Nanocomposites of Cellulose and Conducting Polymer for Electrical Energy Storage

HENRIK OLSSON
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Abstract

The world’s increased energy storage demand, as well as the environmental concerns related to the combustion of fossil fuels, has triggered a transition to intermittent renewable energy sources as well as to electrical and hybrid vehicles. Current day rechargeable batteries are, due to the invention and development of lithium ion batteries, technologically well positioned to answer to some of these demands. Conventional batteries, however, utilize inorganic materials of limited supply that require large amounts of energy during refining and processing. The materials also add a significant cost to the final product, making the rechargeable batteries less attractive for large scale applications. During the last decade, significant efforts have been made to find suitable organic matter based electrode materials that can replace the inorganic materials. One class of organic materials that can be used for electrical energy storage, or be included as components in organic matter based energy storage systems, is conducting polymers.

The aim of this thesis was to investigate the possibilities and limitations of using the conducting polymer polypyrrole in energy storage applications. The polymer was synthesized onto cellulose extracted from the Cladophora sp. algae, and the result was a flexible composite material. Symmetrical energy storage devices constructed with the composite material were shown to exhibit a pseudocapacitive behavior. The resistance in the cells was investigated and was found to scale linearly with the separator thickness. Cells could be cycled for 4,000 cycles without significant capacitance loss and cells that were overcharged to 1.8 V cell potential, were found to be protected by a resistive potential drop. Devices were constructed as proof-of-concept and were used to power a remote control and a digital thermometer.

The self-discharge in polypyrrole was studied extensively. It was found that oxygen was responsible for the oxidation of the reduced electrode, while the positive electrode self-discharged due to a faradaic reaction. Through spectroscopy and the temperature dependence of the self-discharge, it was suggested that the self-discharge of oxidized polypyrrole is linked to the degradation at high potentials, commonly referred to as overoxidation.

Keywords: Polypyrrole, Nanocomposites, Energy storage, Conducting polymers, Cellulose

Henrik Olsson, Department of Engineering Sciences, Nanotechnology and Functional Materials, Box 534, Uppsala University, SE-75121 Uppsala, Sweden.

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I am somewhat exhausted; I wonder how a battery feels when it pours electricity into a non-conductor?

-Sir Arthur Conan Doyle
List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


Reprints were made with permission from the publishers.
My contribution to the included papers

**Paper I:** The planning and performance of the experimental work was shared equally between me and G. Nyström. I wrote the initial draft, contributed to the analysis of data, and the continued manuscript writing process.

**Paper II:** I participated in the planning, and performed the majority of the experimental work. I wrote the initial draft, contributed to the analysis of data, and the continued manuscript writing process.

**Paper III:** I participated in the planning, and performed the majority of the experimental work. I wrote the initial draft, contributed to the analysis of data, and the continued manuscript writing process.

**Paper IV:** I participated in the planning, and performed all the experimental work. I wrote the initial draft, contributed to the analysis of data, and the continued manuscript writing process.

**Paper V:** I participated in part of the planning, and performed part of the experimental work. I participated in the writing of the initial draft, contributed to the analysis of data and the continued manuscript writing process.
Also Published

**Journal articles**


**Conference contributions**


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<th>Full name</th>
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<tbody>
<tr>
<td>AC</td>
<td>Alternating current</td>
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<tr>
<td>CE</td>
<td>Counter electrode</td>
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<td>CV</td>
<td>Cyclic voltammetry</td>
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<td>DC</td>
<td>Direct current</td>
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<td>LIB</td>
<td>Lithium ion battery</td>
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<td>OCP</td>
<td>Open circuit potential</td>
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<td>OLED</td>
<td>Organic light-emitting diode</td>
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<tr>
<td>PPy</td>
<td>Polypyrrole</td>
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<tr>
<td>RE</td>
<td>Reference electrode</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>WE</td>
<td>Working electrode</td>
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<table>
<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>C</td>
<td>Capacitance</td>
<td>F = C/V</td>
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<td>E</td>
<td>Applied potential</td>
<td>V</td>
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<td>E&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Formal potential</td>
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<td>E&lt;sub&gt;a&lt;/sub&gt;</td>
<td>Activation energy</td>
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<td>F</td>
<td>Faraday constant</td>
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<td>Current</td>
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<td>Rate constant</td>
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<td>k&lt;sub&gt;B&lt;/sub&gt;</td>
<td>Boltzmann constant</td>
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<td>R</td>
<td>Gas constant</td>
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<td>R</td>
<td>Resistance</td>
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<td>T</td>
<td>Temperature</td>
<td>K</td>
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<tr>
<td>t</td>
<td>Time</td>
<td>s</td>
</tr>
<tr>
<td>U</td>
<td>Potential drop</td>
<td>V</td>
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<tr>
<td>v</td>
<td>Potential scan rate</td>
<td>V/s</td>
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General introduction

Conducting polymers constitute a class of polymers that are electronic conductors. Generally, conducting polymers are insulators in their neutral state and conductivity is achieved by oxidizing or reducing (doping) the polymer chain. The nature of the conductivity implies that the polymers are also redox active, which opens up to a large variety of interesting applications, apart from those arising from their conductivity. Conducting polymers have been used for applications such as ion extraction, actuators, electromagnetic radiation shielding, organic light-emitting diode (OLED) displays, and sensors. They can also be used as the active material in energy storage applications.

Conducting polymers are often used in composites, with substrates such as cellulose, carbon nanotubes, and graphene. The use of substrate materials can improve various properties of the polymers such as the mechanical strength, flexibility, porosity, surface area, rate capability and capacitance.

The work in this thesis is focused on energy storage using the conducting polymer polypyrrole (PPy). A PPy composite electrode material with cellulose extracted from Cladophora sp. algae as the substrate, first described by Mihranyan et al., will be presented and its characteristics depicted. The unique features of the material will be discussed, along with its intrinsic limitations as electrical energy storage material. Finally, it will be shown that the material can be used as electrodes in all-organic energy storage devices, and proof-of-concept devices will be presented.

A more extensive introduction and background to each topic will be given in the beginning of each chapter.
Aims of the thesis

The work presented in this thesis focuses on the properties of a PPy/cellulose composite for electrical energy storage and aims at understanding some of its more fundamental characteristics. Environmental friendliness and all-organic energy storage are the two concepts forming the basis of my entire PhD project.

The specific aims of the work presented are:

- To investigate the chronopotentiometric behavior of two-electrode symmetrical devices based on PPy/cellulose composites, their stability during cycling, and uses in electric energy storage applications (Paper I and V).

- To study how the cellulose substrate and different ways of chemical polymerization influence the electrochemical properties of PPy composites in aqueous solution (Paper I, II and V).

- To understand the mechanisms involved in different types of degradation of conducting polymers (Paper I, III and IV).

- To examine the self-discharge behavior of two-electrode symmetrical devices based on PPy/cellulose composites, understanding the underlying mechanism, and minimizing its occurrence in these devices (Paper III and IV).

- To examine the limitations and resistances in sandwich type two-electrode symmetrical devices based on PPy/cellulose composites, and how their design can be improved (Paper V).
Given the finite nature of fossil fuels and the world’s increasing demand for energy, there is currently a worldwide interest in finding renewable alternatives of producing energy. Because of the intermittent nature of many renewable energy sources (e.g. solar, wind and wave power), there is a growing need to be able to store energy so that it can be used during peak energy consumption.

