Nanocellulose and Polypyrrole Composites for Electrical Energy Storage

GUSTAV NYSTRÖM
Dissertation presented at Uppsala University to be publicly examined in Häggsalen, Ångström laboratorium, Lägerhyddsvägen 1, Uppsala. Friday, March 30, 2012 at 09:30 for the degree of Doctor of Philosophy. The examination will be conducted in English.

Abstract

To meet the predicted increase in demand for energy storage in tomorrow’s society, the development of inexpensive, flexible, lightweight and sustainable energy-storage materials is essential. In this respect, devices based on electroactive organic molecules, such as conducting polymers, are highly interesting. The aim of this thesis was to evaluate the use of nanocellulose as a matrix material in composites of cellulose and the electroactive polymer polypyrrole (PPy), and the use of these composites in all-polymer paper-based energy-storage devices.

Pyrrole was polymerized using FeCl₃ onto cellulose nanofibers in the form of a hydrogel. The resulting PPy-coated fibers were washed with water and dried into a high surface area, conductive paper material. Variations in the drying technique provided a way of controlling the porosity and the surface area of wood-based cellulose nanofibers, as the properties of the cellulose were found to have a large influence on the composite structure. Different nanocellulose fibers, of algal and wood origin, were evaluated as the reinforcing phase in the conductive composites. These materials had conductivities of 1–6 S/cm and specific surface areas of up to 246 m²/g at PPy weight fractions around 67%.

Symmetrical supercapacitor devices with algae-based nanocellulose-PPy electrodes and an aqueous electrolyte showed specific charge capacities of around 15 mAh/g and specific capacitances of around 35 F/g, normalized with respect to the dry electrode weight. Potentiostatic charging of the devices was suggested as a way to make use of the rapid oxidation and reduction processes in these materials, thus minimizing the charging time and the effect of the IR drop in the device, and ensuring charging to the right potential. Repeated charging and discharging of the devices revealed a 10–20% loss in capacity over 10 000 cycles. Upon up-scaling of the devices, it was found that an improved cell design giving a lower cell resistance was needed in order to maintain high charge and discharge rates.

The main advantages of the presented concept of nanocellulose-PPy-based electrical energy storage include the eco-friendly raw materials, an up-scalable and potentially cost-effective production process, safe operation, and the controllable porosity and moldability offered by the nanocellulose fiber matrix. Integrating energy storage devices into paper could lead to unprecedented opportunities for new types of consumer electronics. Future research efforts should be directed at increasing the energy density and improving the stability of this type of device as well as advancing the fundamental understanding of the current limitations of these properties.

Keywords: conducting polymer, polypyrrole, cellulose, nanocellulose, porosity, composite, energy storage, battery, supercapacitor

Gustav Nyström, Uppsala University, Department of Engineering Sciences, Nanotechnology and Functional Materials, Box 534, SE-751 21 Uppsala, Sweden.

© Gustav Nyström 2012

ISSN 1651-6214
urn:nbn:se:uu:diva-168664 (http://urn.kb.se/resolve?urn=nbn:se:uu:diva-168664)
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 respective publishers.
Summary of my contribution to the papers included in this Ph.D. thesis:

**Paper I:** I participated in the planning and performed most of the experimental work, wrote the initial manuscript and contributed to the continued manuscript writing process.

**Paper II:** The planning and performance of the experimental work was shared equally with H. Olsson, who wrote the initial manuscript. I contributed to the analysis of data and to the continued manuscript writing process.

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

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

**Paper V:** The planning and performance of the experimental work and the writing of the initial manuscript were shared equally with D. O. Carlsson. I contributed to the analysis of data and to the continued manuscript writing process.
Also published

**Journal articles**


**Conference contributions**


## Contents

1. Introduction .................................................................................................................. 11  
   1.1 Nanocellulose ........................................................................................................... 11  
   1.2 Polypyrrole ............................................................................................................. 13  
   1.3 Cellulose and polypyrrole composites .................................................................... 15  
   1.4 Electrical energy storage ....................................................................................... 16  

2. Aims of the thesis ......................................................................................................... 19  

3. Materials and Methods ............................................................................................... 20  
   3.1 Synthesis .................................................................................................................. 20  
      3.1.1 PPy-Cladophora cellulose composites (I–III) ...................................................... 20  
      3.1.2 NFC paper (IV) ................................................................................................. 21  
      3.1.3 PPy-wood cellulose composites (IV–V) ............................................................. 21  
      3.1.4 Drying of TEMPO-NFC PPy composites (V) .................................................... 22  
   3.2 Supercapacitor cell assembly (I–III) ....................................................................... 22  
   3.3 Primary material characterization ........................................................................... 24  
      3.3.1 Scanning electron microscopy (I–II, IV–V) ....................................................... 24  
      3.3.2 Transmission electron microscopy (I) ............................................................... 24  
      3.3.3 Electronic conductivity (I, III–IV) .................................................................... 24  
      3.3.4 Specific surface area and pore volume (I, IV–V) ............................................... 25  
      3.3.5 Thermogravimetric analysis (I, IV–V) ............................................................... 25  
      3.3.6 Elemental analysis (I, V) .................................................................................. 26  
      3.3.7 Viscosity measurements (V) ............................................................................. 26  
      3.3.8 Density and porosity measurements (V) ......................................................... 26  
      3.3.9 Tensile strength (V) .......................................................................................... 26  
   3.4 Electrochemical characterization ............................................................................ 26  
      3.4.1 Cyclic voltammetry (I, III–V) ........................................................................... 27  
      3.4.2 Chronopotentiometry (I–III) .......................................................................... 27  
      3.4.3 Chronoamperometry (III, V) .......................................................................... 28  
      3.4.4 Electrochemical impedance spectroscopy (III) ............................................... 28  

