Operating Organic Electronics via Aqueous Electric Double Layers

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During the course of the research underlying this thesis, Henrik Toss was enrolled in Forum Scientium, a multidisciplinary doctoral program at Linköping University, Sweden.

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Abstract

The field of organic electronics emerged in the 1970s with the discovery of conducting polymers. With the introduction of plastics as conductors and semiconductors came many new possibilities both in production and function of electronic devices. Polymers can often be processed from solution and their softness provides both the possibility of working on flexible substrates, and various advantages in interfacing with other soft materials, e.g. biological samples and specimens. Conducting polymers readily partake in chemical and electrochemical reactions, providing an opportunity to develop new electrochemically driven devices, but also posing new problems for device engineers.

The work of this thesis has focused on organic electronic devices in which aqueous electrolytes are an active component, but still operating in conditions where it is desirable to avoid electrochemical reactions. Interfacing with aqueous electrolytes occurs in a wide variety of settings, but we have specifically had biological environments in mind as they necessarily involve the presence of water. The use of liquid electrolytes also provides the opportunity to deliver and change the device electrolyte continuously, e.g. through microfluidic systems, which could then be used as a dynamic feature and/or be used to introduce and change analytes for sensors. Of particular interest is the electric double layer at the interface between the electrolyte and other materials in the device, specifically its sensitivity to charge reorganization and high capacitance.

The thesis first focuses on organic field effect transistors gated through aqueous electrolytes. These devices are proposed as biosensors with the transistor architecture providing a direct transduction and amplification so that it can be electrically read out. It is discussed both how to distinguish between the various operating

mechanisms in electrolyte thin film transistors and how to choose a strategy to achieve the desired mechanism. Two different strategies to suppress ion penetration into, and thus electrochemical doping of, the organic semiconductor are presented.

The second focus of the thesis is on polarization of ferroelectric polymer films through electrolytes. A model for the interaction between the remnant ferroelectric charge in the polymer film and the mobile ionic charges of the electrolyte is presented, and verified experimentally. The reorientation of the ferroelectric polarization via the electric double layer is also demonstrated in a regenerative medicine application; the ferroelectric polarization is shown to affect cell binding, and is used as a gentle method to non-destructively detach cells from a culture substrate.

Populärvetenskaplig Sammanfattning

Upptäckten av ledande polymerer på 1970-talet blev startskottet för forskningsområdet ledande plaster och senare också för organisk elektronik. Möjligheten att använda polymera material, det vill säga plaster, som elektrisk ledare och halvledare i elektroniska komponenter innebär en rad olika fördelar med avseende på processteknik för tillverkning av komponenter och kretsar, men öppnar också upp för helt nya elektroniska komponenter och användningsområden. De organiska elektronikmaterialen går ofta att enkelt lösa upp i lösningsmedel och dessa lösningar kan användas för tillverkning som utnyttjar till exempel traditionella tryck- eller bstrykningsmetoder. De är relativt mjuka och elastiska vilket innebär att materialen kan användas på flexibla substrat och ofta passar bättre, inte minst rent mekaniskt, ihop med andra mjuka system, exempelvis biologiska system eller som elektronik på papper. Ofta är de ledande och halvledande polymererna elektrokemiskt aktiva vilket också möjliggör utveckling av helt nya komponenter och applikationer.

Arbetet som ligger till grund för denna avhandling har fokuserats emot att nyttja vattenbaserade elektrolyter i kombination med elektroniska komponenter baserade på polymerer för att realisera nya sensorer och aktuatorer för tillämpningar inom medicin och bioteknologi. Syftet är att utnyttja elektroniska funktioner i dessa komponenter för att detektera, karakterisera och reglera processer i biologiska system, samtidigt som elektrokemiska reaktioner undertrycks. I biologiska system och miljöer är i normalfallet vatten närvarande vilket både innebär en möjlighet men samtidigt en utmaning. Vid gränsskiktet mellan elektrolyter och andra elektroaktiva material bildas ett elektriskt dubbellager av laddningar vilket i sin tur innebär att vi kan erhålla mycket höga kapacitanser. Egenskaperna utmed och i det elektriska dubbellagret är mycket känsligt för små förändringar av orientering och struktur av de

inkluderade laddningarna. Denna egenskap kan utnyttjas som en känslig och eventuellt selektiv reaktionsmekanism i olika sensorer och aktuatorer. Då elektrolyten kan representeras av olika biologiska system och vätskor öppnas en rad olika möjligheter med inom biologi och medicin.

Organiska fälteffekttransistorer vilka inkluderar elektriska dubbellager som isolator för styret kan användas som sensorer där transistorstrukturen både kan överföra och förstärka en sensorsignal till en elektriskt mätbar signal. För en tydlig signal i sådana fälteffektkomponenter krävs ofta att elektrokemiska (sido-)reaktioner undviks eller undertrycks. I denna avhandling diskuteras och realiseras två olika strategier för att undertrycka penetration av joner från elektrolyten in i de polymera elektronikmaterialen för att minimera att sensorsignalen går förlorad i elektrokemiska signaler.

Den laddning som kan lagras i det elektriska dubbellagret används också till att polarisera tunna ferroelektriska polymerfilmer. Samspelet och kopplingen mellan laddningen i det elektriska dubbellagret och de ferroelektriska dipolerna i polymeren modelleras och simuleras för att förstå och möjliggöra nya användningsområden inom bioteknologi. Beroende på orienteringen av de ferroelektriska dipolerna så kan affinitet och frisättning av levande celler till den ferroelektriska polymerytan styras helt elektroniskt. Detta öppnar nya möjligheter med så kallade elektroniska odlingsskålar inom regenerativ medicin samt inom biologi.

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List of Included Papers

Paper I

On the mode of operation in electrolyte-gated thin film transistors based on different substituted polythiophenes

Henrik Toss, Clément Suspène, Benoît Piro, Abderrahim Yassar, Xavier Crispin, Loïc Kergoat, Minh-Chau Pham, and Magnus Berggren

Organic Electronics 15, pp. 2420–2427 (2014)

Contribution: Designed experiments, performed most of the experimental work, wrote most of the manuscript.

Paper II

Copolythiophene-based water-gated organic field-effect transistors for biosensing

Clément Suspène, Benoit Piro, Steeve Reisberg, Minh-Chau Pham, Henrik Toss, Magnus Berggren, Abderrahim Yassar, and Gilles Horowitz

Journal of Materials Chemistry B 1, pp. 2090-2097 (2013)

Contribution: Fabrication and electrical characterization of devices, wrote part of the manuscript and contributed to the editing of the final manuscript.

Paper III

Phospholipid film in electrolyte-gated organic field-effect transistors

Serafina Cotrone, Marianna Ambrico, Henrik Toss, M. Daniela Angione, Maria Magliulo, Antonia Mallardi, Magnus Berggren, Gerardo Palazzo, Gilles Horowitz, Teresa Ligonzo, and Luisa Torsi

Organic Electronics 13, pp. 638–644 (2012)

Contribution: Fabrication and electrical characterization of devices, contributed to experimental design, initial analysis of data, wrote part of the manuscript and contributed to the editing of the final manuscript.

Paper IV

Polarization of ferroelectric films through electrolyte

Henrik Toss, Negar Sani, Simone Fabiano, Daniel T Simon, Robert Forchheimer, and Magnus Berggren

Manuscript in preparation

Contribution: Created models, wrote simulation protocols, designed experiments, performed most of the experimental work and wrote most of the manuscript.

Paper V

Ferroelectric Surfaces for Cell Release

Henrik Toss, Susanna Lönnqvist, David Nilsson, Anurak Sawatdee, Josefin Nissa, Simone Fabiano, Magnus Berggren, Gunnar Kratz, and Daniel T. Simon

Submitted manuscript

Contribution: Contributed to experiment design, fabrication and electrical characterization of devices, wrote the first draft and contributed to editing of the final manuscript

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“Remember kids;
the only difference between
screwing around and science
is writing it down”
- *Adam Savage*

Part I

Background

1. Introduction

1.1 Organic Electronics

Electronics represent a corner stone in modern society and is integrated and represented into almost every aspect of our lives. This appears as a natural continuation of the early electronic era that started in 1947 with the invention of the first transistor achieved by John Bardeen and Walter Brattain at Bell Laboratories ^[1], USA.

The transistor enabled the further development of great many applications and technologies; most notably the computer science era, and the transistor device is now the basic building block of all modern electronics. To make transistor-based technologies various inorganic materials have traditionally been used, such as metal conductors and silicon and germanium as semiconductors.