Electrical energy can be converted and stored in different ways – e.g. water can be split into oxygen and hydrogen that can be used as fuels, or the water can be pumped into a reservoir at higher altitude to be used in a hydroelectric power plant. Another way of storing energy is by the utilization of batteries, for example the widely used lithium ion battery (LIB). In a battery, two electrodes are separated by an electrolyte that allows for ion movement. In the case of the LIB, the negative electrode usually consists of graphite with intercalated lithium ions. The positive electrode usually consists of a metal oxide, e.g. Li$_x$CoO$_2$. During discharge of the battery, electrons move from the negative to the positive electrode to compensate for the potential difference between the electrodes. At the same time, charge compensation takes place as Li$^{+}$ ions move from the negative electrode to the positive electrode.

While LIBs are among the top performing battery types today, they are not free from problems and limitations. For instance, lithium and the materials used in the positive electrode of LIBs are found in the earth’s crust and require mining and purification at high temperatures. These processes consume a large amount of energy and are the cause of a large carbon footprint in the manufacturing of LIBs. An estimate showed that electric cars have to be used for approximately 120 charge cycles before their total carbon emission (including production of the battery) becomes lower than that of a traditional car using fossil fuels. Furthermore, LIBs consist of brittle and inflexible materials, which is one of the reasons why batteries used today typically are rigid. For many applications, such as wearable electronics, it would be advantageous to have flexible batteries that could withstand bending during cycling. The intrinsic properties of the components used in LIBs today make this a tough challenge, but there are successful attempts reported.

By constructing batteries from organic materials, energy storage devices with a lower carbon footprint could be achieved. Synthetic organic chemistry makes it possible to produce an incredibly wide array of organic molecules
through low temperature processes. If the starting materials are produced from renewable sources (e.g. plants or trees) the carbon emission from production and synthesis can be minimized. Another advantage with using organic materials in batteries could be their higher flexibility, which further opens up for use in applications where traditional inorganic batteries have a hard time functioning.

Figure 1. Timeline for lithium based batteries. “Lithium Batteries” by xkcd.com is licensed under CC BY-NC 2.5.

Electrochemistry as a tool

The use of electrochemistry is essential when studying battery materials. The most common setup for such measurements involves three electrodes connected to a potentiostat. The first electrode, the working electrode (WE), is the main electrode at which the electrochemistry of interest occurs. It can be used to probe electroactive molecules in the electrolyte solution, or molecules attached to the electrode surface. During the various electrochemical measurements that can be performed using the potentiostat, electric current flows between the WE and the counter electrode (CE). When a molecule on the WE is oxidized, electrons move through the circuit (producing current) and something is reduced at the other end, that is, on the CE. The third electrode is the reference electrode (RE) which allows for controlling or monitoring the potential of the WE against a known reference redox couple. The potential of the WE is strictly controlled by the potentiostat and reported to the user, while the potential of the CE is chosen to balance the current during the experiment. If insufficient conversion is occurring at the CE, the potentiostat will change the potential accordingly to ensure that the CE is not limiting in the measurement. This means that it is difficult to know exactly which
electrochemical reactions are taking place at the CE. This can cause a pH shift in aqueous electrolytes, or the formation of unwanted species, which is why the CE is often kept in a separate compartment equipped with an ion-permeable membrane.

Cyclic voltammetry
The most commonly used technique in electrochemistry is cyclic voltammetry (CV). In a CV measurement the potential is scanned at a constant rate (see left side of Fig. 2) and the current response is measured. Depending on the species and electrodes, this response can vary and give rise to different distinctive peaks. Commonly, the species under study is dissolved in the electrolyte, and the WE is a metallic electrode immersed in the solution. In order for the redox reaction to take place the species must be transported to the electrode, which gives rise to a CV peak with a characteristic tail. Transportation can take place through migration in the electric field, diffusion and convection. The right side of Fig. 2 shows a cyclic voltammogram with the redox peaks for ferrocene/ferrocenium in solution, where the diffusion tail is clearly visible after each peak. The peak potential for such reversible systems is given by

$$E_p = E_{1/2} + 1.109 \frac{RT}{nF}$$

where \( R \) is the gas constant, \( T \) the temperature, \( n \) is the number of electrons and \( F \) is the Faraday constant. \( E_{1/2} \) is equal to the formal potential \( E^0 \) if the diffusion coefficient is the same for both the reduced and oxidized species.\(^{24}\)

The formal potential is practically equivalent to the redox potential, \( E^0 \), but with a small correction stemming from differences between activities and concentrations.\(^{24}\) It should be mentioned that reactions and equations in electrochemistry are often given for the reduction. However, since the experimental results presented in this thesis are for PPy, it is more convenient to give the equations for the oxidation. All potentials are however reported as reduction potentials, according to convention, throughout the text.
Figure 2. Potential program (left) and the respective CV response (right) for dissolved ferrocene. The arrows denote the direction of the sweep, and the peaks in the voltammogram have tails typically seen for diffusion controlled measurements in solution.

Electrodes can be made with the redox active species attached to the surface. If the layer is sufficiently thin (e.g. monolayer), so that there is no diffusion limitation through the film, the diffusion tail will be absent in the cyclic voltammogram. The obtained voltammogram could look like the left one in Fig. 3, with the peak potential given by the potential of maximum conversion, i.e. the redox potential in this case.

A careful look at the left voltammogram in Fig. 3 reveals a small constant current present even at potentials with no redox activity. This is a capacitive current originating from the charging of the double layer at the electrode, as given by

\[ i_c = vC_{dl} \]  \hspace{1cm} (2)

where \( i_c \) is the current, \( v \) is the potential scan rate, and \( C_{dl} \) is the double-layer capacitance.

So far, the voltammograms discussed in this chapter have been for species with facile kinetics. Another case worth discussing is that of a surface-confined species with slower redox kinetics. In this case, the obtained results look more like the right voltammogram in Fig. 3. Because the system can no longer be said to be at equilibrium at all times, the peak potential is given by

\[ E_p = E^0 + \frac{RT}{(1 - \alpha)nF} \ln \left( \frac{(1 - \alpha)nFv}{Rk^0} \right) \]  \hspace{1cm} (3)

where \( \alpha \) is the transfer coefficient and \( k^0 \) is the exchange rate constant. The equation above holds for reactions with slow kinetics where the oxidation and reduction peaks are well separated, and the back reaction can be neglected. It can also be used for irreversible reactions, where no back reaction is possible. Usually, the capacitive current remains the same as it depends on
the electrode and electrolyte, but it can also be affected by the redox reaction. For instance, the polarity or porosity of the surface may change upon oxidation/reduction – thus affecting the capacitance.

Figure 3. Simulated CV responses for a modified electrode with the redox active species attached to the surface. The $E^0$ for the reaction was set to 0.5 V. The only difference between the figures is that $k^0$ was reduced by a factor of 1000 in the right voltammogram.

