow R} c_O$ and the rate of the reverse reaction is $v_b = k_{R \rightarrow O} c_R$. The net conversion rate (v_{net}) of O to R can be expressed in the form

$$v_{net} = v_f - v_b = k_{O \rightarrow R} c_O - k_{R \rightarrow O} c_R \quad (4.4.2)$$

The coefficients $k_{O \rightarrow R}$ and $k_{R \rightarrow O}$ are depending on material properties of the species, electrolyte, electrode as well as on the applied potential $\Delta\varphi = \varphi_{\text{electrode}} - \varphi_{\text{electrolyte}}$ between electrode and electrolyte. Butler-Volmer assumption implies the following dependence of reaction rate coefficients

$$k_{O \rightarrow R} = k^0 \exp[-\alpha n f(\Delta\varphi - \varphi^0)], \quad (4.4.3)$$

$$k_{R \rightarrow O} = k^0 \exp[(1 - \alpha) n f(\Delta\varphi - \varphi^0)], \quad (4.4.4)$$

where k^0 is the standard rate constant, α is the transfer coefficient and φ^0 is the formal potential. Combining equations 4.4.3, 4.4.4 and 4.4.2 the net conversion rate is obtained as

$$v_{\text{net}} = k^0 (c_R e^{(1-\alpha)n(\Delta\varphi - \varphi^0)F/RT} - c_O e^{-\alpha n(\Delta\varphi - \varphi^0)F/RT}) \quad (4.4.5)$$

The current density associated with the electrochemical reaction at the electrode given by

$$i = nF v_{\text{net}} = k^0 (c_R e^{(1-\alpha)n(\Delta\varphi - \varphi^0)F/RT} - c_O e^{-\alpha n(\Delta\varphi - \varphi^0)F/RT}) \quad (4.4.6)$$

Equation 4.4.6 describes a current-voltage characteristic in the electrochemical cell and widely used in the treatment of the problems of heterogeneous kinetics at electrode surfaces.

Equilibrium for one step electrode process is achieved when net conversion rate is zero ($v_{\text{net}} = 0$) and surface concentrations are equal to the bulk. Under these conditions, the equation 4.4.5 yields to the Nernst equation for equilibrium potential

$$\Delta\varphi_{\text{eq}} = \varphi^0 - \frac{RT}{F} \ln \frac{c_R^*}{c_O^*}, \quad (4.4.7)$$

where c_R^* and c_O^* are bulk concentrations of reduced and oxidized species, respectively. In the case when bulk concentrations of reduced and oxidized are equal to each other, the formal potential φ^0 defines the equilibrium potential $\Delta\varphi_{\text{eq}}$.

4.5 Ion exchange membranes

Ion exchange membranes are made of a polymer with fixed ionic groups such as sulfite or ammonium groups. The membranes are used for transporting dissolved ions from one solution to another in desalination, drug delivery and chemical recovery applications. There are two types of ion exchange membranes: a cation exchange membrane (CEM) and an anion exchange membrane (AEM). The membranes with immobilized anionic groups repel anions and attract cations to compensate their fixed charges. They are known as cation selective or cation exchange membranes. Schematics of the cation exchange membrane system is shown in Figure 4.5.1 a. Similarly, the membranes with fixed cationic groups are known as anion selective or anion exchange membranes. Mobile ions of opposite charge to the membrane immobilized group are called counterions while ions with same charge as fixed groups are called coions.

Figure 4.5.1: (a) Schematics of a CEM system (b) Equilibrium ion concentration and potential profiles in a CEM. c_+ , and c_- correspond to the concentration of mobile cation and anion.

A three-layer system composed of a membrane and two diffusion boundary layers contacting either sides of the membrane is commonly referred to as a membrane system. The concept of diffusion boundary layer is associated with surrounding electrolyte reservoirs connected to the electrodes. According to this concept, an unstirred diffusion boundary layer with width δ is formed at the solution/membrane interface. The solution outside the diffusion boundary layer is assumed to be completely stirred and, thus, has the concentration of the bulk solution.

Donnan Equilibrium Consider a cation exchange membrane (CEM) with uniformly distributed fixed groups that have concentration c_{fix} and charge number $z^M = -1$ in contact with binary symmetric electrolyte dissociating completely into cations (+) and anions (-). We assume that the electrochemical potential for ions in the electrolyte and membrane can be written in the same form

$$\tilde{\mu}_{\pm} = \pm F\varphi + RT \ln c_{\pm} \quad (4.5.1)$$

The equilibrium distribution of ionic species between an external solution (superscript w) and a membrane (superscript M) is achieved when the electrochemical potentials become equal in two phases

$$\tilde{\mu}_{\pm}^w = \tilde{\mu}_{\pm}^M \quad (4.5.2)$$

When equation 4.5.1 and equation 4.5.2 are combined this becomes the equation for distribution equilibria

$$c_{\pm}^M = c_{\pm}^w e^{\mp F \Delta \varphi_D}, \quad (4.5.3)$$

where $\Delta \varphi_D = \varphi^M - \varphi^w$ is the Donnan potential and $c_{\pm}^w = c_+^w = c_-^w$ is the bulk ion concentration. Using local electroneutrality condition inside membrane ($c_+ - c_- + z^M c_{fix} = 0$) and equation 4.5.3 one can obtain ionic concentration in the membrane phase

$$\begin{aligned} c_+^M &= \frac{c_{fix}}{2} + \left[\left(\frac{c_{fix}}{2} \right)^2 + (c_{\pm}^w)^2 \right]^{1/2} \\ c_-^M &= \frac{c_{fix}}{2} - \left[\left(\frac{c_{fix}}{2} \right)^2 + (c_{\pm}^w)^2 \right]^{1/2} \end{aligned} \quad (4.5.4)$$

In strongly charged membranes $c_{fix} \gg c_{\pm}^w$ and equation 4.5.4 implies that counter ions compensate the fixed membrane charges and its concentration is $c_{+}^M \approx c_{fix}$ while concentration of coions is low.