Polymer materials, commonly known as plastics, were for a long time considered to only be insulators with respect to electrical current. This view changed in the late 1970s when Alan Heeger, Alan MacDiarmid and Hideki Shirakawa discovered that the conductivity of polyacetylene could be improved through chemical doping ^[2]. It is the alternating single and double chemical bond-structure of

polyacetylene and other so called conjugated polymers that gives them their conducting properties [3]. This discovery marks the starting point of the scientific field of conducting polymers, which then led also to the area known as organic electronics.

Polymers are easily processed and can be tailored to carry and represent a vast range of different chemical and mechanical properties. By just glancing at the examples of the synthetic fibers and acrylic glasses gives a hint to the range of applications in which we can find polymeric materials today.

Organic electronic materials combine the desired processability of polymers with the electrical and optical features of metals and semiconductors. Classic semiconductor devices such as Light Emitting Diodes (LEDs) [4], Field Effect Transistors (FETs) [5-6] and solar cells [7-10] including electronic polymers as the semiconductor have already been developed. Moreover, some of the organic semiconductors (OSC) are also electrochemically active, which enables the development of organic electrochemical transistors (OECTs) [11], super capacitors [12-13], electrochromic display cells [14-15] and light emitting electrochemical cells (LECs) [16-17]. In addition, organic materials express several unique features making them suitable for biological and biochemical applications. They are relatively soft and can be made to be both electronically and ionically conductive [18]. These features make them excellent as the interface between technology and soft living materials both for recording as well as transmitting signals in biology, and potentially also in medicine.

1.2 Aim and outline of the thesis

In all sensor or actuator systems some kind of transducer is needed to translate and/or interpret the signals from one end of the system to the other. As electronics are becoming a more and more integral part of our lives, and in technology, it is desired to utilize electrical transduction mechanisms as it would open up for the possibility of a direct interfacing, including that of electronics, that

record or control biological signal patterns. As mentioned above, organic electronics appears to be a very good fit with respect to interfacing with many biological and biochemical systems. Water is a fundamental component of life as we know it and will thus be present in many of these systems. With this, both challenges and opportunities arise. Electrically active devices operating in aqueous environment results in that charge polarization is established along the active interfaces. This might, in turn, result in electrochemical side-reactions. Depending on the design, of a sensor or actuator in question, the electrochemical reactions can be desired or not. In any case, it is crucial to understand the characteristics along the electronic-aqueous interface in order to fully be able to control, predict and understand the behavior of these types of devices while operating as a sensor or actuator.

The first part of this thesis serves as an introduction and a brief summary of the background information needed to understand the scientific findings presented in the papers and manuscripts, included in the second part of the thesis.

2. Materials

2.1 Organic semiconductors

Polymers are linear macromolecules built up by, as the name suggests, many (Poly) repeating subunits (mers) connected by covalent bonds. For a long time polymers were considered being only electronic insulators as this is the case for many of the more common polymers or plastics we encounter. However, in 1977 Alan Heeger, Hideki Shirakawa and Alan G MacDiarmid reported the possibility to enhance the conductivity of the polymer polyacetylene by exposing it to iodine vapor ^[2]. With this experiment, they discovered that polymers with an alternating single and double bond structure, i.e. conjugated polymers, could be made electronically conductive due to their molecular structure. This finding was then the starting point of two completely new fields of research – Conducting Polymers and Organic Electronics.

2.1.1 Orbitals

A characteristic of organic molecules is that they include one or several carbon atoms in combination with other atoms. In organic polymers the carbon has a crucial role in that it forms bonds to other carbon atoms, which leads to the formation of longer chains.

Atoms are constituted by a dense nucleus, of positively charged protons and (for most atoms) also neutral neutrons, surrounded by a cloud of negatively charged electrons. By the laws of quantum mechanics we find that the electrons only can occupy certain states in space and energy, which we call atomic orbitals. These orbitals describe the probability of finding an electron at a certain position. According to the Pauli principle, a maximum of two electrons, which then must have opposite spin, may occupy the same orbital. The orbitals are denoted by shell (K/1, L/2, M/3, N/4 etc.) and orbital type/shape (s, p, d, f etc.). In the ground state of an atom the electrons occupy the orbitals with the lowest energy.

Figure 2.1 Illustrations of s-orbital (left) and p-orbital (right).

For an isolated carbon atom the ground state is $1s^2 2s^2 2p^2$ denoting that the electrons are distributed over the first and second s- and p-orbitals. The superscript denotes the number of electrons occupying each state. The s-orbitals are spherical in shape and the three orthogonal p-orbitals have a dumbbell like shape with their two ellipsoid shaped lobes and a node located at the nucleus (Figure 2.1). It is the orbitals that are containing only a single, unpaired, electron (valence electrons) that generally dictate the chemistry of the atoms and molecules. When two atoms are brought close

together the orbitals of the valence electrons can start to overlap and form a chemical bond due to interactions between valence electrons. The resulting molecular orbitals can be approximated as linear combinations of the two atomic orbitals and their nature depend on the properties of, and the relationship, between the involved atomic orbitals. If the bond is symmetrical, with respect to the rotational axis of the bond, it is called a σ -bond (Figure 2.2). If the resulting bond is not symmetrical it is called a π -bond. Furthermore, the energy levels of the combined atomic orbitals can split into a bonding and an antibonding molecular orbital. The resulting energy of a bonding orbital, of a molecule, is lower than the energy of the individual atomic orbitals and thus stabilizes the molecule, while the antibonding orbital has a relatively higher energy than the atomic orbitals and expresses destabilizing characteristics. The antibonding orbitals are often denoted with an asterix (σ^* , π^*). A lower binding energy level indicates a stronger molecular bond and, as indicated by the name, the bonding orbitals thus have lower energy than the antibonding. The overlap between atomic orbitals is generally larger in a σ -bond than in the corresponding π -bond and the energy of the σ -bond is thus often lower in energy. In the ground state the electrons will occupy the orbitals with the lowest energy. The molecular orbital, with the highest energy, occupied by an electron is called the Highest Occupied Molecular Orbital (HOMO). The molecular orbital, without electrons, with the lowest energy is called the Lowest Unoccupied Molecular Orbital (LUMO) [19].

Figure 2.2 Overlap of two atomic *s*-orbitals forming two molecular orbitals, one bonding (σ) and one anti-bonding (σ^*).

2.1.2 Hybridization

At first glance, when considering the electronic structure, it appears as carbon only has two unpaired electrons and should thus be able to form only two molecular bonds. This is however not the case. In the presence of other atoms the outermost *s* and *p* orbitals of carbon become distorted into a set of hybridized orbitals. One *s*-orbital can together with one, two or all three, *p*-orbitals form two *sp*, three *sp*² or four *sp*³ hybrid orbitals, respectively [20]. The carbon atoms in conventional polymers, such as alkanes, are *sp*³-hybridized. In this case four, identical and equally distributed, orbitals are formed, thus giving a tetrahedral configuration of bonds. Each of these orbitals can form a σ -bond with a neighboring atom in which the electrons taking part in that bond are strongly localized between the two atoms. In e.g. alkenes the orbitals are *sp*²-hybridized. In this case the hybridized orbitals form a σ -bond with the neighboring carbon atom and the unhybridized *p*-orbitals, which are perpendicular to the *sp*²-orbitals, are able to overlap to form a π -bond, which then results in a double bond formed between the two atoms (Figure 2.3). In this case the three hybridized orbitals, of one atom, are oriented in one plane, which gives an angle between them (and thus the resulting bonds) of 120°.

Figure 2.3 (left) illustration of sp^2 -hybridized carbon atom orbitals with the three sp^2 -orbitals (shaded) and one p -orbital (dotted outline). (right) the formation of a molecular bond between two adjacent sp^2 -hybridized carbon atoms forming one σ -bond and one π -bond.

2.1.3 Electronic structure of conjugated polymers

In a chain of sp^2 -hybridized carbon atoms the electrons of the sp^2 -orbitals are strongly localized in σ -bonds between the atoms while the electrons in the orthogonally oriented p -orbitals are free to overlap with the p -orbitals of the adjacent carbon atoms (Figure 2.4). If the carbon atoms were equally spaced, along the chain, the electrons of these overlapping p -orbitals would be de-localized as the energy states would be equal and thus have the same probability. This would then lead to a one-dimensional conductor. The total energy of the molecular chain can however be lowered by alternating the bond length leading to a, so called, conjugated structure with alternating double and single bonds. This creates an energy gap between the filled π -orbitals and the empty π^* -orbitals.