**Chronopotentiometric and -amperometric methods**

Three other techniques used frequently in electrochemistry are chronopotentiometric (constant current), chronoamperometric (constant potential), and zero current methods. In the first two techniques, the potential or current is measured vs. time while a constant current or potential is applied. Apart from being useful techniques for electropolymerization (described in a later section) or obtaining information about an electrochemically active system, these techniques can be used to simulate the operation of a battery or a capacitor. The chronopotentiometric measurement allows for simulating the discharge of an energy storage device at different currents, corresponding to usage in applications with different current demands. It is also a good way of simulating the recharging of a battery, since most of today’s chargers use a constant current during the initial charging step.

The chronoamperometric procedure, on the other hand, is often used at the end of a charge cycle to ensure full charging. When only a constant current is used to charge a battery, the iR-drop is troublesome to account for, which is solved by switching to a chronoamperometric technique in the end of the charge cycle. Chronoamperometric measurements can also be used to obtain the RC time constant of a capacitor, according to

\[ i = \frac{E}{R} e^{-t/RC} \]

(4)
where $R$ is the resistance, $C$ is the capacitance, $t$ is the time and $E$ is the applied potential. Apart from giving the resistance and the capacitance of a capacitor, the RC constant (unit of seconds) also sets the lower limit for the time that the capacitor needs to charge. It can be noted that $3RC$ is the time needed for charging the capacitor to 95% of the applied potential,\textsuperscript{24} as seen from the following equation

$$V(t) = V_A(1 - e^{-t/RC})$$

(5)

where $V_A$ is the applied potential. Since large capacitive contributions can be troublesome in electrochemical measurements, it is sometimes beneficial to reduce the RC constant. One way to accomplish this is to use small electrodes, often called microelectrodes. Microelectrodes are electrodes with a small surface area, typically with diameters of 10-100 µm. The small surface area limits the current and microelectrodes are often used when it is important to do measurements in small A/V conditions. For disk electrodes with a small radius $r$, the resistance is proportional to $1/r$ while the capacitance is proportional to $r^2$. Hence, the RC time constant decreases with electrode size.

Finally, in the zero current procedure the potential is measured as a function of time, in the absence of applied current. When working with energy storage devices, this technique is useful for measuring the self-discharge in the device. The self-discharge can be studied from the potential drop occurring in a charged battery or capacitor when it is not being used. Due to the energy contained in the chemistry of a charged energy storage device, leaking current, degradation, or side reactions can occur – all of which act to lower the energy stored in the device.

Two-electrode measurements

There are situations where three-electrode experiments are problematic since the CE just compensates for the reaction at the WE without regard to its potential. Instead it is often better to perform a two-electrode measurement, in which the CE is connected to the RE. In this way, the potential between the two electrodes is controlled, so that the device can be cycled within the desired cell potential region. The potential of the electrodes against a known reference potential is, however, not monitored. This means that unless the open circuit potential (OCP) and the capacitances of each electrode are known in advance, there is no way of determining if the electrodes will reach potentials outside of their stability window. This problem can be solved by the introduction of an external RE. The RE is connected to one or both of the electrodes in the device through a voltmeter which measures the potential between the device electrode and the RE. This enables two-electrode cycling.
of the device, while the potentials of the device electrodes are monitored against a known reference. A schematic drawing of this setup can be seen in Fig. 4.

*Figure 4.* Schematic drawing of a two-electrode cell, connected to a potentiostat, with potential monitoring through a RE connected to voltmeters in an external circuit.
Conducting polymers

Polymers are large molecules constructed from smaller units, usually called monomers.²⁶ They are generally electrical insulators, used in all sorts of applications ranging from laptops to frying pans.

Conducting polymers constitute a subclass of polymers with very special properties in form of intrinsic electrical conductivity. Although polyaniline (one of the more common conducting polymers) was synthesized as early as 1862,²⁷ the research field is generally viewed to have started with the famous paper by Shirakawa, MacDiarmid and Heeger,²⁸ showing for the first time high conductivity in doped polyacetylene. In the article, the authors anticipated that

“We believe the polyacetylene halides may be the forerunners of a new class of organic polymers with electrical properties which may be systematically and controllably varied over a wide range by chemical doping.”

The contribution by Shirakawa, MacDiarmid and Heeger was awarded the Nobel Prize in Chemistry in 2000,²⁹ which led to an increased activity in the field.

Research carried out within the field of conducting polymers has led to the discovery of a large variety of polymers that share the intrinsic property of doped polyacetylene, the most common being PPy,³⁰ polyaniline,³¹ and polythiophene.³² In addition to fundamental research, there has been a large interest in utilizing conducting polymers for energy storage,³³-³⁷ ion separation,¹,² actuators,³ sensors,⁶,⁷ and OLEDs.⁵

Polyacetylene as a model

The simple chemical structure of polyacetylene makes it a suitable example for discussing the intrinsic conductivity seen in conducting polymers. Polyacetylene consists of repeating CH-units ordered in a cis- or trans-form – the structure of the latter can be seen in Fig. 5.³⁸

The fact that polyacetylene can be readily doped after synthesis, stems from the open morphology and the weak interchain interactions that allow for diffusion of charge compensating ions in the polymer.³⁸
In order to understand the conduction mechanism in these polymers, it is useful to consider their electronic band structure. The electrons in a single isolated atom are described by atomic orbitals, which have discrete sets of energies. When atoms combine in a molecule, the atomic orbitals interact and form molecular orbitals, which have different energies compared to the atomic orbitals. The combination of more atomic orbitals will eventually cause the discrete energy levels to form a continuum – a band. Gaps in the band structure, seen for certain materials, are essentially ranges of energy that are not covered by any available states.

A polyene (i.e. a polyunsaturated organic compound) like polyacetylene with equal bond lengths has no bandgap. The absence of a bandgap would lead to metallic conduction in neutral (undoped) polyacetylene, which is not seen experimentally (see top part in Fig. 5). The reason why neutral polyacetylene behaves like an insulator is the occurrence of a Jahn-Teller distortion called the Peierls distortion, which shortens every second bond in the chain (see middle part in Fig. 5). This leads to a decreased energy of the occupied $\pi$ orbitals, and a simultaneous increased energy of the occupied $\sigma$ orbitals. The overall energy (when considering both the occupied $\pi$ and $\sigma$ orbitals) determines the distortion and thus the band gap. Since the width of the gap is larger than the thermal energy available at room temperature, neutral polyacetylene is an insulator.

Upon oxidation of the chain, new thermally accessible states are formed in the band gap, allowing conduction to occur at room temperature. Such states are illustrated in the bottom part of Fig. 5.
Polyacetylene used as a model for understanding the band gap and mid-gap states in conducting polymers. The Peierls distortion shortens the double bonds and creates a band gap (middle part of figure). Oxidizing the polymer introduces two new levels in the mid-gap (bottom part of figure).

Figure 5. Polyacetylene used as a model for understanding the band gap and mid-gap states in conducting polymers. The Peierls distortion shortens the double bonds and creates a band gap (middle part of figure). Oxidizing the polymer introduces two new levels in the mid-gap (bottom part of figure).

Polypyrrole

The synthesis of PPy dates back to at least 1966, and since the discovery of its conducting properties it has become one of the most studied conducting polymers. The reason for its popularity is likely the ease of synthesis in water and high stability in air.

This chapter will be dedicated to introducing the polymerization procedure and electrochemical behavior of PPy.