By combining local electroneutrality condition inside the membrane with equation 4.5.3 we could find a relation between the Donnan potential and the concentration of fixed charges

$$-z^M c_{fix} = c_{\pm}^w (e^{-f\Delta\varphi_D} - e^{f\Delta\varphi_D}) = \sinh(-f\Delta\varphi_D/2) \quad (4.5.5)$$

This equation implies that Donnan potential is negative for CEM and positive for AEM.

The Donnan potential $\Delta\varphi_D$ is the difference in an electric potential between membrane and electrolyte phases that have uniform potentials φ^M and φ^w , respectively, far from membrane/solution interface. Somewhere between membrane and electrolyte phases the potential must show a nonlinear spatial variation from φ^w to φ^M and according to the Poisson equation, space charge density should have non zero value. The regions at the membrane/solution interface where the Donnan potential drop takes place is called electrical double layers. In order to find how the potential and ionic concentrations are distributed in the membrane system we need to obtain solution of Nernst-Planck 4.1.8, Poisson's 4.2.1 and mass balance 4.3.3 equations. Figure 4.5.1 b shows a typical spatial variation of potential and ionic concentration in a CEM system in zero electric field. Since a fixed groups are negatively charged, the potential in membrane phase is negative. As expected, the most significant potential drops occur at the solution/membrane interfaces due to the formation of double layers at these regions and local electroneutrality assumption is valid everywhere except the double layers regions.

Steady state transport across ion exchange membrane When a potential bias is applied to the diffusion boundary layers the ionic current starts to flow through the membrane system. Under steady state condition the phenomenon known as a concentration polarization occurs. On the left side, where cations enter, the ion concentration decreases next to the membrane while the concentrations increases on the opposite side as shown in Figure 4.5.2 a. This phenomenon is related to the fact that both diffusion and migration terms contribute to the ion flux densities in the electrolyte phase.

The total current density of ionic species in a membrane system is the sum of two contribution describing anion and cation current densities

$$\mathbf{i}_{total} = F(z_+ \mathbf{j}_+ + z_- \mathbf{j}_-) = \mathbf{i}_+ - \mathbf{i}_- \quad (4.5.6)$$

At the steady state regime ionic flux density is independent of the position but diffusion and migration contributions to fluxes can depend on the position. According to the Nernst-Planck equation and the electroneutrality condition at the diffusion boundary layer, non zero total current implies that concentration gradients must evolve on both sides of the membrane. Figure 4.5.2 c shows diffusion and migration contribution to ion current densities for counter and coions at the end diffusion boundary layer for different applied voltages. For counter ions (+) diffusion and migration contributions to the current density are approximately the same magnitude and direction while for coions (-) the migration flux cancels diffusion flux.

Figure 4.5.2: (a) Concentration polarization in CEM. c_+ and c_- correspond to the concentration of mobile cation and anion; (b) Total (j_{total}), cation (j_+) and anion (j_-) steady state fluxes in CEM as function of applied voltage; (c,d) Diffusion ($j_+^{Diffusion}$ and $j_-^{Diffusion}$) and migration ($j_+^{Migration}$ and $j_-^{Migration}$) contribution to the cation and anion fluxes (c) at the end of diffusion boundary layer and (d) at the middle of the membrane

In membrane phase the diffusion and migration contributions to ion current densities are completely different due to presence of the fixed charges. Since counter ions compensate fixed charges in the membrane phase, its concentration is much higher than the concentration of coions which are mostly excluded. This implies that the counterion migration current contributes mostly to the total current in the membrane region while other contributions are low as shown in Figure 4.5.2 d.

The total current density in CEM is mostly contributed by counterions while coions reveals low leakage current (Figure 4.5.2 b). The current voltage characteristics of the membranes reveals two regimes. In the linear regime, the ions concentration in the electrolyte at the side where counter ions enter membrane linearly decreases with applied voltage until it reaches zero. And when coion concentraion reaches zero the limiting current density (j_{lim}) is achieved. The further increasing of applied voltage leads to relatively slower current growth and membrane start to operate in overlimiting regime ($j > j_{lim}$). In this regime an extended space charge layer with high electric field is formed at the electrolyte/membrane interface.

Chapter 5

First principal study of the molecular systems

5.1 The Schrödinger equation

In quantum mechanics[79] (QM), a system of particles can be described by wave function Ψ . This function depends on the position of each particle and time. The probability distribution function for the particles to be found at given position corresponds to absolute squared value of the wave function $|\Psi|^2$. Observable quantities in QM such as energy, positions, momenta are associated with operators. The property of the systems can be obtained by acting with corresponding operator on wave function of the system.

The wave function of the system can be found as a solution of the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = \hat{H} \Psi(\vec{r}, t), \quad (5.1.1)$$

here i is an imaginary unit and $\hbar$ is the reduced Planck constant and $\hat{H}$ is the Hamiltonian operator which is associated with total energy of the system. In the case when Hamiltonian does not depend on time the wave function can be expressed as a product of spatial and temporal parts. Spatial part of the wave function can be obtained by solving the time-independent Schrödinger equation

$$\hat{H} \Psi(\vec{r}) = E \Psi(\vec{r}), \quad (5.1.2)$$

here E is the energy of the state, and the total wave function has time dependency and can be written in the form

$$\Psi(\vec{r}, t) = \Psi(\vec{r}) e^{iEt/\hbar}. \quad (5.1.3)$$

Defining the hamiltonian of a complex system and solving the resulting equation requires a lot of efforts and usually various simplifications and approximation are taken into account.

5.2 The many body problem

The hamiltonian operator of the molecular systems contains at least five contributions [79, 80]

$$\hat{H}_{tot} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ee} + \hat{V}_{en}. \quad (5.2.1)$$

The first and second terms describe the kinetic energy of nuclei and electrons, respectively. The last three terms correspond to the electrostatic potential energy due to Coulomb interaction between nuclei (third term), electrons (fourth term) and electron-nuclei (last term).