Figure 2.4 Energy diagram of two atomic p orbitals forming molecular π orbitals.

The number of π -orbitals, and thus the number of possible energy states, increases with the number of atoms along the chain, resulting in a band-like structure similar to that of inorganic and crystalline semiconductors. The energy gap between the π - and π^* -orbital bands, E_g , is called the band gap. As the π -band is lower in energy it will be filled in the ground state. The electronic state, within this π -band, with the highest energy constitutes the HOMO. In the ground state the π^* -band will be empty and the electronic state in this band with the lowest energy constitutes the LUMO (Figure 2.5). An analogy to the conduction/valence band of inorganic semiconductors is often made for the HOMO/LUMO of conjugated polymers.

Figure 2.5 Energy splitting and band formation in transpolyacetylene.

A small E_g is a significant property of a semiconductor while it is larger for an electrical insulator and non-existent for a conductor. The band gap for OSCs are typically 1.5 – 3 eV [21]. This can be compared to the wide band gap 5.5 eV of diamond which is sp^3 -hybridized [22].

2.1.4 Charge carriers

In order for conduction to occur mobile charge carriers are needed [23]. Some polymers, like trans-polyacetylene, have a degenerate ground state. This means that there are two (or more) bond conformations which all give the lowest possible energy. Having the same energy makes these conformations equally probable and they can thus coexist on the same polymer chain. At the boundary between two conformations the bond lengths will be equal leading to a localized nonbonding orbital with an electronic energy level in the middle of the band gap. This creates a quasi particle called a soliton. The soliton can move along the polymer chain and thus function as a charge carrier.

Most conducting polymers do however not have degenerate ground states, but instead have a preferred conformation of the single/double bond alternation. Solitons can therefore not be found

in these. If a charge is introduced into a conjugated polymer with a non-degenerate ground state it will be stabilized by a local rearrangement of the single/double bond alternation around the point of the charge. This introduces localized states around the deformation that are called polaron states. It can be energetically favorable to have two such deformations locally configured and coupled to each other. Such a localized double-charged state is referred to as a bipolaron.

The charge carriers can move along a polymer chain as a localized package, which alternates the bond conformation as it is transported along the chain. This explains the conduction mechanism that occurs along the individual polymer chains. To have conduction in a bulk material the charges also have to cross from one chain to another. In systems with low order at normal temperature this intermolecular charge transport is typically dominated by phonon-assisted hopping [24].

2.1.5 Doping

The conductivity of the conjugated polymer bulk is dependent on mobility and the number of charge carriers. Due to the relatively large band gap of most conjugated polymers, the number of thermally induced charge carriers is rather limited, making them in fact poor conductors in their intrinsic state. To increase the conductivity more charge carriers must be introduced into the system. This can be achieved by charge injection, as is the case of electronic devices such as diodes and field-effect transistors, by photoexcitation, as in photovoltaics or by doping of the polymer [25]. Doping is the charge-compensation mechanism performed by introducing a dopant species into the host material, which can add/donate or remove/accept electrons to, and from, the conjugated system. If the dopant adds electrons, i.e. reduces the polymer, it is called n-doping. If it removes electrons from the polymer, i.e. oxidizes it, it is called p-doping. These redox processes can be induced both chemically and electrochemically [26-27]. In electrochemical doping a voltage is applied between the conjugated system and a counter

electrode connected through some solution containing ions, i.e. an electrolyte. The voltage drives injection of charges into the conjugated system and ions, of opposite charge, migrates into the material from the electrolyte to compensate and preserve charge neutrality ^[28]. Doping a material can improve the conductivity by several orders of magnitude ^[27].

2.2 Polarity of molecules

2.2.1 Electronegativity

The tendency of a chemical element to attract electrons can be described by a property called electronegativity ^[19-20]. When two atoms form a molecular bond, the nature of that bond, and its included electrons, is decided by the difference in electronegativity of the two atoms involved. If they have the same electronegativity they will share these involved electrons equally in a covalent bond. If, on the other hand, there is a difference in electronegativity the electrons will be more attracted to one of the atoms and an electric dipole, along the bond axis, is established. This is called a polar bond. It is also possible that the difference in electronegativity is so large that the electrons of the bond will almost completely be located at one of the atoms alone. That is then called an ionic bond.

2.2.2 Dielectric polarization

When a conductor is placed in an electric field, charges will flow as a current through the conductor to counter and compensate for the field. For an electrical insulator charges cannot flow. Instead, electronic charges involved in bonds of the insulating matter can only be slightly displaced from their equilibrium position thus minimizing the field inside the material. This phenomenon is called dielectric polarization. Depending on the nature of the material the dielectric polarization can consist of distortion of the electron cloud around the atoms, the molecular orbitals or, can even lead to a reorientation of permanent dipoles within the material ^[29].

Reorientation of permanent dipoles is associated with physical displacement of atoms, which must be accompanied with some sort of inertia. Thus, the orientation polarization is frequency dependent. In some cases there is even an apparent energy threshold needed to overcome before the actual initialization of the dipole reorientation can occur. These characteristics can give the material so-called ferroelectric properties and the threshold energy is related to the amplitude of the internal field of the material that is needed to cause reorientation of the dipoles. This internal field quantity is called the coercive field E_c [30-31]. Ferroelectric properties can also be achieved in materials, such as ionic crystals, through ionic polarization [32-33].

The change of orientation of the dipoles in ferroelectric materials is associated with the electric field. From this it follows that any mechanically induced distortion caused to these materials will typically also induce a change of the electric field inside these materials. This gives that ferroelectric materials are also both piezoelectric and pyroelectric [34]. Additionally the internal orientation of the dipoles will be possible to detect as any change of them will have a strong effect on the surface charge of the material.

2.3 Electrolytes

An electrolyte is a material system that contains mobile ions thus making it electrically conductive. Generally speaking, an electrolyte could be said to consist of salt that dissociates into ions as it is introduced into a solvent. Positive and negative ions are often referred to as cations and anions, respectively. Ions are transported in the electrolyte either by diffusion or migration [19]. Diffusion is the thermodynamically driven process that leads to spontaneous dispersion of the ions over time. Migration on the other hand is the ionic transport caused by the force exerted on the ions in the presence of an electric field.

Depending on the fraction of the salt that dissociates into ions the electrolyte can be said to be strong (high fraction) or weak (low fraction). Different types of electrolytes, that are relevant in organic

electronics, are electrolyte solutions, molten salts, ion gels, polyelectrolytes and polymer electrolytes. Out of these the most common are probably electrolyte solutions.

For electrochemical experiments it is sometimes preferred to use an organic solvent due to their electrochemical stability. However, for most biological systems the typical electrolyte solvent is water. Water is in itself a weak electrolyte as it dissociates into hydroxide and hydronium ions, through autoionization, to a concentration of about 0.1 μM at neutral conditions (hence pH 7).

2.3.1 Electric double layer

A difference in electric potential between an electrode and an electrolyte will result in the formation of a so called electric double layer (EDL) at the electrode/electrolyte interface. In the simplest model, the EDL can be described as a thin layer of charges on the electrode surface being compensated by a layer of solvated ions, of opposite charge, in the electrolyte next to the surface. In reality, a more complex model is necessary to describe the fundamentals of the actual EDL. Commonly the Gouy-Chapman-Stern model (GCS) [35-36] is used. In the GCS model the charges in the electrolyte are divided into two layers. Closest to the electrode the ions and solvent molecules are organized in a rigid planar structure called the Helmholtz layer. In this layer all the ions are of opposite charge to those on the electrode. Between the electrode and the Helmholtz layer the field is constant and the potential drop over this layer is thus linear. Further away from the electrode the net charge is still of opposite sign to that of the electrode, but ions of both polarities are present. This makes the structure more diffuse stretching it out into the electrolyte. The electrical potential drops exponentially in this diffuse double layer (Figure 2.6). The total capacitance across an EDL is typically on the order of tens of $\mu\text{F}/\text{cm}^2$ [36-37].

Figure 2.6 Illustration of the structure (top) and potential distribution (bottom) of the EDL according to the Gouy-Chapman-Stern model. The empty circles represent solvent molecules and the black and white circles, with the charge marked, represent cat-ions and an-ions respectively. ϕ_M and ϕ_S are the electric potentials of the Metal and bulk of the Solution respectively.