Electropolymerization

Polymerizing pyrrole using an electrochemical procedure is arguably the best way to ensure full control of the polymerization procedure. A drawback is that the polymerization is limited to conducting electrodes, which may not be a viable route when synthesizing certain composites. It is, however, the best route for understanding the fundamental mechanisms of the polymerization procedure, and electropolymerization of pyrrole has been thoroughly studied in the literature.
It is common to see the polymerization mechanism described in an oversimplified way in the literature. In these descriptions, the pyrrole monomer is oxidized to a radical monomer which reacts with an identical species to form a dimer. Propagation is then described similarly to radical polymerization where the oligomer and a new monomer are oxidized, and propagation proceeds through addition of monomeric units to the chain. This mechanism is unlikely, because measurements show that while the reactivity for monomers is initially high, it drops drastically for oligomers. Monomer oxidation requires higher potentials than oligomer oxidation, and the monomers also react with much more facile kinetics. A more likely mechanism is therefore the dimerization, with subsequent steps to a tetramer and then to an octamer. A part of this mechanism is shown in Fig. 6 for clarity. It should be noted that despite significant efforts, the polymerization mechanism is still not fully understood.\textsuperscript{46}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{mechanism.png}
\caption{One proposed mechanism for polymerization of pyrrole.\textsuperscript{46} The polymerization propagates in steps where the formed dimers react with each other to form tetramers which then react to form octamers.}
\end{figure}

\textbf{Chemical polymerization}

An alternative approach to the electrochemical polymerization described above, is the chemical polymerization route. In this approach, an oxidizing agent, typically an iron(III) salt, is added to a solution of pyrrole monomer. Even though there are large differences compared to the electrochemical approach, the polymerization can be assumed to proceed similarly (Fig. 6).

Chemical polymerization is typically good for producing larger quantities of PPy, since polymerization occurs throughout the entire bulk of the solution, and is not restricted to the electrode surface or to the currents that can be drawn. It is also a very applicable method for producing PPy composites, also widely discussed in the literature.\textsuperscript{15, 47-50} The PPy/cellulose composites under study in this thesis were synthesized using a solution of either FeCl\textsubscript{3} or Fe(NO\textsubscript{3})\textsubscript{3}. During the polymerization Fe(III) oxidizes the pyrrole monomers while undergoing reduction to Fe(II). This reaction proceeds quickly at room temperature, and the solution turns black by PPy formation almost immediately. The main drawback with this type of polymerization is that a large amount of iron is needed, which may be hard to get rid of despite rigorous washing.\textsuperscript{51} Washing with an acidic solution has proven to be more successful because the solubility of iron is higher in solutions with a lower pH.
Electrochemical behavior

The charging (p-doping) of PPy can be seen as the removal of electrons from a number of subunits on the polymer chain, charge-balanced by an anion (dopant ion) from the electrolyte. Figure 7 shows a schematic view of the cycling between reduced and oxidized PPy. When an electron is taken from the polymer, it becomes positively charged and an unpaired radical is formed. In order to maintain charge neutrality, an anion from the electrolyte moves in to compensate for the charge. The chain in the lower part of Fig. 7 corresponds to the polaron state, and as the polymer is oxidized further, bipolarons are formed.

Figure 7. Schematic doping of PPy. When an electron is removed from the neutral polymer, an ion from the electrolyte moves in to compensate the charge.

Since PPy is insoluble in most solvents, electrochemical characterization is typically performed with PPy attached to the electrode surface. This can be done by electropolymerization, where the formed polymer is precipitated onto the electrode, or by connecting PPy powder or a PPy composite to a conductive substrate. Figure 8 shows a cyclic voltammogram with a PPy composite material attached to a platinum wire in a three-electrode setup. If Fig. 8 is compared with the simulated surface cyclic voltammogram in Fig. 3, it becomes evident that the response from PPy differs significantly from the ideal response for a redox species attached on a surface. Indeed, conducting polymers in general do not have one unique redox potential, resulting in the smeared out and largely capacitive looking voltammogram. It is reasonable to think of PPy as a set of superimposed redox states, where some regions may be easier to oxidize. Additionally, the more the chains are oxidized, it becomes increasingly difficult to oxidize the material further. This explains the steep oxidation onset and capacitive looking current decay after the oxidation peak.46
Figure 8. Typical CV response for PPy. This voltammogram was obtained with a composite where pyrrole was chemically polymerized onto cellulose. The current has been normalized with respect to sample weight.
Cellulose

Cellulose is one of the most abundant polymers on earth, and has been used by humans for thousands of years. In fact, the word ‘material’ is derived from the Latin word for ‘trunk of tree’. Cellulose is produced naturally as part of the biomass by numerous organisms, including trees, plants, algae, bacteria, tunicates and fungi.

Apart from well-known uses of cellulose (e.g. paper, building material and cotton fabric), there are numerous applications requiring sophisticated methods of refining the raw materials containing cellulose. Applications include the use of cellulose as filters, reinforcement material in polymers, transparent films, substrate for OLED screens, material for medical implants, and – as will be shown later in this thesis – substrate for conducting polymer-based energy storage devices.

Figure 9. Chemical structure of the cellulose repeating unit.

Cellulose is a linear polymer consisting of glucose units – its structure is shown in Fig. 9. The linearity is promoted by intrachain hydrogen bonding between the hydroxyl groups and the oxygens of neighboring glucose rings. From a bottom-up perspective, summarized in Fig. 10, cellulose chains make up the smallest cellulose building element – the elementary fibril. These fibrils, in turn, make up the microfibril which is bunched together to form a cellulose fiber. The microfibrils can consist of regions of crystalline and amorphous character. The degree of crystallinity (i.e. the fraction of crystalline cellulose in the fibrils) varies depending on the source of the raw material, and the degree of crystallinity is typically high in cellulose of algal origin. Crystalline cellulose has a lower water uptake com-
pared to amorphous cellulose, since water only has access to the surface of the crystallites. This fact will have implications later on in the thesis when different types of cellulose were used in the synthesis of PPy composites.

Figure 10. A bottom-up perspective of the cellulose fiber. The cellulose repeating units build up elementary fibrils that form microfibrils, which in turn form the cellulose fiber.

Refinement procedures, which vary for the different cellulose sources, are needed in order to separate the cellulose from the other constituents of the organisms. Furthermore, additional processing is required to separate the microfibrils from the larger cellulosic fibers. Depending on the cellulose source, different mechanical and chemical refinement procedures may be more or less viable. Since this is an extensive topic in an active research field, this section merely aims to mention some of the methods used in the refinement of cellulose. For an extensive review on the topic, see Moon et al.

Mechanical processes include high-pressure homogenizers, grinders and ultrasonic treatment. These methods have been used predominantly for cellulose of wood origin in the production of microfibrillated cellulose, often called MFC. Because this process requires a lot of energy, it is common to pretreat the fibers either enzymatically or by introducing surface charges, thereby reducing the energy consumption in the subsequent homogenization treatment. Another process is acid hydrolysis, in which the cellulose is treated with acid for a set amount of time. This process, although not fully understood, removes the amorphous regions of the cellulose. Acid hydrolysis is therefore especially interesting when used on cellulose with a high degree of crystallinity. The Cladophora cellulose used in the papers included in this thesis was extracted through acid hydrolysis.
Polypyrrole/cellulose composites

The making of composites with conducting polymers is a commonly used method to improve the properties of the conducting polymer. It has been shown that composites can be used to improve characteristics like the cyclability, conductivity, capacity, thermal stability, flexibility, and rate capability of conducting polymers. Indeed, electrode materials used in LIBs are mixed with additives to improve their properties. Therefore, it should not come as a surprise that the properties of conducting polymers can be dramatically improved in a similar manner.