According to the commonly used Born–Oppenheimer approximation, nuclei movement is negligible on the time-scale of the electron movements, since the mass of the nuclei is much larger than mass of an electron. Hence, the kinetic energy of the nuclei $\hat{T}_n$ can be neglected in the hamiltonian $\hat{H}_{tot}$ and only the electronic part of the hamiltonian

$$\hat{H}_e = \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ee} + \hat{V}_{en} \quad (5.2.2)$$

may be used for the solution equation 5.1.2. The Born–Oppenheimer approximation significantly reduces the complexity and increases feasibility of the calculations.

5.3 Linear combination of atomic orbitals and basis sets

For atomic and molecular system the many body problem may be solved numerically and the total wave function Ψ can be constructed as a combination of molecular orbitals (MO) ψ_i . Each MO may be expanded in terms of basis functions χ_α called atomic orbital (AO)[79]

$$\psi_i = \sum_{\alpha=1}^N c_{i\alpha} \chi_\alpha. \quad (5.3.1)$$

Such construction of the MOs from a linear combination of AOs (MO-LCAO) is the typical way of obtaining many-electron wave functions, and various methods can be used to determine the coefficient $c_{i\alpha}$, as discussed in subsequent sections.

There are two types of one electron atomic orbitals commonly used in electronic structure calculation: Slater-type orbitals (STO) and Gaussian-type orbitals (GTO). Slater-type orbitals have the following functional form [79]

$$\chi_{\xi nlm}^{STO} = N r^{n-1} e^{-\xi r} Y_{lm}, \quad (5.3.2)$$

here N is the normalization constant, n, l, m are quantum numbers, ξ is a constant related to the corresponding nucleus charge, r is the electron's distance from the nucleus, and Y_{lm} are the spherical harmonics functions.

Gaussian-type orbitals with functional form [79]

$$\chi_{\xi nlm}^{GTO} = N r^{2n-2-l} e^{-\xi r^2} Y_{lm} \quad (5.3.3)$$

are widely used for calculating the electronic structure of molecules because the evaluation of integrals with these orbitals requires less effort than calculation using Slater-type orbitals. Typically, a linear combination of GTOs called contracted Gaussian-type orbital (CGTO) are used to emulate STOs. In particular, STO- n G basis set uses linear combination of n GTO to be fitted to a single STO and known as minimal basis set. Valence electrons which principally take part in the molecular bonding are often represented by more than one basis function. The basis sets with more than one CGTO per valence electron are known as split valence basis sets. In the case of two CGTOs per valence electron it is called the double-zeta, for three CGTOs it is called triple-zeta, *etc.* Furthermore, polarization functions can be included to the basis set. The polarization functions represents a higher subshell with quantum number $l + 1$. For example, adding a d -type ($l = 3$) to a p -shell ($l = 2$) electron corresponds to d -type polarization function. In order to reduce computational cost, the core (nonvalence) electrons can be also treated as an effective charge distribution rather than with explicit basis functions.

Pople-type basis sets with notation X-YZg(d) are used in the Paper III, IV. In this basis set X is the number of linearly combined GTOs in each CGTO for the core electrons. The valence orbital contains two basis function each, Y is the number of GTOs for the first basis function, and Z for the second valence basis function. It also includes d-type polarization functions.

5.4 Self-consistent field theory: Hartree-Fock approximation and variation principle

Electron spin is commonly introduced as an *ad hoc* quantum effect when relativistic effects in the Hamiltonian are neglected. The spin dependence of MO are employed by multiplication $\psi_i(\vec{r}_i)$, with a spin function α or β representing the up- or down-spin of the electron. The resulting one electron spin orbitals can be written in the form $\psi_i(\vec{q}_i)$ (here $\vec{q}_i = \{\vec{r}_i, \sigma_i\}$ and σ_i denotes spin of electron). The total wave function Ψ for a N electron system is generally built using one electron spin orbitals combined in the form of Slater determinants (SD)[79, 80]

$$\Psi(\{\vec{q}_i\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{q}_1) & \cdots & \psi_N(\vec{q}_1) \\ \vdots & \ddots & \vdots \\ \psi_1(\vec{q}_N) & \cdots & \psi_N(\vec{q}_N) \end{vmatrix} \quad (5.4.1)$$

The total many electron wave function constructed in the form of Slater determinants satisfies the requirement of anti-symmetry for electrons. It also obeys the Pauli exclusion principle stating that two electrons cannot have all quantum numbers equal. It means that at most one α and one β electron can occupy a single MO.

The total wave function of the many electron system expressed in the form of Slater determinants depends on the coefficient in the LCAO described in the section 5.3. The coefficients that provide the “best” approximation for total wave functions can be obtained by employing the variational principle. The

variational principle here states that the calculated ground state energy

$$E_e = \langle \Psi | \hat{H}_e | \Psi \rangle \quad (5.4.2)$$

of the system described by an approximate wave function has an energy equal to or above the exact energy. The equality holds only in the case when the wave function is the exact function. Obtaining of the “best” approximate wave function can be achieved by iterative minimization of the energy as function of the coefficients.