3.Devices

3.1 Capacitors

Capacitance is a property that describes the ability of a body or device to store charge. Two electrical conductors separated by some insulator will constitute a capacitor where the capacitance, C , between them is defined through the potential, V , between them and the charge, Q , at each conductor as

$$C = \frac{Q}{V}$$

3.1.1 Electric double layer capacitors

Figure 3.1 Illustration of the polarization mechanism in dielectric materials (left) and electrolytes (right) sandwiched between two electrodes. The dipoles of the dielectric align with the field. The ions of the electrolyte migrate along the field towards the electrodes.

If a potential is applied across an electrolyte, sandwiched between two conductors, the ions in the electrolyte will migrate along the field. This will result in the polarization of the electrolyte and the buildup of EDLs at each of the electrodes. The field and potential distribution in this kind of capacitor is thus quite different from that of a capacitor instead including an insulating dielectric layer (Figure 3.1 and Figure 3.2). At very short timescales the ions do not have time to move and the electrolyte behaves like a normal dielectric material with a uniform potential drop over the electrolyte. At a somewhat longer timescale the ions start to migrate along the electric field and EDLs build up along the electrode surfaces. As the ions migrate the electric field is reduced within the electrolyte and the potential drop becomes more and more concentrated to the EDLs at the electrode/electrolyte interfaces. Applying a constant electric field during a timescale long enough to establish a steady state

condition, the potential drop will be entirely concentrated to the EDLs and the electric field will thus be very high at the interfaces and effectively zero within the bulk of the electrolyte (Figure 3.2) [38].

Figure 3.2 Charge distribution, electric potential (U) and field (E) in an electrolyte capacitor during charging. (a) before voltage is applied, (b) before, (c) during and (d) after charge redistribution.

3.1.2 Super capacitors

The EDLs at the electrodes of an electrolyte capacitor can each be viewed as a very thin parallel plate capacitor. The capacitance of a parallel plate capacitor is described by the equation

$$C = \varepsilon \frac{A}{d}$$

where ε is the permittivity of the material between the capacitor electrodes, A is the overlapping area of the electrodes and d is the distance separating the electrodes. The thickness of the EDL corresponds to d when considering the EDL as a parallel plate capacitor. Since this is a very small distance the capacitance of the EDL can get very high. To further increase the capacitance, the area of the electrode can be increased. By making the electrodes porous it is possible to achieve very large effective electrode areas in electrolyte-based capacitors relative to the volume/weight of the capacitor, thus yielding capacitors with extraordinary high energy densities. This type of capacitor is called electrolyte supercapacitors.

In electric double layer capacitors, such as these electrolyte supercapacitors, the charge is stored electrostatically [39-40].

3.1.3 Pseudo capacitors

Another way of storing large amounts of charge in electrolyte-based capacitors is to include electrodes that are electrochemically active. Charge can then be stored throughout the entire bulk of the electrodes by reducing or oxidizing the actual electrode material. In such capacitors, this gives that the entire volume of the electrode material dictates the capacitance value of the resulting capacitor and not just the surface area of the electrode. This type of capacitor is sometimes called a pseudocapacitor as the voltage transients during charge and discharge are similar to what is found in batteries. In pseudocapacitors the charge is stored electrochemically [39, 41].

It is also possible to make hybrid capacitors where the charge is stored electrostatically at one electrode and electrochemically at the other [42].

3.2 Transistors

Transistors can generally be described as three-terminal devices in which the resistance, and thus the current, between two of the terminals can be regulated by addressing the third. This way the current level between the first two terminals can be modulated and the transistors can be used in circuits to achieve electronic digital gates and switches. Transistors can also be used in circuits for analogue applications to achieve amplifiers. The first transistor, a type of point contact bipolar junction transistor made from germanium, was reported in 1947 by Bardeen, Brattain and Shockley at Bell labs [1], in the US. The transistor could then replace the fragile and power consuming vacuum tube triodes. Today transistors are part of almost every piece of electronic equipment.

3.2.1 Thin film transistors

Transistors can also be made from organic materials. Typically a thin film transistor configuration is then used (TFT) ^[43]. These types of transistors have a special configuration where the semiconductor channel is deposited as a thin film on some form of insulating carrier substrate. The TFTs are generally speaking field effect transistors (FET), but in this work we will also discuss yet another type of thin film transistor, the organic electrochemical transistor (OECT). The OECT does not operate according to a FET mode of operation but has many similarities to the FET device with respect to layout and output characteristics. In fact, the very first organic TFT was an OECT ^[44]. In TFTs the channel semiconductor is usually intrinsic (undoped).

3.2.2 Field effect transistors

The field effect transistor was first predicted and patented already in 1925 by Lilienfeld ^[45]. It took, however, until 1959 for such a device to finally be realized ^[46]. What had then been constructed was a silicon-based Metal Oxide Semiconductor FET (MOSFET). FETs are now the most common type of transistor and are included in all kinds of computers and communication devices. The first FET including an OSC was reported in 1986 by Tsumura et al ^[47].

A FET is a three-terminal device where the current between the source and drain electrodes can be modulated through a voltage applied to the gate electrode. The source and drain electrodes are connected by a semiconducting material, which defines the transistor channel. The gate electrode is separated from the transistor channel by an electronically insulating material. This insulator is sometimes referred to as the gate dielectric, but it can also be, e.g. an electrolyte and we thus call it just the gate insulator. Figure 3.3 shows a schematic illustration of a thin film transistor where the important geometric features and components, such as channel length, L , and width, W , are also marked.

Figure 3.3 Schematic illustration of an organic thin film transistor with channel length L and width W .

3.2.3 Transistor operation

The gate/insulator/channel stack can be viewed as a capacitor. The properties of this capacitor is important as it predicts the number of charges present in the channel and thus the number of charge carriers, which in turn dictates the conductivity and throughput of the transistor. For capacitors we know that the capacitance is given by

$$C = \frac{Q}{V}$$

If the capacitance, C_i , of the insulator is independent of the voltage applied, we thus get the very simple relation between the charges induced in the semiconductor and the voltage applied to the gate

$$Q = C_i * V$$

The charges in the semiconductor are mostly concentrated to the semiconductor/insulator interface and an applied voltage creates a, more or less, two-dimensional, conducting transistor channel, between the source and drain electrodes, close to this interface ^[43]. The conductivity of the transistor channel can thus be modulated through changes in the applied gate voltage.

However, charges can be present along the semiconductor, also without applying an external voltage, due to e.g. doping of the

semiconductor, trapped charges that exists along the semiconductor interface and that there exists a difference in work function between the gate electrode and the semiconductor material. This means that there might be some level of the applied gate voltage that needs to be exceeded before the channel becomes conducting ^[48]. This voltage is termed the threshold voltage, V_T , and the number of mobile charges as a function of the applied Gate-Source Voltage, V_{GS} , in the channel is thus given by the equation

$$Q = C_i(V_{GS} - V_T)$$

If the V_{GS} applied is positive the induced charges within the channel will be negative and vice versa. A positively charged channel is referred to as a p-channel and a negatively charged channel as an n-channel.

In some cases it is possible to use an electrolyte as the gate insulator. The gate/insulator/channel stack then constitutes an electric double layer capacitor and the associated capacitance can thus be very high. As can be seen in the equation above, a high insulator capacitance means that the number of induced charges in the channel will be much larger and sensitive to changes in the gate voltage, making it possible to produce transistors operating at very low voltages. This kind of transistor is called electrolyte-gated FETs (EGFET). If the semiconductor material is organic they are commonly referred to as EGFETs where the added 'O' marks organic.

Assuming that the source electrode is grounded there are two transistor electrode voltages that can be varied and controlled in an FET, the Gate-Source Voltage (V_{GS}) and Drain-Source Voltage (V_{DS}). Transistor characteristics curves can be produces by keeping one of these voltages constant while sweeping the other at the same time measuring the drain current response. The current at the three terminals (I_G , I_D , I_S) are defined as being positive while entering into the transistor and Kirchhoff's current law tells us that the sum of them should be zero. Plotting I_D against V_{GS} yields the classical transfer characteristics. By plotting the I_D versus V_{DS} the so-called output characteristics are achieved (see Figure 3.4).

The transfer characteristics are usually plotted with I_D on a log scale versus V_{GS} as the current can vary with several orders of magnitude. Below V_T of the transistor the current is dominated by diffusion instead of drift and there is an exponential relationship between I_D and V_{GS} [6] determined by the insulator capacitance and the density of trap states, at the interface between the semiconductor and insulator materials, as well as temperature. Filling of traps is typically crucial in determining the I_D versus V_{GS} evolution. This subthreshold region is quantified by the subthreshold swing S

$$S = \frac{\partial V_{GS}}{\partial (\log_{10} I_D)}$$

At even lower gate voltages there is no longer any noticeable modulation of the current and the measured current can be attributed to leakage and charging. The particular voltage point, below which there is no current modulation, is called the switch-on voltage (V_{SO}) [49]. At voltages below V_{SO} the transistor is said to be in the off state.