This chapter mainly focuses on a PPy/cellulose composite made with algal cellulose extracted from the Cladophora sp. algae. Specific properties of this composite will be discussed in detail, and some obtained results can be extended more generally to PPy or conducting polymers.

Synthesis

The synthesis procedure used for the composites described herein involves the chemical oxidation of pyrrole to PPy using an iron salt. All papers included in this thesis are based on composites with PPy/Cladophora cellulose. The synthesis procedure will be described briefly, as a detailed description can be found in the experimental section in the papers included in this thesis, and an illustration of the procedure can be seen in Fig. 11. One study included in this thesis uses composites made with a different procedure, using filter paper as the cellulose substrate. Details on this can be found in the experimental section of Paper II.

![Synthesis Procedure](image)

*Figure 11. The synthesis procedure for the PPy/cellulose composite described in this section.*
By sonicating the cellulose in a water solution, using a probe sonicator, a homogenous dispersion of cellulose with an almost gel-like structure could be obtained. The dispersion was then mixed with a pyrrole monomer solution before the polymerization was started by adding a solution of iron salt, either Fe(NO$_3$)$_3$ or FeCl$_3$. The polymerization proceeds rapidly at room temperature, and the mixture turns black almost immediately after addition of the iron solution. After polymerization, the mixture was transferred to a funnel and washed thoroughly to get rid of residual iron. Washing with an acidic solution has been proven to improve the amount of iron removed,$^5$ and this procedure was adopted in the later papers (Paper III, IV and V). After thorough washing, a short additional sonication was performed in order to achieve a more homogenous composite material. Finally the mixture was dried onto a filter paper in the funnel. The composite material is stable in air, and was therefore dried further under ambient conditions. Figure 12 shows the composite material being cut into rectangular pieces in preparation for assembly in a cell.

![Figure 12. Photograph of the PPy/cellulose composite as it is being prepared for assembly in a cell.](image)

**Characterization**

**Scanning electron microscopy**

Electron microscopy techniques are extremely useful for studying the morphology of nanostructured materials, such as the PPy/Cladophora cellulose composite in this thesis. In scanning electron microscopy (SEM), the sample is put in a vacuum chamber and an electron beam is scanned across a small part of the sample surface. The contrast can be obtained in two primary ways – either by backscattered or secondary emitted electrons. In the first case, the electrons from the primary source are reflected back by interaction (elastic
scattering) with the sample. Heavy elements backscatter electrons more strongly and will therefore look brighter (higher intensity) than light elements.\textsuperscript{66}

In the second detection mode, electrons from the source interact with (inelastic scattering) and knock out electrons from the sample. These electrons, called secondary electrons, have a lower energy than the primary electrons. The brightness again depends on the amount of electrons that reach the detector. Depending on if the primary electrons enter perpendicular to the sample (a flat surface) or at an increased angle of incidence, where a higher amount of secondary electrons can escape from the sample and be picked up by the detector, a topographical contrast is obtained where sharp edges appear brighter in the micrograph.

Figure 13. Surface SEM micrograph of the PPy/Cladophora cellulose composite (left) and a micrograph of the cross-section of an identical sample (right).

Apart from being one of the most important tools for analyzing how different synthesis conditions affect the morphology of the composites, the most important conclusions that could be drawn from SEM was that the polymerization takes place on the fibers, covering them rather smoothly as well as resulting in some regions where PPy forms ball-like clusters on the surface of the fibers. Additionally, SEM micrographs of the cross-section of the material revealed that the composite can be considered a homogenous material with PPy throughout the entire bulk of the material. The latter result is not surprising, considering that the synthesis takes place on dispersed cellulose, but it is an important confirmation that the protocol used for synthesis is viable. A micrograph of the surface, as well as of the cross-section, can be seen in Fig. 13.

Elemental analysis

Composite materials prepared in different ways were subjected to CHN elemental analysis performed by a commercial laboratory. Since the only contribution of nitrogen comes from the PPy, it was possible to calculate the weight percentage of PPy in the different composites. When the capacity (obtained from CV) of each composite material was plotted as a function of
PPy concentration, proportionality was found. The results can be seen in Fig. 14, and it is important to note that the capacity was normalized with respect to the sample weight in order to obtain size independent results.

The results clearly show that the same fraction of the PPy is active regardless of synthesis procedure, which is a strong indicator that there are no inactive regions in the materials. This is supported by the SEM results described earlier, where the material was shown to be homogenous throughout the bulk of the composite.

![Graph](image)

**Figure 14.** The specific charge capacity for different composites as a function of the weight fraction of PPy in the sample. The specific charge capacity is based on the total weight of the composite and the capacity is evaluated from CV at 5 mV/s. The dotted line is a fit to the data points, and the corresponding equation is displayed in the graph.

**Electrochemical response**

When using an electrical energy storage device, *e.g.* a battery, it is generally favorable that the discharge occurs at a relatively constant potential. This is the case for most batteries, with well-defined redox reactions that occur at fixed potentials. Capacitors do not share this property with batteries – their potential drops linearly with charge consumption, meaning that it may be difficult to utilize all the available charge in a capacitor since the last charge will be available only at a low cell potential.

Traditional capacitors consist of two metal plates separated by an insulating but polarizable material (often called a dielectric material). The energy is stored by separation of the charges to the respective plate. Capacitors of
this type are widely used in electronic circuits for various purposes, e.g. blocking of direct current (DC).

Supercapacitors are another class of capacitors that are electrolyte-based and bridge the gap between dielectric capacitors and batteries. The charge can be stored by separation of charge in the double-layer (double-layer capacitance) and/or through redox reactions and electron transfer (pseudo-capacitance).

The response obtained for PPy is pseudocapacitive. Charge is stored through electron transfer and redox reactions in PPy (doping/dedoping). The charging/discharging of PPy, however, should not be seen as a single well-defined redox potential, but should rather be seen as a distribution of redox states. This leads to a capacitive response, i.e. rather linear potential dependence with time when subjecting the polymer to a constant current, as opposed to a discharge potential plateau observed for batteries. The normalized capacitance, from a constant current measurement, is given by

$$C = \frac{i}{\frac{\Delta E}{\Delta t} m}$$

where m is the mass. It should be noted that capacitance values given in the literature can vary significantly, depending on how the equation above is used. In the case of composite electrodes, the mass m, often refers to the total sample weight for a composite but is sometimes taken as the mass of the active material only. In composites with a large amount of inactive substrate, the latter gives very favorable values. Secondly, capacitance values from two-electrode devices found in the literature are sometimes given as specific capacitance, where the measured capacitance has been multiplied with a factor four. Assuming that both electrodes in the device are of equal mass, a factor two comes from the normalization with the weight from only one of the electrodes. Another factor two is introduced because a two-electrode device can be seen as two capacitances connected in series. Assuming that the capacitance for both electrodes is equal (as in a symmetrical device), the capacitance is given by

$$C_m = \frac{1}{\frac{1}{C_s} + \frac{1}{C_s}} = \frac{1}{2} C_s$$

where $C_m$ is the measured capacitance of a two-electrode device and $C_s$ is the specific capacitance. An alternative way of thinking is that every electron will cause a potential increase and decrease, respectively, on each electrode. Since capacitance is charge per potential, this means that a measured cell capacitance will be half of the capacitance measured for one electrode.
The absence of a standard way for reporting capacitances in composite devices makes it important to pay attention when comparing values in the literature. Even though specific capacitances reflect the property of the material, it is the measured device capacitance that can be used in actual cells.