The Hamiltonian operator within Born–Oppenheimer approximation described qualitatively in section 5.2 and can be expressed as [79, 80]

$$\hat{H}_e = - \sum_k \frac{\hbar^2}{2m} \nabla_k^2 + \sum_k V(r_k) + \sum_{kk'} \frac{e^2}{8\pi\epsilon_0 |\vec{r}_k - \vec{r}_{k'}|} \quad (5.4.3)$$

The last term in the equation is the electron–electron interaction term. The evaluation of this term is the most challenging, as it cannot directly operate on the one-electron wave functions. However, employing Hartree-Fock (HF) approximation allows to reduce this term to a sum of one-electron operators which can be applied to the individual molecular orbitals. In HF approximation each electron experiences only the average self-consistent field generated by the other electrons. Applying variational principle to the ground state energy of the system with Hamiltonian 5.4.3 and the total wave function in the form of SD one can obtain the following Hartree-Fock equation [79, 80]

$$\begin{aligned} \left(-\frac{\hbar^2}{2m} \nabla_i^2 \right) \psi_i(\vec{r}) + V(\vec{r}) \psi_i(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \sum_{k \neq i} \int \frac{|\psi_k(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r}' \psi_i(\vec{r}) \\ - \frac{e^2}{4\pi\epsilon_0} \sum_{k \neq i} \int \frac{\psi_k(\vec{r}) \psi_i(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \psi_i(\vec{r}) = E_i \psi_i(\vec{r}) \end{aligned} \quad (5.4.4)$$

First term in the right side of the equation 5.4.4 corresponds to the kinetic energy of electron with mass m , the second term is the attractive potential energy between the electron and field created by nuclei, the third term represents the coulombic repulsion between electrons and the last term represents the exchange energy between electrons.

The Hartree-Fock equation 5.4.4 may be written as [79, 80]

$$\hat{F}_i \psi_i(\vec{r}) = E_i \psi_i(\vec{r}), \quad (5.4.5)$$

where $\hat{F}_i$ is the Fock operator and its eigenvalues is the energies of the corresponding MO. Since the Fock operators depends on unknown functions $\psi_i(\vec{r})$ the equation 5.4.5 should be solved iteratively. Using some initial guess of $\psi_i(\vec{r})$ one can formulate $\hat{F}_i$ and obtain a new function $\psi_i(\vec{r})$ as a solution of the equation 5.4.5. The updated $\psi_i(\vec{r})$ then is used for constructing an updated $\hat{F}_i$ and the process is repeated until the change in wave functions and energy of the system with each iteration is smaller than some predefined value. At this point the Hartree-Fock equation achieves self-consistency. Thus, the Hartree-Fock method is called as a self-consistent field (SCF) method.

5.5 Density functional theory

Density functional theory (DFT) method is based on Hohenberg–Kohn theorems [81]. They state that properties of the many body electron system in a ground state can be obtained from the electron density ρ . The first theorem demonstrates that the electron density is uniquely determined by the external potential. According to the second theorem an energy functional for the many body electron system can be defined and a ground state electron density minimizes the energy functional.

The framework suggested by Kohn and Sham[82] is the foundation for using DFT in computation electronic properties of chemical systems. In the Kohn-Sham method the many body electron system is considered under assumption of non-interacting electrons moving in a effective potential. The general DFT energy functional can be written as[79, 83]

$$E_{DFT}[\rho] = T_S[\rho] + E_{ne}[\rho] + J[\rho] + E_{xc}[\rho]. \quad (5.5.1)$$

The first term in equation 5.5.1 is the kinetic energy of non-interacting electrons, the second term describes nuclei-electron potential energy and the third term is the Coulomb electron-electron repulsion. The last term represents the energy of exchange correlation interaction. The exchange correlation energy is defined as a part that remains after subtraction of non-interacting electrons kinetic energy, electron-nuclei, and electron-electron Coulomb potential energies from exact energy. Once DFT energy functional is formed the single-particle eigenvalue equations similar to Fock equation 5.4.5 can be formulated[79, 83]

$$\left(-\frac{\hbar^2}{2m} \nabla_i^2 + v_{eff}(\vec{r}) \right) \psi_i(\vec{r}) = E_i \psi_i(\vec{r}). \quad (5.5.2)$$

Here the single electron orbitals $\psi_i(\vec{r})$ are called Kohn-Sham orbitals. The Kohn-Sham electron density determined as

$$\rho(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2 \quad (5.5.3)$$

used for obtaining effective potential[79, 83]

$$v_{eff}[\rho](\vec{r}) = \frac{\delta E_{ne}[\rho]}{\delta \rho} + \frac{\delta J[\rho]}{\delta \rho} + \frac{\delta E_{xc}[\rho]}{\delta \rho} = v_{ne}(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \int d\vec{r}' \frac{\rho(\vec{r}', t)}{|\vec{r} - \vec{r}'|} + v_{xc}(\vec{r}), \quad (5.5.4)$$

where the second term in the sum is Hartree potential. The Kohn-Sham equations 5.5.2 solved iteratively analogous to SCF method.

The main difficulty with implementation of DFT is formulation of an unknown exchange-correlation energy functional $E_{xc}[\rho]$. Various attempts have been made to find “good” approximation for $E_{xc}[\rho]$ [79, 83]. The Local Density Approximation (LDA) assumes that $E_{xc}[\rho]$ is a local function of the density. In a more general case when electron spin densities are not equal to each other, LDA is replaced by the Local Spin Density Approximation (LSDA). In LSDA $E_{xc}[\rho]$ is given as the sum of two terms and each depends on the individual spin density. LDA and LSDA successfully describes nearly free-electron-systems but is not sufficiently accurate for calculating properties for most chemical systems.

Exchange-correlation energy functionals with additional terms that depend on the gradient of charge density are called generalized gradient approximation (GGA) functionals. These functionals improve accuracy and can be used for the prediction of geometries and energies of many strong bound systems.

LDA, LSDA and GGA functionals are commonly denoted as Density Functional approximation DFA functionals[84]. DFA employed localized model for exchange correlation interaction and do not take into account non local effects.

The hybrid DFT methods, which combine the Kohn-Sham and the Hartree-Fock methods are commonly used for incorporating non local exchange-correlation effects into DFA. These methods can provide reasonable accuracy for large molecular systems. The general form of hybrid exchange-correlation density functional is[84].

$$E_{xc} = c_x E_x^{HF} + E_{xc}^{DFA}, \quad (5.5.5)$$

where c_x is the fractional number, typically ranging from 0.2 to 0.6. However, using the general hybrid density functionals can lead to errors since exchange-correlation potential decays as $-c_x/r$ (not as correct $-1/r$ decay).