Figure 3.4 Typical current-voltage characteristics of an organic field effect transistor. (Left) output characteristics with linear and saturation regimes marked out. (Right) Transfer characteristics with on/off current ratio, switch-on voltage (V_{SO}), threshold voltage (V_T), subthreshold swing (S) as well as the different regimes marked out.

At voltages greater than V_T the behavior of the current response can be estimated as following the transistor equations derived and given below.

For the equation presented above which predict the number of mobile charges within the channel we assume that the source and drain voltages are both grounded. If a voltage is applied to the drain electrode there will be a drop of the voltage from drain to source and the difference in voltage between the gate and the channel, and thus the number of induced charge carriers, will therefore differ along the channel. The charge density, at some position x along the channel, is given by

$$Q(x) = C_i[V_{GS} - V_T - V(x)]$$

If the Drain-Source Voltage, V_{DS} , is small, so that $V_{DS} \ll V_{GS} - V_T$, the potential difference between the gate and the channel will more or less be uniform along the whole channel. Because of this the mobile charge density, and thus the conductivity, will also be almost uniform along the whole channel and the Drain current, I_D , will increase linearly with the applied V_{DS} . This is called the linear regime of the transistor. As V_{DS} approaches $V_{GS} - V_T$ the density of mobile charges will get noticeably lower towards the drain electrode, which also means that the conductivity reduces close to the drain electrode and the slope of the I_D vs. V_{DS} becomes less and less steep. When $V_{DS} = V_{GS} - V_T$ the mobile charge density at the edge of the drain electrode will theoretically be zero. The point in the channel where the potential is equal to $V_{GS} - V_T$ is referred to as the pinch of point (P). Increasing V_{DS} even further will then move P further away from the drain electrode, towards the source electrode and thus increases the fraction of the channel that has a low conductivity. This gives that I_D will saturate, i.e. I_D more or less stops increasing with an increase of V_{DS} and this is thus called the saturation regime of the transistor (Figure 3.5).

Figure 3.5 Schematic illustration of the operating regimes of a field effect transistor. Voltage characteristics (top) and illustration of charge distribution (bottom) for (a) linear regime, (b) onset of saturation at pinch-off point and (c) saturation regime.

The equations describing the current characteristics of the transistor behavior can be derived by assuming constant mobility, μ , along the entire channel, and that there is no leakage so that the drain current, I_D , is constant throughout the channel. By simply using Ohms law we have that

$$J = \sigma E$$

Or more specifically

$$\frac{I_D}{W} = \mu Q(x) E(x)$$

where $E(x)$ is the electric field in the direction along the channel at a point x along the channel. Setting $E(x) = dV(x)/dx$ and $Q(x) = C_i(V_{GS} - V_T - V(x))$, and since I_D is constant along x we can integrate along the entire length, L , of the channel from source ($x=0$) to drain ($x=L$) and get

$$I_D = \frac{\mu W}{L} C_i \left[(V_{GS} - V_T) V_{DS} - \frac{V_{DS}^2}{2} \right]$$

In the linear regime ($V_{DS} \ll V_{GS} - V_T$) this equation can be simplified to

$$I_{Dlin} = \frac{\mu W}{L} C_i (V_{GS} - V_T) V_{DS}$$

The saturation current can be calculated by simply setting $V_{DS} = V_{GS} - V_T$

$$I_{Dsat} = \frac{\mu W}{2L} C_i (V_{GS} - V_T)^2$$

Considering the transistor characteristics and fitting the data of the transfer characteristics to the transistor equations makes it possible for us to extract transistor parameters such as the mobility and the threshold voltage.

Another transistor characteristic, which is often considered one of the most crucial and representative, is the transconductance g_m . It describes how the output current I_D is modulated by the input voltage V_{GS} , such that $g_m = \partial I_D / \partial V_{GS}$ at a constant V_{DS} [6]. The transconductance is thus different in the linear and saturation regimes

$$g_{mlin} = \frac{\mu W C_i}{L} V_{DS}$$

$$g_{msat} = \frac{\mu W C_i}{L} (V_{GS} - V_T)$$

3.2.4 Electrochemical transistors

In EGOFETs the EDL at the electrolyte/semiconductor layer interface is well defined. This means that the ions in the electrolyte and the induced electronic charges in the semiconductor are

separated and constrained to their respective medium along the interface [37].

It is sometimes possible for ions from the solution to breach the interface and then migrate into the bulk of the organic semiconductor material [50]. This gives a less well, or even ill-, defined EDL and the mechanisms that modulate the transistor current is no longer constrained to just the surface of the semiconductor, but also occur throughout the entire bulk. The introduction of charged species into the semiconductor material can be viewed as doping of the entire bulk and, as the process is driven by an electrical potential, transistors modulated in this manner are called (organic) electrochemical transistors (OECT). We can speculate over what mechanism is responsible for the transistor modulation for different cases and kinds of OECTs. It could in some cases be due to electrochemical redox reactions of the polymer channel in which charge transfer actually takes place between the introduced ions and the OSC. It could however also be speculated that the OECT mode of operation is due to ion exchange and charge compensation. The latter mechanisms would then define a transistor that operates according to principles more similar in nature to the mechanism of modulation taking place in EGOFETs. Regardless of which mechanism that governs the operation in the OECTs, the drain current level in the transistors will scale with the thickness of the semiconductor layer as the gate potential modulates the conductivity of the entire bulk. Furthermore, the OECTs modulation is generally slower as it not only depends on the time it takes to form the EDL, which depends on the diffusion rate in the electrolyte, but also the diffusion or migration rate of the entering ions inside the OSC. As ions propagate further and further into or out from the semiconductor film, more or less of the semiconductor material will take part in the formation of the transistor channel, and conduction of charges, through the transistor and with this propagation an evolution of the I_D will follow. The fact that the charges need to be moved in and out of the semiconductor thus gives some memory/hysteresis effects that typically appear at high frequency biasing.

3.2.5 Electrolyte gated thin film transistor sensors

The channel conductivity in a FET is highly dependent on the induced charge carriers established along the channel. From this, one can achieve an amplified response to any voltage change recorded at the gate terminal or to modifications of the charge transport characteristics occurring along the channel itself. Such an event could e.g. be an actual change in the gate potential, but it is possible to also conceive of other origins for such a change. For this reason, TFTs are considered, and heavily explored, as an attractive component in different sensors as they can provide an amplified signal, and thus an increased sensitivity, for a variety of sensors. Several different sensors utilizing a TFT to amplify the sensor signal have been proposed.

Chemical and biochemical reactions that take place on the surface or within the semiconductor bulk can potentially be transduced by a TFT if these reactions are accompanied with a change in the electric charge carrier density. This will then impact the conductivity and the drain current of the channel. Examples of such reactions could be the binding or release of charged species on or adjacent to the semiconductor channel ^[51]. This type of sensor could be made as a simple two-terminal chemresistor device where the bound charges would mimic the role of an applied gate voltage in the corresponding three-terminal transistor. The concentration of the bound charges could then be thought of as corresponding to the amplitude of said applied gate voltage. A reference electrode is however often added in the electrolyte as this gives a much better defined system with more reliable sensing. Adding an actual gate terminal to such chemresistor sensors could make it possible to control the sensitivity of the sensor as biasing the gate voltage will have impact on which part of the transfer characteristics that will correspond to the baseline of the sensor ^[52]. It is possible that this type of TFT sensor could function for both OFETs and OECTs. For OECTs, the whole bulk of the semiconductor takes part in the formation of the transistor channel. This gives that the majority of the possible transistor charge carriers could be completely unaffected by a changes occurring only on the surface. The charges, taking part in the sensing event, thus need to

also migrate throughout the entire semiconductor bulk or the sensitivity would be significantly reduced.

If the TFT semiconductor layer is thin enough a sensing event could also take place on the side of the semiconductor layer that is not in contact with the gate dielectric. A prerequisite for this is also that the change in charge, induced by the sensing event, induces a large enough field to significantly affect the entire semiconductor film.