For battery materials with a fixed potential, it is common to report potential against specific capacity. Such a plot, taken from Song et al., is shown in Fig. 15, with the specific capacity of PPy added. The capacity for PPy was taken from Fig. 14. It should be noted that PPy compares reasonably well to supercapacitors, but it is clear from the figure that there are materials available with much higher specific capacities. Ideally, PPy could be coupled to a high capacity organic compound to obtain an electrically conducting material with a high specific capacity.

Figure 15. Potential against specific capacity for various inorganic and organic electrode materials. PPy has been added to the figure, to indicate the approximate position of the material under study in this thesis. Reprinted with permission from the publisher.

Devices

The composite material was used as both electrodes in a symmetrical capacitor device. This allows for two-electrode characterization of the material, and is the first step towards building prototypes that can be tested in real applications.
Cell design is important and influences the behavior of the device. The initial cells were constructed by stacking the active material between two microscopy glass slides (Paper I). The current collectors were made of platinum foil, and a filter paper was used as separator. The glass slides were then wrapped in Parafilm in order to keep the cell assembled, and the device was immersed in a beaker with electrolyte (see left hand side of Fig. 16). There are two fundamental problems with this cell design. First of all, because of its open design, the amount of electrolyte available greatly exceeds the amount that can be used in a real device. Secondly, platinum foil as current collector is a poor choice because of its cost and catalytic properties.

An improved device (see right hand side of Fig. 16) was made using graphite foil current collectors and commercial separator paper in a similar stacking manner. The cell was sealed in an aluminum pouch that was filled with electrolyte. This design offers a more realistic alternative since there is only a finite amount of electrolyte present, and the sealed environment prevents gases from entering or leaving the device. While this device design offers many improvements compared to the cell based on glass slides, it is still far from being a viable option for a final cell. Commercial supercapacitors usually consist of very long electrodes that are rolled up to achieve a more practical size. Typically, commercial capacitors have DC resistances in the mΩ range. Furthermore, the active electrode layer in commercial capacitors is very thin (µm) compared to the active PPy/cellulose composite (mm). The paper making of the PPy/cellulose composite is however not optimized, and it is therefore likely that the sheets could be compacted significantly without losing a detrimental amount of the porosity in the material. A slight decrease in porosity would likely be advantageous since it would decrease the amount of electrolyte needed to soak the material, thus decreasing the amount of inactive weight.
Figure 16. Two-electrode devices using PPy/cellulose composites as electrode material. The left panel shows an early cell design using platinum current collectors and glass slides. A newer type of cell is shown in the right panel, using graphite current collectors and an aluminum pouch for encapsulation.

The improved device design was investigated with both DC and alternating current (AC) techniques to further understand the limitations and possible improvements that can be made. When a constant current is drawn through a circuit, a drop in voltage (called iR-drop) will occur, as described by Ohm’s law

$$U = iR$$

where $U$ is the potential drop, $i$ is the current and $R$ is the resistance. If a device is cycled with a constant current, the potential drop seen when switching from charging to discharging can therefore be used to calculate the resistance of the device. When the separator thickness was varied in the PPy/cellulose devices, a linear increase of $1.5 \, \Omega/mm$ was observed and the intercept at $0 \, mm$ separator was $1.6 \, \Omega$ (see Fig. 17). Since graphite was used in the devices, the limited conductivity of the current collectors gives a significant contribution to the cell resistance. It is not trivial to calculate the exact contribution from the current collectors, since they contact the electrodes over a large surface. However, by using four-probe conductivity measurements, the contribution could be estimated to be in the range of $0.4 – 1.1 \, \Omega$. The remaining resistance (in the range $0.5 – 1.2 \, \Omega$) was attributed to the contact resistance between the PPy/cellulose electrode and the current collector.

A somewhat surprising observation was that the overall cell resistance was approximately the same as when platinum current collectors were used to construct cells. Since platinum has a much higher conductivity than graphite, a lower cell resistance was expected. Earlier results showed that cells using platinum current collectors exhibited higher resistances when
smaller electrodes (~40 mg) were used. Cells with larger electrodes (~400 mg) had much lower resistances, and the difference was attributed to large contact resistances between PPy/cellulose composites and platinum current collectors. AC impedance data from Paper V confirm this conclusion.

![Graph of cell resistance vs separator thickness](image)

*Figure 17.* The resistance dependence on separator thickness for the pouch cells described in this section. Pressure was added to the cells plotted in this figure, which reduced the intercept but left the slope unaffected. The dashed line represents a linear fit to the data, and the equation for the fit displayed in the figure.

It was observed that the radius of the semi-circle in a Nyquist plot (commonly associated with the charge-transfer resistance) is approximately twice as large for platinum current collectors. Furthermore, the semi-circle radius is suppressed when pressure was added to the cells, which also indicates that the charge transfer resistance is linked to the contact between the current collector and the electrode.

Another interesting feature detected from the AC impedance is that the onset of finite length diffusion takes place at the same frequency regardless of the parameters varied in Paper V. In other words, a variation of the electrode thickness or separator thickness had no effect on the frequency at which the vertical line appears in the Nyquist plot. Finite length diffusion is seen at very low frequencies, for very thin samples or for large diffusion coefficients. Since the onset of the behavior is observed at the same frequency for different electrode thicknesses, this indicates that the electrode thickness in this case is represented not by the macroscopic thickness, but by the fiber thickness in the composite (see characterization section). While the electrodes were made macroscopically thicker, the porous nature of the composite material remains constant and ions from the pores filled with electrolyte will have the same distance to travel before being blocked.
Cyclability

Another important property of capacitors is their high cyclability and lifetime. Normally, capacitors can be used for hundreds of thousands of cycles because no faradaic reactions take place.\textsuperscript{73} PPy is known for its relatively good cyclability, but the nature of PPy charging/discharging makes it unlikely to reach cyclability comparable to commercial electrolyte-based capacitors. The potential applications where a device based on PPy may be used are therefore limited. The cyclability of the PPy/cellulose composite device was tested with chronopotentiometric charging/discharging with promising results. The left panel in Fig. 18 shows the measured capacitance, evaluated from the discharge slope, against cycle number. After 4,000 cycles, the device retained 99.3\% of its initial capacitance (\textbf{Paper I}). When three-electrode experiments were conducted, a dramatic improvement in stability was observed when an acidic electrolyte was used, compared to an electrolyte with neutral pH, as seen in the right panel of Fig. 18. It should be noted that the results from Fig. 18 (\textbf{Paper I}) were obtained with composite samples synthesized in the absence of acid. This is contrary to the latter papers (\textbf{Paper III – V}) where acidic conditions were used during the synthesis and the washing step. The fact that composites from the latter papers are acidic will have implications later, when results regarding the self-discharge of the composite are discussed.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure18.png}
\caption{Stability during cycling, seen as the capacitance \textit{vs.} the cycle number. A two-electrode symmetrical device was stable for 4,000 cycles (left). The same experiment performed in a three-electrode setup (right) yielded significantly different results depending on the pH used in the electrolyte. The electrolyte was 2.0 M NaCl (triangles) and 2.0 M NaCl + 0.01 M HCl (squares).}
\end{figure}

When the devices were cycled to high potentials (1.8 V cell potential), degradation due to overoxidation of the positive electrode was expected. A degradation of one of the electrodes in the cell would lead to a reduced capacitance, but this was not observed even after 600 cycles. By introducing a RE into the device, the potential of the individual electrodes could be monitored. This showed that while reducing the negative electrode as part of charging the device, the loss of conductivity in the material leads to a drop in poten-
tial. Since this drop adds to the total cell potential, the negative electrode protects the positive electrode from attaining potentials where overoxidation takes place. A resistive potential drop of the same magnitude would not be seen if an electrically conducting substrate was used.