The long range corrected (LC) hybrid density functionals have been developed in order to accurately describe exchange-correlation interactions. LC hybrid density functionals retain full Hartree-Fock exchange for long-range (LR) electron-electron interaction while for short-range (SR) interaction only c_x fraction of Hartree-Fock exchange is taken into account. In Paper III and Paper IV we used the long range corrected (LC) hybrid density functional $wB97XD$ with following exchange-correlation term[84, 85]

$$E_{xc}^{wB97XD} = E_x^{LR-HF} + c_x E_x^{SR-HF} + E_x^{SR-DFA} + E_c^{DFA} + E_{disp}. \quad (5.5.6)$$

The last term in equation 5.5.6 describes empirical atom to atom dispersion correction for non-covalent interaction that does not involve the sharing of electrons. Introduction of this term is highly useful for systems where such weak interactions are important, for example, stacked molecular systems.

5.6 Optimization

For obtaining the most realistic electronic structure of molecular system the knowledge of the minimum energy structure is required. DFT and HF formalism described above can be also exploited for obtaining such optimized geometry[79].

The minimum energy structure can be described by a vector of the nuclei positions. Forces acting on these nuclei is proportional to the gradient of the potential energy $\frac{\partial V}{\partial \vec{r}_i}$. The nuclei geometry is optimized when $V(\vec{r})$ is at local minimum. The computational model that provides approximate geometry uses numerical calculation of potential energy gradients from HF or DFT calculations. In the case if forces are less than predetermined threshold and second derivative matrix $\frac{\partial^2 V}{\partial \vec{r}_i \partial \vec{r}_j}$ of the system is positive definite, the geometrical structure of the molecule corresponds to the minimum energy. Otherwise, nuclei are moved along the forces vectors using some algorithm. For updated geometry one can obtain new electronic structure and potential energy gradients. This optimization procedure iteratively repeats until convergence criteria are met.

DFT optimized geometries are generally good for description of electronic and optical properties of the molecular systems.

5.7 Time dependent density functional theory

Time dependent density functional theory (TDDFT) is based on the idea that a complicated time-dependent Schrödinger equation for the many body system can be replaced by a set of time-dependent single-particle equation. The formal foundation of TDDFT is Runge-Gross theorem[86] that is an analog of Hohenberg-Kohn theorems. Runge-Gross theorem proves that the time-dependent density for a system with specified interactions and initial density uniquely determined by the external time dependent potential.

Properties system of interest in TDDFT can be obtained by solving the time-dependent Kohn-Sham (TDKS) equations[87, 83, 88]

$$\left(-\frac{\hbar^2}{2m} \nabla_i^2 + v_{eff\sigma}[\rho](\vec{r}, t) \right) \psi_{i\sigma}(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \psi_{i\sigma}(\vec{r}). \quad (5.7.1)$$

that describes dynamic of non interacting electrons with Kohn-Sham orbitals $\psi_{i\sigma}(\vec{r}, t)$ in the effective uniquely chosen $v_{eff\sigma}[n](\vec{r}, t)$ Kohn-Sham potential defined as[83, 88]

$$v_{eff\sigma}[\rho](\vec{r}, t) = v_{ext\sigma}(\vec{r}, t) + v_{ne\sigma}(\vec{r}, t) + \frac{e^2}{4\pi\epsilon_0} \int d\vec{r}' \frac{\rho(\vec{r}', t)}{|\vec{r} - \vec{r}'|} + v_{xc\sigma}(\vec{r}, t), \quad (5.7.2)$$

where $v_{ext\sigma}(\vec{r}, t)$ is the external time-dependent potential. In this approach the spin variable σ ($\sigma = \alpha, \beta$) is introduced to take into account spin dependence of $v_{ext\sigma}(\vec{r}, t)$. The Kohn-Sham spin densities used for calculation of Kohn-Sham potential is given by

$$\rho_{i\sigma}(\vec{r}) = \sum_i |\psi_{i\sigma}(\vec{r}, t)|^2. \quad (5.7.3)$$

In our works (Paper III, IV) we consider perturbation of molecular systems by oscillating electric field

$$V(\vec{r}, t) = \vec{r} \vec{F} \cos(\omega t), \quad (5.7.4)$$

with frequency ω and field of strength $\vec{F}$. Such perturbation in usual situation can be treated as weak and one can use linear response approximation for extracting the optical adsorption spectrum of the molecular systems. Since the external electric field is the periodic function of time, Fourier transform can be applied to the Kohn-Sham spin densities. The resulted Kohn-Sham spin densities in frequency domain may be expressed as series[83, 88]

$$\rho_{\sigma}(\vec{r}, \omega) = \rho_{\sigma}^0(\vec{r}) + \rho_{\sigma}^1(\vec{r}, \omega) + \rho_{\sigma}^2(\vec{r}, \omega) + \dots \quad (5.7.5)$$

where $\rho_{\sigma}^0(\vec{r})$ is the ground state spin density. In the case of arbitrary weak electric field, the first order density response $\rho_{\sigma}^1(\vec{r}, \omega)$ is widely used for estimating

properties of molecular systems since it depends only on ground state Kohn-Sham orbitals and parameters of the field. First order density response can be parametrized as follows[83, 88]

$$\rho_{\sigma}^1(\vec{r}, \omega) = \sum_{a,p,\sigma} P_{pa\sigma}(\omega) (\psi_{a\sigma}^0(\vec{r}))^* \psi_{p\sigma}^0(\vec{r}) + P_{ap\sigma}(\omega) (\psi_{p\sigma}^0(\vec{r}))^* \psi_{a\sigma}^0(\vec{r}), \quad (5.7.6)$$