TFTs can be operated using an electrolyte as the gate insulator. This provides us with an opportunity to introduce the analyte, through the electrolyte, in between the gate and the channel. This then offers an even greater opportunity to achieve sensors with very high sensitivity. Further, in EGOFET sensors the introduction of charges via sensor reactions in direct proximity of the transistor channel would naturally provide an opportunity for high sensitivity. A sensing event involving immobilization of charge could also possibly take place at the gate electrode ^[53] (see Figure 3.6d). The EDLs, at the channel and gate, can be viewed as two separate capacitors connected in series and we know from Kirchhoff's laws that the charge stored in both these capacitors then must be the same. A change in charge at the gate should then thus effectively also mean an equivalent change in the charge at the channel. Not only direct changes or switching of the charge in the gate-electrolyte-semiconductor configuration could possibly be monitored and sensed by an EGOFET sensor. If for instance uncharged species bind to the surface of the channel it could distort the EDL at the channel in various aspects, such as effectively increasing the distance that separates the charges of the semiconductor and the electrolyte in the EDL ^[54]. This then lowers the actual capacitance value of the EDL at this interface and thus affects the transistor current. This sensing approach would most likely be more effective for EGOFETs than for OECTs as the current modulation in OECTs is dependent on charges penetrating into the semiconductor bulk. The static drain current level of an OECT is expected to be relatively more insensitive to such in-binding occurring along the surface of the semiconductor. One

could however imagine that the analyte (if small enough), could also penetrate into the bulk of the semiconductor material and thus change the possible concentration of the dopant charges that predicts the drain current level. Another sensing approach for the OECTs is if the bound analyte blocks the doping ions from migrating in or out of the semiconductor. This would then suppress the possibility to modulate the drain current of the transistor. This approach would then probably have the drawback of only be able to give a binary, e.g. detection, response to some threshold value of the analyte and would therefore not be suitable for quantitative analysis [55].

Immobilizing charges on the channel or the gate electrode should ideally be detectable as a shift in the threshold voltage. Disturbing the EDL at the channel (without immobilizing charge) should ideally only change the effective C_i which would be seen as change in the slope of the transfer curve [54].

Figure 3.6 Different architectural designs for thin film transistor sensors. The dotted line in each image marks the location of the sensing event.

In Figure 3.6 an effort is made to illustrate the different approaches of using OTFTs in sensor devices. In Figure 3.6a the transistor is not gated through the electrolyte, including the analyte, and thus the electrolyte is not an active component of the transistor architecture [56-57]. Analytes present in the electrolyte that attaches to the OSC can however still affect the density of charges and traps in the OSC and the gate electrode can then be used to make the transistor operate at optimal sensitivity and amplification. In Figure 3.6b there is a dielectric layer introduced between the OSC and the electrolyte. Analytes attaching to, or reacting with, this dielectric material may then change the voltage drop over the dielectric layer which in turn can be observed as a change in the transistor behavior. The transducer mechanism can in this case originate from the effect of charges entering into the dielectric, equivalent to mode of operation present in Ion Selective FETs (ISFET), or simple displacement of the charges established along the dielectric/electrolyte interface [54, 58]. Excluding the dielectric layer in this type of device yields the architecture given in Figure 3.6c. Here, the OSC is in direct contact with the electrolyte, thus typically providing relatively higher sensitivity. However such a sensor approach is also associated with the risk that ionic species from the electrolyte can penetrate or directly react with the OSC. This gives that the measured sensor effect on the conductivity of the transistor channel is no longer just a result of a field effect [59-61], but can instead be attributed to electrochemical doping, the introduction of traps or rearrangements of the polymer chains. Further, the sensing event can also be introduced at the gate electrode, see Figure 3.6d, as this may change the charge or the effective work function (potential) of the gate, which in turn would influence the charging of the transistor channel [62]. There are also successful approaches where the sensing event has been entirely separated from the transistor channel and instead utilizes charging of a floating gate [63]. In such an approach, the sensor reaction is chemically completely de-coupled from the transistor channel-insulator-gate configuration.

3.3 Ferroelectric surfaces

Since the net surface charge, defined by the orientation of the included dipoles, of ferroelectric thin films are fixed on the surface, and thus non-Faradaic, they may not spontaneously be able to rearrange if the film is placed in contact with an electrolyte. Instead the charges in the electrolyte will have to adapt to the film and the EDLs of such systems can thus be said to be more well defined, as compared to, e.g. the EDL along a metal surface ^[64].

A ferroelectric thin film can be placed in between two electrodes to define a two-electrode switch device. By applying a voltage between the conductors, so that the electric field in the ferroelectric becomes larger than the coercive field (E_c) the dipoles will switch and align ^[65-66]. An electrolyte layer can be placed between the ferroelectric thin film and one of the electrodes. In this case the potential distribution will be somewhat different as compared to the former electrode-ferroelectric-electrode case. As the voltage, applied to the two electrodes, is increased and finally expresses an electric field inside the ferroelectric layer larger than E_c , ferroelectric polarization will still occur and dipoles will thus align with the field. Once removing the applied potential the induced polarization of the ferroelectric dipoles will remain, meaning that the EDL at the ferroelectric surface will again be stabilized, without an externally applied voltage, but of opposite polarization as before.

Surfaces with different surface energy or charge can have major impact on e.g. chemical and biological species, such as self-organized layers, cells and tissues, in an aqueous solution. It is possible to create and redefine regions of different polarity, and thus different surface energy and charge, on the surface of a ferroelectric thin film placed in an electrolyte ^[64]. This could provide an opportunity for spatiotemporal and active control over the adhesion, growth, organization and release of chemical and biological systems while interacting with the ferroelectric surface as it undergoes switching. In addition, the regions of different polarity will be stable without having to connect the system to an electrical circuit with any external voltage source, which means that no power is consumed simply to

preserve a polarization state. Also, as the electroactive surface is switching, the ferroelectric layer does not cause any charge transfer with the aqueous solution, thus limiting undesired electrochemical side reactions.

4. Experimental Methods

4.1 Fabrication

All of the devices presented in this manuscript are based on a substrate of some form with one or more thin layers of material. Some of these layers comprise an “active” component of the device, while others comprise passive or encapsulating materials. In addition, each of the device’s layers generally involve some form of macroscopic or microscopic patterning to define individual features. The following sections describe the various techniques used to fabricate the devices in Papers I-V.

4.1.1 Thermal evaporation

Thermal evaporation is one form of physical vapor deposition, in which a material is evaporated from a source in vacuum and condensed onto a target substrate forming a thin film. Keeping the source and target in vacuum both creates a free path for the evaporated particles to travel directly from the source to the target (Figure 4.1), and reduces the required evaporation or sublimation temperature. Placing a quartz crystal microbalance (QCM) in the evaporation chamber, close to the target, makes it possible to record deposition in real time, and precisely control the evaporation rate

and resulting film thickness. It is possible to transfer patterns onto the target substrate by using stencils, sometimes referred to as shadow masks.

Figure 4.1 Deposition of a thin film through thermal evaporation. The deposition material is placed in the source and is evaporated through heating of the source. A shadow mask can be placed in between the source and the target substrate as to create patterns in the resulting film.

4.1.2 Photolithography

One versatile method for creating highly precise patterning on a substrate is through photolithography. The surface to be patterned is first covered in a photosensitive material known as a photoresist. A mask with the desired pattern is placed over the substrate so that only some parts can be exposed to light. Exposing the photoresist to a light source (typically UV) triggers a chemical reaction (generally either a cross-linking, strengthening reaction, or a degrading reaction) in the resist, only in the areas exposed through the mask pattern. The exposed substrate can then be developed, similar to developing an exposed photograph, using a chemical developer specific to the photoresist used [67]. If the exposed areas of the photoresist become more soluble in the developer solution, it is called a positive photoresist. If the exposed areas become less soluble it is called a negative photoresist. After processing with the developer solution, some regions will still be covered with photoresist, while other will not. The exposed areas can thus be processed, e.g. through wet or dry etching (i.e. removing material by exposing it to some reactant gas, plasma or solution), while the

covered parts remain protected by the photoresist. After processing the exposed areas, the remaining protective photoresist can be removed using an additional solvent (often called a remover) (Figure 4.2).

Figure 4.2 Schematic illustration of photolithographic patterning process.