Prototype device

As part of the development of the PPy/cellulose composite material, prototype cells were assembled and used to power real devices as proof-of-concept of the working principle of the energy storage device. An early prototype was made in collaboration with ETC – Battery and FuelCells Sweden AB, where several symmetrical two-electrode devices were connected in series to increase the output potential. The rechargeable cell pack was used to power a remote control. The energy storage device and the remote control are shown in Fig. 19.

![Prototype device](image)

*Figure 19. Prototype device consisting of several sandwich type cells connected in series to increase the output potential. The battery pack was able to power a remote control for a limited time as a first proof-of-concept.*

Another prototype device, shown in Fig. 20, was manufactured by VTT in Finland and shown at the Nanotech Conference and Expo 2013 in Washington, D.C. The device consisted of four individual cells connected in series and was used to power a digital thermometer. The device could power the thermometer for five hours after being charged for less than a minute.
Self-discharge

Significant effort was made to study the underlying cause of self-discharge in the PPy composite devices. In this thesis, self-discharge denotes a change in potential toward the discharged state, which in two-electrode devices is seen as a drop in cell potential. This potential drop can be due to a potential change of both electrodes or due to a potential change of one individual electrode (also possible in three-electrode setups). Monitoring the potential of each electrode against a common reference, inserted in the cell, enables a better understanding of the processes responsible for the self-discharge.

A rapid self-discharge is severely limiting in most situations, unless the energy storage device can be charged immediately before usage. Although the rapid self-discharge seen in conducting polymers has been known for a long time, it is most often not discussed in papers with an application focus towards energy storage. Some papers on conducting polymers mention self-discharge, but do not discuss it in detail, while others try to explain the underlying cause. Examples of the latter include papers that attribute the self-discharge to electrolyte impurities, electrolyte decomposition, and faradaic reactions.

Two papers included in this thesis (Paper III and IV) are focused on the self-discharge seen in the PPy/cellulose composite devices discussed above. Through spectroscopic and electrochemical analysis we have proposed a mechanism responsible for the self-discharge, and this chapter will be devoted to explaining the findings in detail.
Initial measurements

The investigation of the self-discharge was started by varying different parameters to investigate how the discharge rate was affected. It was found that the self-discharge rate remained constant when changing the electrode size, and when changing the electrolyte, either by substituting the salt or lowering the pH. It should be noted that the composite material itself is slightly acidic after synthesis – hence the electrolyte in the cells had a slightly lowered pH. Measurements were also performed in an inert atmosphere in a glovebox, and some preliminary tests were done using organic electrolytes in a glovebox. Despite the efforts in varying all the mentioned parameters, the only thing observed to affect the self-discharge rate was pre-cycling of the device prior to self-discharge (from here on called pretreatment). Pretreated cells were found to discharge significantly slower, and by introducing an external RE in the two-electrode device, it was possible to identify the first reason for this behavior.

Figure 21 shows typical self-discharge curves in a two-electrode device with an inserted RE. At the start ($t = 0$), the cell is charged to 0.6 V which is seen as the potential difference between the two curves in the figure. It is evident that the potential drop with time on the positive electrode is more rapid in the beginning (high potentials). It was found that as cells were pretreated, each cycle would shift the positive electrode to lower potentials vs. Ag/AgCl, with a subsequent shift of the negative electrode in the same direction. Thus, while pretreated cells were charged to the same cell potential, the electrode potentials against the RE would be different.

![Figure 21. Self-discharge of a two-electrode PPy/cellulose composite device. The potential drop on the individual electrodes was monitored against a Ag/AgCl reference inserted into the cell.](image-url)
Apart from helping with the explanation of the lower self-discharge rate seen in pretreated devices, Fig. 21 shows that the positive and negative electrodes seem to be discharging with different rates and magnitudes. This result justifies treating the electrodes separately for elucidation of the mechanisms.

**Negative electrode**

The self-discharge of the negative electrode was suspected to be connected to the presence of residual oxygen in the electrolyte, as previously proposed. By measuring the self-discharge at the relevant potentials, in a three-electrode setup, it was confirmed that thorough degassing of the electrolyte and subsequent measurements under a nitrogen blanket reduced the self-discharge dramatically to almost negligible rates. The results of these measurements are shown in Fig. 22.

*Figure 22. The effect of thorough degassing of the electrolyte on the self-discharge of the negative electrode. The measurement was done with a three-electrode setup, at potentials that match the negative electrode in a two-electrode device.*

These results also explain why pretreatment had an effect on the self-discharge rate. During the assembly of the devices, the electrolyte contains oxygen despite degassing prior to assembly. Residual oxygen is likely trapped in the pores of the composite electrodes and may be difficult to get rid of. Since pretreatment involves cycling of the cell between its charged and discharge state, oxygen will be consumed, which leads to a lowered self-discharge rate for the negative electrode. This effect was also verified in a two-electrode cell, where a significant reduction of the self-discharge rate on the negative electrode was seen after pretreatment.
Positive electrode

As seen from Fig. 21, the majority of the self-discharge in a two-electrode device occurs on the positive electrode. It was found that the potential drop was well described by Eq. 9, representing a faradaic potential dependence, which is derived from the Tafel equation (a full derivation is available in the supporting information of Paper III). This agreement was the first indication that a faradaic reaction is responsible for the self-discharge of the positive electrode

\[ \Delta E = -\frac{RT}{\alpha F} \ln \left( \frac{\alpha Fi_0}{RTC} \right) - \frac{RT}{\alpha F} \ln \left( t + \frac{KC}{i_0} \right) \]  

(9)

where \( i_0 \) is the exchange current, and \( K \) is given by

\[ K = \frac{RT}{\alpha F} e^{-\frac{\alpha F}{RT} \Delta E_i} \] 

(10)

where \( \Delta E_i \) is the initial potential at \( t = 0 \). A three-electrode setup was devised so that the charge leakage, pH and UV-Vis spectrum were recorded during potential steps to potentials where self-discharge of the positive electrode normally occurs. It was found that the degradation product maleimide\(^{81, 82} \) was released together with protons.