where $P_{pa\sigma}(\omega)$, $P_{ap\sigma}(\omega)$ is the unknown parameters and $\psi_{a\sigma}^0(\vec{r})$, $\psi_{p\sigma}^0$ is the ground state Kohn-Sham orbitals. In this notation the indices a, b and p, q corresponds to virtual orbital and occupied orbitals respectively, while indices k, l, m, n stand for general orbitals. The unknown parameters $P_{pa\sigma}(\omega) = X$, $P_{ap\sigma}(\omega) = Y$ and excitation energies ω_I in the linear response approximation can be determined as self-consistent solution of the following eigenvalue problem[83, 88]

$$\begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega_I \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \quad (5.7.7)$$

where matrices A and B is given by

$$A_{pa\sigma, qb\sigma'} = \delta_{\sigma\sigma'} \delta_{pq} \delta_{ab} (\epsilon_{a\sigma} - \epsilon_{p\sigma}) + K_{pa\sigma, qb\sigma'}, \quad (5.7.8)$$

$$B_{pa\sigma, qb\sigma'} = K_{pa\sigma, qb\sigma'} \quad (5.7.9)$$

with

$$K = \frac{e^2}{4\pi\epsilon_0} \int d\vec{r} d\vec{r}' (\psi_{k\sigma}^0(\vec{r}))^* \psi_{l\sigma}^0(\vec{r}) \left(\frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta^2 E_{XC}}{\delta\rho_{\sigma}(\vec{r})\delta\rho_{\sigma'}(\vec{r}')} \right) (\psi_{n\sigma}^0(\vec{r}'))^* \psi_{m\sigma}^0(\vec{r}) \quad (5.7.10)$$

Oscillator strength in linear response approximation that correspond to the excitation energies ω_I may be calculated from eigenvectors (X, Y) as[87]

$$f_I = \frac{2m}{3\hbar} \omega_I |\langle 0 | \vec{r} | I \rangle|^2 \quad (5.7.11)$$

The computed oscillator strength determines the absorption strength of a molecular system in the electric field. However, in order to obtain absorption spectra from calculated oscillator strengths and excitation energies, it is required to make some assumptions about the shape of the peak. The common approach is using Gaussian broadening of the calculated transitions. The broadening width can be arbitrary assumed or estimated from experiments. It should be noted that TDDFT calculations usually performed at zero temperature while absorption measurements is commonly obtained at room temperature. At the finite temperature, a molecular ensemble will exhibit a distribution of conformations, which is slightly different on average than the optimized structures at zero temperature. Due to this fact absorption peaks of molecular systems reveals broadening at finite temperature.

5.8 Polarizable continuum model

Various solvation models have been developed in order to take into account effects of the environment on molecular systems. Solvation models could use molecular mechanics for describing the environment effects or continuum approximation, which treat environment as the dielectric media.

Continuum based models[79] consider molecular systems placed in molecular cavity with dielectric permittivity $\varepsilon_m(\vec{r}) = 1$ that build within dielectric media with dielectric permittivity $\varepsilon_d(\vec{r}) = \varepsilon_d$. In this case the total potential V is the sum of the potential induced by molecular system V_m and potential caused by surface charge distribution ρ_s on the boundary between molecular cavity and dielectric media V_{ρ_s}

$$V(\vec{r}) = V_m(\vec{r}) + V_{\rho_s}(\vec{r}), \quad (5.8.1)$$

where

$$V_{\rho_s}(\vec{r}) = \frac{1}{4\pi\varepsilon_0} \iint d^2s \frac{\rho_s(\vec{r})}{|\vec{r} - \vec{s}|} \quad (5.8.2)$$

In the polarizable continuum model (PCM), the surface charge distribution ρ_s obtained using the equation for the charges induced on the surface connecting two regions with different dielectric permittivities

$$\rho_s(\vec{r}) = \varepsilon_0 \frac{\varepsilon_d - 1}{\varepsilon_d} \frac{\partial}{\partial \vec{n}} (V_m(\vec{r}) + V_{\rho_s}(\vec{r})) \quad (5.8.3)$$

Using the equations given above one can self-consistently calculate $\rho_s(\vec{r})$ and $V_{\rho_s}(\vec{r})$. It should be noted that the size and shape of the molecular cavity strongly influences calculation results. One of the most common approaches is employing molecular shaped cavities with characteristic size that is proportional to Van der Waals radii.

Chapter 6

Experimental techniques

Experimental approaches, which represent the basics of the main experimental techniques used in the papers, are discussed in this chapter.

6.1 Electrochemical characterization

Electrochemical techniques are widely used for characterization of electroactive species[74]. It is also commonly used for the synthesis of conducting polymers by oxidation of the monomer units at the electrode surface[89].

The instrumentation needed for electrochemical characterization consists of the potentiostat connected to the electrochemical cell (see Figure 6.1.1). A waveform generator in the potentiostat is used for generating of electrical signals and current-to-voltage converter is utilized for the current measurements. The potentiostat applies a chosen form of potential signal between the working electrode and the reference electrode. The capacitive or/and faradaic process occurs at the working electrode. The reference electrode (e. g. Ag/AgCl electrode) provides a constant, well known potential. A counter electrode is used to measure a current flow through the electrochemical cell. The surface area of a counter electrode is much larger than the area of the working electrode and, thus, the total current is limited by the process at the working electrode.

Cyclic voltammetry is one of the most versatile techniques used for investigating the redox reaction and capacitive charging of electrode materials[74]. In cyclic voltammetry the potential applied to the working electrode varies linearly with time between the limits V_{max} and V_{min} as shown in Figure 6.1.1 b. The current in the electrochemical cell is measured as a function of applied potential. The typical form for obtained voltammograms is shown in Figure 6.1.1 c, d. In the case of the capacitive process at a working electrode (double layers formation) the voltammogram typically have a box shape (see Figure 6.1.1 c). For faradaic processes the voltammogram reveals current peaks corresponding to the oxidation and reduction electrochemical reactions at working electrode as shown in Figure 6.1.1 d.

The different form of applied potential can be chosen in electrochemical measurements. For example, small sinusoidal excitation signal is used in electrochemical impedance spectroscopy, a potential step is used in chronoamperometry technique etc.