4.1.3 Spin coating

Spin coating is a method used to produce uniform thin films on a flat substrate from materials in solution or suspension. Thus, it is commonly used for polymer-based thin films. The substrate is placed on a spin coater, which is basically a rotating sample holder with its

rotational axis connected to a motor with controllable rate. The substance that should form the film is then dispensed from dispersion or solution onto the substrate. Often the spinning cycle of the process is preceded by a spreading step in which the sample rotates a lower rate (typically 500 rpm) for a couple of seconds. This is to make sure the solvent wets the entire sample. This step is followed by the main, spinning step, which has a much higher rate (typically 1000-6000 rpm) (Figure 4.3). Factors that affect the resulting film thickness and uniformity are, e.g. solvent viscosity and boiling point, humidity and temperature (as this also affects the evaporation rate of the solvent) and, of course, spin rate [68-69].

Figure 4.3 Deposition of a thin film by spin coating.

4.1.4 Typical fabrication of devices used in this thesis

The typical substrates used for the devices presented in Papers I-V have been flat, smooth and electrically insulating, such as thermally grown SiO_x on top Si wafers, glass or PET foil. On top of these substrates metal has been deposited through thermal evaporation. The metal has then been patterned using photolithography to form bottom contacts of the devices. The active organic films were spin coated from solution on top of the patterned metal. In most cases the final steps for completing the devices was to simply pipette a droplet of aqueous electrolyte large enough to cover the desired areas of the bottom electrode pattern. Top electrodes (e.g. gate electrode)

generally consisted of a metal wire or foil, dipped into the droplet and kept in place by a probe holder (see Figure 4.4).

Figure 4.4 Illustration of the typical fabrication steps used in this thesis.

4.2 Characterization

4.2.1 Current-Voltage measurements

Most of the electrical characterization of the devices described within this thesis was performed using a semiconductor parameter analyzer equipped with several source-measurement units (SMUs). Each SMU can supply a user defined current or voltage while at the same time measuring both the voltage of the SMU as well as the current passing through it. Note that there can sometimes be discrepancies between the set supply values and measured values if,

e.g. the power supply exceeds the limits of the equipment. Current-Voltage (I-V) measurements are a fundamental tool for characterizing and elucidating device dynamics. It is used to characterize all kinds of electrical devices ranging from transistors to solar cells and memory devices.

4.2.2 Impedance spectroscopy

Impedance spectroscopy is a technique that can be used to characterize a material's or device's various electrical properties, such as transfer resistance, ohmic resistance and double layer capacitance of an electrolyte [36, 38]. The materials or compound of materials to be investigated is placed between two electrodes thus creating some kind of capacitor-like structure. A sinusoidal voltage signal of known amplitude, frequency and offset is applied between the electrodes and the current response is recorded. From this the complex impedance for the entire sample at the specified frequency can be calculated. By scanning a range of frequencies it is possible to elucidate various properties of the sample being investigated. The complex impedance as a function of frequency f , or more commonly angular frequency $\omega=2\pi f$ is given by,

$$Z(\omega) = \frac{U^*}{I^*}$$

where U^* and I^* are the complex voltage and current respectively. The complex impedance can also be represented by its real and imaginary components as,

$$Z(\omega) = Z_{Re} + jZ_{Im}$$

Due to the complex impedance, there can sometimes be a shift in phase between the voltage and current signals. This shift is defined as the phase angle,

$$\theta = \tan^{-1} \left(\frac{Z_{Re}}{Z_{Im}} \right)$$

As a continuous AC signal is applied it is possible to use a special case of the Laplace transform (sometimes referred to as the $j\omega$ -method) to analyze the current response as a function of angular frequency. To do this one must set up a theoretical equivalent circuit. The equivalent circuit should take materials as well as interfaces between materials into account. For a purely conductive material the equivalent circuit element is a simple resistor and for a purely dielectric material the corresponding circuit element would be a capacitor. At the interface between an electrolyte and a metal electrode it is usually not the case that the interface can be described as either a pure capacitor or a pure resistor. As mentioned in Section 3.1.2, the EDL at the electrolyte/electrode interface can be viewed as a capacitor (C_D) but there could also be some charge transfer, e.g. due to electrochemical reactions which then looks like a resistive contribution (R_{CT}) in parallel with the EDL capacitor.

Charge transfer processes between different interfaces can however be limited by mass transfer and thus be diffusion limited, which means that the impedance of these interfaces will be frequency-dependent. In the case of the faradaic impedance at the electrode/electrolyte interface, an equivalent circuit element called the Warburg impedance (Z_W) is often used to represent this resistance to mass transfer. Another commonly used, non-ideal circuit element is called a Constant Phase Element (CPE). The CPE is an empirically derived impedance element and can be used to describe, e.g. other diffusion-limited processes in solid and liquid electrolytes or interfaces between different electrolytes as charge transport in those materials is non-ideal. Impedance expressions and phase angles for different circuit elements is given in Table 4.1.

Circuit Element	Impedance (Ω)	Phase angle ($^\circ$)
Resistor	$Z_R = R$	0
Capacitor	$Z_C = 1/(j\omega C)$	-90
Inductor	$Z_L = j\omega L$	90
Warburg Impedance	$Z_W = A/(j\omega)^{0.5}$	-45
Constant Phase Element	$Z_{CPE} = 1/[Q_\alpha(j\omega)^\alpha]$	$-90^\circ \alpha$; $\alpha \in [0, 1]$

Table 4.1 Impedance expressions and phase angles of commonly used circuit elements.

Note that R , C and Z_W can all be viewed as special cases of CPE with $\alpha = 0, 1$ and 0.5 respectively.

To illustrate the data from the impedance spectroscopy the two most common ways are through either Nyquist or Bode plots. In a Nyquist plot the negative of the imaginary part of the complex impedance ($-\text{Im}[Z]$) is plotted on the vertical axis against the real part ($\text{Re}[Z]$) on the horizontal axis. This representation can be very useful for constructing equivalent circuits as the shapes of the curves can often easily identify suitable circuit elements for the equivalent circuit.

In many cases, however, it can be of interest to more explicitly illustrate the frequency dependence of the complex impedance. Then a Bode plot is more suitable in which the logarithm of the impedance ($\log|Z|$) and the phase angle (θ) are plotted against the logarithm of the angular frequency ($\log[\omega]$). From the Bode plot it can thus be seen at which frequencies a sample is dominated by, e.g. capacitive or resistive behavior. Figure 4.5 Typical impedance data of a Randles equivalent circuit (inset top) represented in Nyquist (top) and Bode (bottom) plots. shows the impedance plots corresponding to a so-called Randles equivalent circuit, which is often used to represent electrochemical cells. The top graph shows the Nyquist plot where the contributions of the different circuit elements can easily be identified. The slight shift from the origin corresponds to the bulk resistance of the electrolyte (R_E). The semicircular shape visible is typical of a capacitor and resistor in parallel, here corresponding to the charge transfer resistance (R_{CT}) and electrolyte double layer capacitance (C_{EDL}). Finally, the 45° linear region towards higher values of $\text{Re}(Z)$ is characteristic for the Warburg impedance (Z_W). The bottom graph of Figure 4.5 shows the frequency dependence in a Bode plot. The dotted line shows how the phase angle varies with the impedance. At high frequencies the double layer capacitance does not have time to fully charge and the behavior of the circuit is completely dominated by the resistance of the electrolyte. Moving towards lower frequencies the EDL starts to form and a more capacitive behavior related to C_{EDL} becomes visible as a decrease in θ . Decreasing the

frequency further saturates the influence of the double layer capacitance and a more resistive behavior can again be seen as charge transfer can start to occur. Finally, at the lowest frequencies, there is another drop in θ where charge transport begins to limit and Z_W starts to dominate the behavior of the circuit.

Figure 4.5 Typical impedance data of a Randles equivalent circuit (inset top) represented in Nyquist (top) and Bode (bottom) plots. Note in the Nyquist plot the characteristic attributes (shifted semicircle and linear region). The Bode plot indicate a peak of capacitance-dominated behavior around $\omega=3 \times 10^2$.

5. Basic cell biology

The devices presented in this thesis have been developed specifically with biological applications in mind. Interfacing biological samples with electronics is often termed bioelectronics and ranges from applications such as sensing biochemical markers [70-71] to stimulation of cells and tissues [72]. In Papers II, III and V electronic devices, either aimed at or utilizing biological systems, are presented. This section aims to serve as a basic orientation of the biological background of said papers to enable better understanding of the mechanisms employed.