Taken together, the faradaic reaction and the detection of maleimide indicate that the self-discharge of the positive electrode occurs through a degradation of the polymer. This result may seem contradictory to the reversibility seen for self-discharge in PPy, \( i.e. \) a self-discharged cell can be recharged without any apparent loss in capacity. Calculations show, however, that loss of potential corresponding to a full self-discharge can be explained by a degradation of only \( \sim 0.04\% \) of the PPy units. Such a small degradation would not be observable, even after multiple self-discharge cycles of the same device. The similarity in the time evolution of charge, protons and maleimide indicates that the degradation products are formed from a common intermediate through a common rate limiting step. The intermediate can then react further to release charge, protons and degradation products including maleimide.

In order to find out more about the rate limiting step, self-discharge measurements were carried out at different temperatures using a thermostat bath and a three-electrode setup. The PPy composite electrode was charged to the potential obtained for the positive electrode in a two-electrode device, and the potential was monitored as the electrode self-discharged. The derivative of the potential-time data (dE/dt) was used to calculate rate constants according to the equations below
\[
\frac{dQ}{dt} = \frac{dE}{dt} C
\]

(11)

\[
\frac{dQ}{dt} = -k_{app} Q
\]

(12)

where \( C \) [F/g] is the capacitance and \( Q \) [C/g] is the charge from an oxidative CV scan up to the potential where \( \frac{dE}{dt} \) was evaluated.

In total, 10 potentials at 7 different temperatures (10 °C to 70 °C) were evaluated, all of which are seen in Fig. 23.

\[k = A e^{-\frac{E_a}{k_B T}}\]

(13)

where \( E_a \) is the activation energy and \( k_B \) is the Boltzmann constant. Only a small error is introduced if the activation energies are used as the driving
force for the reaction (a more extensive discussion about this can be found in Paper IV). With the driving force known, it is possible to calculate the redox potential for the reaction. This calculation can be done independently at each evaluated potential, and the results are shown as the circles in Fig. 24. $E^0$ was found to be independent of applied potential, and the average value for the redox reaction was found to be $E^0 = 0.89 \text{ V vs. Ag/AgCl}$. 

Figure 24. The activation energy obtained for the different potentials (squares) determined from the temperature dependence of the self-discharge. The redox potential (circles) was determined by treating the activation energies as the driving force for the reaction.

The potential dependence of the rate constant exhibits an exponential form, and the values obtained at 20 °C were extrapolated to the value of $E^0$ to obtain the rate constant at zero driving force. This rate constant was found to be 0.43 s$^{-1}$.

With the evaluated redox potential in mind, a CV measurement on PPy suggests that the overoxidation is a likely candidate for the rate limiting step of the self-discharge. CV measurements were performed on PPy films obtained by electropolymerization of pyrrole onto carbon microelectrodes to obtain fast response times and enable the use of high scan rates. A selection of the obtained voltammograms is shown in Fig. 25, where the large second peak is the degradation often referred to as overoxidation.
Figure 25. CV measurements of PPy on carbon microelectrodes at different scan rates. This time, the potential was swept up to potentials where PPy degrades and the peak potential for the overoxidation was extracted.

It was found that the scan rate dependence of the peak potentials was described well by a kinetically limited redox reaction, see Eq. 3, with $k_0$ evaluated to 9 s$^{-1}$. The two extracted rate constants differ by approximately an order of magnitude, but considering the experimental uncertainty and the extrapolation done in order to obtain the first rate constant, there is a fair agreement between the two. This further supports the assumption that the self-discharge reaction in PPy is linked to the overoxidation.
Future work

The use of a PPy/cellulose composite material in energy storage applications has been presented in this thesis, along with successful proof-of-concept devices. However, there are several key points that need to be addressed if the devices are to be made commercially viable. As the project progresses, efforts are already being made to improve some of these points. It is clear that organic energy storage is an interesting field of research that will most likely continue to develop in the future.

**Capacity and energy.** Based on data presented in this thesis (our PPy synthesis), the amount of charge that can be stored per unit mass of PPy is 76 mAh/g. If the stability issues that could be problematic at such high doping levels are ignored, the charge capacity is not so low when compared to materials used in batteries today. For example, cathode materials used in today’s LIBs have capacities in the range 100 to 300 mAh/g.¹⁸³ There is, however, a major drawback with PPy that is not evident when only comparing capacities. PPy does not have a fixed redox potential, which means that the discharge of a PPy device will not take place at a potential plateau, but will rather give a capacitive response. This issue can be solved by utilizing the conductive backbone of the polymer, and attaching organic redox active groups covalently to the chain. This approach is currently being used in the continued work of the project.

**Asymmetrical systems.** The current cell design uses PPy as both positive and negative electrode. This is not optimal, since PPy cannot be n-doped. Neutral PPy is insulating which means that it is a bad choice as backbone for redox pending groups on the negative side. Other conducting polymers, with a conducting reduced form, could be used in an asymmetrical device.

**Electrolyte.** The current cells use water as electrolyte, which severely limits the maximum potential of the device. This works for symmetrical devices based on PPy, since the stability of the polymer becomes an issue before the potential window of water is reached. However, if asymmetrical cells are to be tested, other electrolytes should be used that allow for higher cell potentials and thus higher energy densities of the devices. It is worth mentioning that moving to alternative electrolytes (e.g. organic electrolytes) would affect the environmentally friendly aspect of the battery in a negative way. It
would, however, still be possible to obtain an all-organic energy storage device.

**Stability.** The results presented in this thesis highlight some aspects that help improve the stability of PPy. There are, however, still severe stability concerns at high potentials (high doping) and issues with self-discharge (caused by a small degradation) even at moderate potentials. Conducting polymers have been around for a long time, but there are still no known ways of solving these issues. Future work should focus on the challenging task of repressing the degradation, or finding ways (*e.g.* the addition of pending groups) of using the polymer for energy storage at low enough potentials to ensure stability.

**Cell design.** The current cell design is sufficient for the proof-of-concept devices shown in this thesis. The resistance values obtained in the cells are, however, much too high for commercial purposes and lead to a large iR-drop even at moderate currents. Improving the cell design will also require further investigation of the active composite material, to find the optimal thickness and porosity.
Sammanfattning på svenska

I takt med ett ökande globalt energibehov behövs nya sätt att lagra elektrisk energi. Ett skäl till detta är att den förnyelsebara energin (t.ex. sol- och vindkraft) inte produceras i jämmtakt, utan endast när solen skinner och vinden blåser. Detta gör det extra viktigt att kunna lagra den producerade energin för användning när den behövs.

Förutom utmaningen i att designa system som är kapabla att lagra stora mängder energi, blir materialvalet i energilagringsshopen eller material som hämtas från gruvor, med stora koldioxidutsläpp och miljöpåverkan som följd. Ett alternativ som på senare tid fått stor uppmärksamhet är möjligheten att använda organiska material för energilagring. En organisk förening är en kemisk förening där grundämnet kol ingår. En fördel med sådana material är att det går att skaldyrsy och framställa funktionella föreningar vid låga temperaturer. Dessutom är de lätt att återvinna då de i princip kan eldas upp med bildande av koldioxid som följd.


Det är tidigare känt att polypyrrol är drabbat av en snabb självurladdning när det används som aktivt material för energilagring. Detta betyder att celler som laddas upp kommer att tappa laddningen även om cellen inte används. Genom att studera självurladdningen i materialet har vi kunnat visa att detta beteende kan kopplas ihop med samma process som ansvarar för degradering av materialet då det laddas till höga potentialer. Denna förståelse kan
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