Figure 6.1.1: (a) Schematics of the electrochemical cell. (b) The potential sweep in cyclic voltammetry and corresponding cyclic voltammogram for the (c) capacitive process and (d) redox process

6.2 UV-Visible spectroscopy and spectroelectrochemistry

Ultraviolet–visible (UV-Vis) spectroscopy is a technique that measures the absorption of electromagnetic radiation in materials as a function of wavelength. In this technique the wavelength of incident light lies in the near-UV, visible, and near-infrared (NIR) ranges.

The absorption of light in a material occurs as a result of a transition from the ground state to the electronically excited state. According to the energy conservation law, the difference in energy between these states must match the energy of the absorbed photon. The energy of the electronic transitions typically corresponds to somewhere in the UV-Vis-NIR range.

Ultraviolet–visible spectroscopy can be particularly useful for the studying of conducting polymers and oligomers[90, 91, 92, 93]. The absorption spectra of oligomers depends on its chain length and thus the number of monomer units in oligomer chain can be estimated by UV-Vis spectroscopy.

UV-Vis spectroscopy can be also used for studying electronic states in conducting polymers and oligomers during the doping/undoping process. The switching from the undoped state to the doped state in organic systems is usually accompanied by a colour change. In the undoped state, the absorption peak usually corresponds to the visible wavelength. Upon doping, the new electronic states such as polarons or bipolarons can be formed, which leads to change in the absorption spectra and to formation of absorption bands in near-infrared ranges. UV-Vis spectroscopy combined with the electrochemical technique utilized for electrical control of the doping level is usually referred to as spectroelectrochemistry technique.

In UV-Vis spectroscopy the measurements are usually performed on a film deposited on a transparent indium-tin oxide coated glass electrode. A conventional electrochemical cell is used for the spectroelectrochemistry measurements.

Prior film characterization, the absorption spectrum of the electrode without deposited film is recorded and used as a reference. In order to obtain an absorption spectrum, the light beam with given wave length and intensity I_o is focused on the electrode and the intensity of transmitted light I is recorded using a photodiode detector. Then, the absorbance A is calculated as $A = \log(I/I_o)$. The resulting absorbance of the film can be obtained by subtracting the reference spectrum from the spectrum of the coated electrode.

Chapter 7

Summary of the papers

7.1 Paper I

In this paper we have performed numerical modeling of the ion bipolar junction transistor (IBJT), which was developed and experimentally studied by Tybrandt *et al* [13]. This npn-IBJT comprises a collector (C), an emitter (E), a base (E), and a neutral junction. The emitter and collector are anions-selective membrane channels, while the base is a cation-selective membrane channel. The transport processes in the IBJT was described using Poisson's and Nernst–Planck (PNP) equations within two dimensional approximation (see Figure 7.1.1 a).

Figure 7.1.1 b shows simulated and measured transfer curves for $V_{EC} = 10$ V and $-1 < V_{EB} < 3$ V. Our calculations demonstrate that I_C is low in cut-off mode ($V_{EB} \lesssim 0.25V$) and linearly depends upon the emitter–base voltage in the active mode ($V_{EB} \gtrsim 0.25V$), while I_B remains low in both modes. The inset in Figure 7.1.1 (a) reveals the high electric field at the junction–collector interface. The high electric field at this interface in combination with the presence of fixed ionic groups in the material has previously been reported to cause electric field enhanced (EFE) water dissociation[94]. The measured collector current is higher than the simulated one because EFE water dissociation is not accounted for in the model. The simulations also verify that the experimentally found threshold voltage can be explained in terms of membrane potentials.

Figure 7.1.1 c shows measured and simulated output characteristics for $0 < V_{EC} < 10$ V and $V_{EB} = -1, 1, 2, 3$ V. Our simulations reveal three modes of operation. In saturation mode, I_C depends upon V_{EC} , while in cutoff and active mode, I_C is independent of V_{EC} . The main features of the experimental data are reproduced by our simulations. The transitions between the different modes are analyzed on the basis of detailed concentration and potential profiles provided by the model. By analysis of the extended space charge region at the collector we found that, the dimensions of the IBJT can be significantly reduced. Our results provide the basis for a detailed understanding of IBJT operation.

7.2 Paper II

Conducting polymer materials consist of the organic macromolecules and can conduct both electronic and ionic charge carriers. The mixed ion-electron con-

Figure 7.1.1: (a) 2D geometry of IBJT used in the computer simulation. (b) Transfer curves are given for simulated data (lines) and experimental data [13]. (squares) for $V_{EC} = 10V$. (Inset) Electric field profile at the collector–junction interface, showing the high electric field at the interface. (c) Output characteristics of the npn-IBJT from numerical simulation (solid lines) and experimental data (dotted lines)[13]. The graph shows active, cutoff, and saturation modes of the operation.

ductor PEDOT:PSS (poly(3,4-ethylenedioxythiophene):polystyrene sulfonate) is commonly included as an electroactive material in various devices such as electrochemical and field effect transistors, sensors, photovoltaic devices, electrochromic displays, implantable drug delivery devices, etc.

The operation principle of several above-mentioned devices relies on the supercapacitive properties of PEDOT:PSS. Despite of thousands of experimental studies devoted to this material, the nature of its intrinsic capacitance is not only poorly understood but also remains highly controversial. Generally, charge storage in supercapacitors can be due to the formation of double layers or to the redox reactions. It is widely accepted, that conducting polymers including PEDOT:PSS belong to the later category. This point of view is however challenged in the studies where the description of the device operation is based solely on the coupling between electronic and ionic motion (doping/de-doping).

In our work we have performed experimental studies and theoretical modelling of polymeric mixed electron-ion conductors PEDOT:PSS. We demonstrate that capacitive charging of the PEDOT:PSS electrode during the cyclic voltammetry, can be understood within a modified Nernst-Planck-Poisson formalism for two phase system in terms of the coupled ion-electron diffusion and migration without invoking the assumption of any redox reactions.