5.1 Cells

The cell studies (also referred to as *in vitro* studies) related to this thesis have mainly been related to skin grafts for burn victims. Human skin primarily consists of two layers. The outermost part is called the epidermis, in which the main cellular component is keratinocytes. The deeper part is called the dermis, where the main cellular component is fibroblasts [73-74]. During the course of this thesis only fibroblasts have been used to demonstrate the techniques as an initial step towards more complex cell cultures. Fibroblast cells

are generally present in connective tissues, where they are often the most numerous cells. Their primary role is to produce the fibers and ground substance of the extracellular matrix [74]. Fibroblasts thus also play an important role in wound healing and reformation of tissues [73].

5.2 Phospholipids and the cell membrane

The outer surface of cells consists of a cell membrane. This membrane separates the inside of the cell from its external environment. The membrane regulates transportation of substances in and out of the cells and also contains means for cells to communicate with their environment and other cells [74].

Figure 5.1 Schematic representation of a phospholipid (left) with the polar head and fatty tails and how they can organize into double layers in solution (right).

The cell membrane is composed primarily of phospholipids; molecules with a polar, hydrophilic phosphate “head” and one or more non-polar, hydrophobic fatty acid “tails” (Figure 5.1). This makes them amphiphilic, and in aqueous environments they thus self-organize tail-to-tail into a double layer, forming the main structure of the cell membrane [74]. Because of the fatty core of the phospholipid bilayer, it is impermeable to ions and large polar

molecules, while at the same time permeable to water and non-polar molecules.

5.3 Membrane proteins

The cell membrane also contains glycoproteins that can either be peripheral, located on one side (inside/outside) of the membrane, or integral proteins, that extend into or through the lipid bilayer. Membrane proteins, together with glycolipids, play a vital role in intercell communication. Indeed, the majority of a cell's interaction with its environment is mediated through its membrane proteins, e.g. transporting specific ions or molecules through the membrane, or as receptors that can recognize and bind to specific molecules [74]. In some cases, the membrane proteins can be seen as cell identity markers playing an important part in, for example, tissue formation or immune response, where cells need to identify and communicate with their adjacent cells and environment.

5.4 Extracellular matrix

The extracellular matrix (ECM) of connective tissues comprises some ground substance (water and large organic molecules) combined with protein fibers. The ground substance can be in fluid, gel or solid state depending on the tissue. The ECM provides a structural framework for the tissue's cells and provides a medium for transportation of substances between the blood and cells. The protein fibers of the ECM thus support and strengthen the tissue and provide anchor points for tissue growth [74-75].

The tripeptide sequence arginine-glycine-aspartic acid ("RGD", in single-letter amino acid code) has been shown to bind to specific receptor proteins in the cell membrane [75]. As the RGD sequence is present on ECM proteins such as fibronectin and fibrinogen, the RGD sites are considered to be primary cell anchoring (binding) points.

5.5 Binding proteins/mechanisms

Because there are certain amino acids sequences of that are required for effective cell anchoring/binding – like the RGD sequence mentioned above – protein conformation, and thus binding-sequence exposure, becomes very important. When a protein adheres to a surface it can change conformation depending on properties such as surface chemistry, energy or charge, which in turn affects the ability of cells to bind to the proteins on the surface [75]. The surface properties may also affect the affinity of the proteins themselves, which then in turn also affects how strongly cells are attached to the surface through binding to these proteins [75]. It is these surface effects that are exploited in Paper V.

5.6 Biorecognition events

Since proteins can act as ID-tags for specific cell types or conditions, many biosensors utilize protein interaction, such as binding and enzymatic reactions, to achieve a high level of specificity. One method that has been very successful throughout the years is using the strong affinity between the enzyme biotin and the protein avidin, discovered in the 1940s [76], and later also to other proteins with similar features such as streptavidin [77]. Through the process of biotinylation, biotin can be attached to different molecules which then can be detected, or be used to detect, through their high affinity to biotin binding proteins, such as avidin or streptavidin [78]. For detection in sensor applications the biotin could e.g. be attached to a fluorescent probe or, as in Paper II, an organic semiconductor.

5.7 Cell detachment

Cells cultured *in vitro* must usually at some point be detached from their substrate for, e.g. analysis, re-seeding or implantation. There are several strategies applied to achieve this detachment. Perhaps the most widely used method today is a treatment with the enzyme trypsin, which cleaves the membrane proteins which bind the cells to the surface [79]. While this technique can be highly

effective at detachment, enzymatic treatment of the membrane proteins can affect the viability of the cells and their ability to bind to subsequent surfaces or tissues [80-81]. Detachment strategies that target the substrate itself, rather than the biochemistry of the cells, have thus been proposed.

Electroactive release of the entire substrate surface is one strategy. In this method, cells are cultured on an intermediate surface which can be electronically released from the main substrate. The cells are thus released along with the intermediate layer, and can subsequently be collected and reseeded [82-85]. Such electroactive strategies also have the potential for spatial as well as temporal control of the release of cells from the substrate surface, as individual release areas or “pixels” could be defined.

Other methods of cell release have also been proposed or demonstrated. For example, changing the surface energy of the substrate via thermally-induced effects has been demonstrated [86-88], and in Paper V we demonstrated an entirely new electroactive cell release method using ferroelectric films.

6. Conclusions and future outlook

The focus of this thesis has been on the challenges and opportunities faced when placing organic electronics in aqueous environments and even using these environments as active components of the devices. We have explored how the polarization of an electrolyte in contact, and circuit, with various electroactive polymer thin films can be exploited to modulate the devices. We have also demonstrated how changes in the EDL, at the interface with the polymer thin films, can be used both for sensing and modulating events at the interface.

Papers I, II and III all touch on the subject of when and how it is possible to make use of the high capacitance of the EDL, and its sensitivity to local changes, in transistor-based sensors. Transistor modulation via EDLs can be complicated – and even diminished – by electrochemical doping of the semiconductor, in competition with the field-effect of the EDL. This could in turn thus also diminish the sensor signal. However, if one can make certain that the dominant modulation mechanism is through field effect, EDL-based systems can be utilized. This restriction to field-effect can be achieved by suppressing the availability of the semiconductor bulk to the ions of the electrolyte. Two strategies are presented within this thesis, the

first being to decrease the ion mobility in the semiconductor by using a co-polymer with a sufficiently large hydrophobic part (Paper I and II). The second strategy involves adding another layer on top of the semiconductor, thus slightly separating it from the electrolyte (Paper III). In the case presented in Paper III it can be seen that there is some form of charge transfer over one of the interfaces as there must be a CPE included in the equivalent circuit model to properly fit the impedance data. In both of the cases it becomes apparent from the impedance data that the frequency of the applied signal has an effect on the behavior of the devices. This should most likely translate into an effective time limit for applying a gate voltage before risking ion penetration into the semiconductor bulk. Taking these design parameters into account should vastly expand the number of possible semiconductor materials and device architectures that can be utilized for aqueous *in situ* transistor-based sensing applications.

In Papers IV and V the focus shifted from how the electrolyte affects the electroactive polymer to how the electroactive polymer can affect the electrolyte, specifically the EDL. We demonstrate how the EDL can be formed at the surface of a ferroelectric film, and how the surface charge of the ferroelectric material affects the total charge of the EDL. The surface charge on the ferroelectric material can thus affect the resulting voltage drop over the EDL. Although the stabilization of the EDL by ferroelectric surfaces has been investigated before, the specific voltage induced over the EDL has not previously been elucidated. It turns out that the (easily measured) overall device voltage is highly sensitive to changes in the properties of the EDL, indicating that we may have found a new means of intimately probing the EDL and events taking place therein. This not only opens up possibilities of investigating the EDL itself but also shows promise for new types of sensors with a direct voltage readout. Such sensors could have extremely low power consumption as there does not need to be any input power once the ferroelectric thin film has been polarized.

Well-defined surface charge has also been suggested as a useful tool for controlling where biological and chemical events can take

place on a patterned ferroelectric surface. We have shown that it is possible to change the polarization of a ferroelectric polymer film by applying a voltage through an electrolyte. This aqueous modulation of the polarization provides the opportunity to continuously redefine surface charge patterns and thus control where said biological or chemical events take place. To demonstrate this ability, we grew cells on ferroelectric polymer thin films and were able to trigger their release from the surface by changing the direction of the ferroelectric polarization *in situ*. The cells used in our experiments were one type of skin cells. Tissues are generally composed of several types of cells, which means that there is still much to explore. Different cell types may react differently to the different surface energies, meaning that the technique might be possible to use for organizing or sorting cells in a culture. Still, ferroelectric cell release represents a promising alternative to contemporary chemical cell release techniques, potentially resulting in healthier cells and tissue for eventual implantation or other regenerative medicine applications.

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Part II

The Papers

Papers

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