We found that it is important to treat PEDOT:PSS as a two phase system consisting of hole-conducting PEDOT-rich grains and ion-conducting PSS-rich grains. Such morphology suggests that the charge storage mechanism is associated with electric double layers formed at the interface between the electron-

Figure 7.2.1: (a) Schematics of the electrode system for two-phase model. (b) Cyclic voltammograms calculated according to two-phase model for different scan rates. (c) Concentrations and (c, d) corresponding potential profiles at $V_0 = 0.5 \text{ V}$ for two-phase model. (c) Concentration profiles are shown along y -axis at $x = 50 \text{ nm}$. c_- , c_+ and c_h correspond to concentration of mobile negative ions, positive ions and holes respectively. (d) Two-dimensional potential profiles at the electrode.

ically conducting PEDOT rich phase and the ionically PSS rich phase. Figure 7.2.1 a shows schematics of the simplest two-phase two-dimensional model representing a nanopore geometry, which is consistent with the main features of the morphology.

The voltammograms calculated within the proposed model are shown in Figure 7.2.1 b. The voltammograms reproduce the main features of the experimental curves including the box shape behavior in the oxidized state without any additional phenomenological assumptions. In our work we analysed voltammograms on the basis of concentration and potential profiles provided by the model. We found that the capacitance originates from charging of the double layers formed on the boundaries between the two phases within the bulk as shown in Figure 7.2.1 c, d.

7.3 Paper III-IV

A self-doped p-type conducting polymer which polymerizes itself in the xylem vascular tissue of the plant have been previously reported[95]. The polymerized conductive wires can be used for forming analogue and digital circuits which operate inside plants (*e-Plants*). Self-doped conducting polymers represent the most promising material for *e-Plant* applications. Such polymers possess an ionisable, negatively charged functional group in their chemical structure which acts as self- dopant anion (usually sulfonate), and is covalently bound to the polymer backbone.

In our work we reported synthesis of a self-doped sodium salt bis[3,4-ethylene-

Figure 7.3.1: UV/Vis spectra of 4 ETE-S oligomers in (a) reduced and (c) bipolaron states. (c) Spectroelectrochemistry of ETE-S film in 0.01 M NaCl(aq) solution

dioxythiophene]3thiophene butyric acid (ETE-S) that can be distributed and forms longer oligomers and polymers in every part of the xylem vascular tissue of a plant, forming long-range conducting wires. Using the plant's natural architecture and conducting wires we manufactured supercapacitors along the stem. The polymer material in wires reveal conductivity up to 10 S/cm and a specific capacitance of 20 F/g.

A detailed study of the electrical properties of this material is essential for developing device applications and improving material performance. In this work we investigated transition from reduced to electrically-conductive oxidized states. This has been done using the spectroelectrochemical measurements combined with electron paramagnetic resonance spectrometry and cyclic voltammetry. Experimental studies were supported by DFT and time-dependent DFT calculations.

Figure 7.3.1 a, b shows the time-dependent DFT computed spectrum together with the optimized structure of ETE-S oligomer with $n=4$ units in the reduced and bipolaron electronic states. The main peak of the absorption spectra for the reduced state is located around 490 nm. The main optical transition is mainly due to the HOMO→LUMO transition but other transitions are also involved. The absorption spectra of the bipolaron state is considerably red-shifted compared to the case of the reduced ETE-S oligomer and reveals a single band around 800 nm.

The absorbance changes of the electrochemically polymerized ETE-S film under an applied bias was studied using spectroelectrochemistry techniques and are shown in Figure 7.3.1 c. The film is reduced in the voltage interval $-1 \text{ V} \lesssim V \lesssim -0.7 \text{ V}$ and reveals a single pronounced peak at 550 nm. As the voltage is increased to $V \lesssim -0.3 \text{ V}$ a single absorption band at 800 nm develops which is attributed to the bipolaronic states. With further increase of the applied voltage $V \gtrsim -0.3 \text{ V}$, in addition to bipolaronic band, broad tail in the absorption spectra ($\lambda \gtrsim 1000 \text{ nm}$) starts to develop. We attribute the origin of the tail to the drastic changes of the band structure and to the strong decrease of the band gap when a polymeric film undergoes oxidation.

Figure 7.4.1: (a) Schematics of simulation domain with a single microband electrode (b) Experimental and simulated cyclic voltammetry (solid and dashed curves, respectively) of ferrocenedimethanol at the graphite microband electrode (0.1 M HCl, 1 mM FcDM, scan rates: 50 mV/s (red and blue curves) and 200 mV/s (black curves)).

7.4 Paper V

Many phenols are hazardous for humans and therefore the determination of the phenolic compounds in raw waters and wastewaters is an important issue. Biosensors presents a promising approach for the specific, rapid and simple detection of the phenolic compounds. A variety of enzyme based biosensors have been developed for a phenol detection[96]. However, previously reported biosensors reveals insufficient detecting limits for phenols in water samples.

In Paper V we report on the development of a laccase-based microband biosensor for *in situ*, total phenol estimation. The using of microband array electrodes allows to increase a faradaic current density due to non linear mass transport on the microscale. The modified diffusion domain approach and periodic boundary conditions were used for modeling of the voltammetric response and the transport processes in the developed microband electrode system. Figure 7.4.1 shows geometry of the simulation domain together with experimental and theoretical cyclic voltammograms.

The microband electrode array was modified with laccase using anodization followed by a covalent immobilization. Mediated and direct laccase bioelectrocatalytic oxidation of catechol was studied on macro- and microscale graphite electrodes. Our results indicate significant improvement of the analytical performance of a microband enzyme biosensor, compared to corresponding macroscale systems, due to the establishment of convergent diffusion in the microband case rather than the planar mass transfer for the macroscale systems. Finally, the developed biosensor was utilized to monitor phenolic compounds in real waste water.

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