4. Results and Discussion ............................................................................................... 30  
   4.1 Energy storage devices with cellulose-based electrodes ....................................... 30  
      4.1.1 Paper I .............................................................................................................. 30  
      4.1.2 Paper II ............................................................................................................ 32  
      4.1.3 Paper III .......................................................................................................... 35  
      4.1.4 Discussion of Papers I–III .............................................................................. 40
4.2 Electroactive composites from wood cellulose ........................................44
4.2.1 Paper IV .....................................................................................44
4.2.2 Paper V .....................................................................................46
4.2.3 Discussion of Papers IV–V .....................................................51

5. Future work ...................................................................................55
6. Summary .....................................................................................57
7. Sammanfattning på svenska ..........................................................60
8. Acknowledgements .......................................................................62
9. References ...................................................................................64
# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of polymerization</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>MFC</td>
<td>Microfibrillated cellulose</td>
</tr>
<tr>
<td>NFC</td>
<td>Nanofibrillated cellulose</td>
</tr>
<tr>
<td>NHE</td>
<td>Normal hydrogen electrode</td>
</tr>
<tr>
<td>PPy</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>RC</td>
<td>Resistor-capacitor</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TEMPO</td>
<td>2,2,6,6-tetramethylpiperidine-1-oxyl</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
</tbody>
</table>
1. Introduction

1.1 Nanocellulose

Cellulose is the most abundant polymer on earth and is, as a part of the biomass, renewed continuously through photosynthesis in quantities in the same order as the world reserves of minerals and fossil fuels.¹ Being readily available, cellulose-based natural materials such as wood, cotton and paper have played an important role in our societies over thousands of years.²

Materials in nature often develop their functionality, flexibility and mechanical strength by utilizing a hierarchical structure of building blocks,² as exemplified for wood in Fig. 1. At the most basic level of this hierarchy, cellulose in the cell wall provides reinforcement for trees, plants, algae and some sea creatures (e.g. tunicates).²

Algae are thallophytes (plants lacking roots, stems and leaves) which have chlorophyll A as their primary photosynthetic pigment, lack sterile vegetative cells around their reproductive cells, and live in, or close to, water.³ This definition is not strict in that it also includes plant forms such as the cyanobacteria, which are more closely related to bacteria than to the rest of the algae. The fibrillar reinforcing component of algal cell walls is usually composed of cellulose; however, other polysaccharides such as mannan and xylan also occur.³ Cladophora sp. are green algae, found in freshwater and marine habitats, from which a highly crystalline cellulose can be produced.⁴, ⁵ Cellulose from Cladophora was used in Papers I–III in this thesis.

To extract the cellulose fibers from, for example, the most important raw material source of cellulose, wood, they must be separated from the other main components of the cell wall: hemicellulose and lignin.⁶ This is achieved in a pulping process where wood is chemically and/or mechanically disintegrated, depending on the desired end product, into discrete fibers.⁷

The resultant pulp fibers can then be further disintegrated into microfibrils (see Fig. 1), or microfibrillated cellulose (MFC), using high shear field homogenization, as shown in the 1980s by Turbak and co-workers.⁸ To facilitate the disintegration of wood pulp into cellulose microfibrils and to minimize the energy consumed in the process, the pulp can be pretreated with enzymes⁹, ¹⁰ or TEMPO-radical-mediated oxidation.¹¹
As MFC contains fibrils with nanoscale dimensions (fibril diameter: \(\approx 2\text{–}40\) nm, fibril length: \(>1\ \mu\text{m}\)), the terms nanofibrillated cellulose (NFC) or nanocellulose are also used. Nanocellulose from wood was used in Papers IV–V in this thesis.

On the molecular level, cellulose is a polymer with two linked D-glucose molecules as the repeating unit, see Fig. 2. The link is established through an oxygen covalently bound to C1 of the first D-glucose and C4 of the second D-glucose, a so-called \(\beta(1\rightarrow4)\) glucosidic bond. The number of repeating units, \(n\), or degree of polymerization, DP, depends on the cellulose source. It is typically 300–1700 for wood-based cellulose and in the range of 800 to 10 000 for cotton and other plant fibers.
Each D-glucose unit has three free hydroxyl groups which can undergo chemical reactions but can also form intra- and intermolecular hydrogen bonds. The ability of cellulose to form hydrogen bonds leads to a parallel arrangement of cellulose chains. The shortening of cellulose fibers observed during acid hydrolysis has inspired a model in which ordered, crystalline regions are linked together by disordered, amorphous, regions of cellulose chains, see Fig. 2. The smallest cellulose building element, the elementary fibril, is made up of 36 cellulose chains; these in turn form the microfibril, see Fig. 1. The term nanofiber will be used in the present thesis as a general descriptor of cellulose fibrils with diameters in the nanometer range.

The crystalline segments in cellulose have a greater axial elastic modulus than the synthetic fiber Kevlar, and their mechanical properties are within the same range as those of other reinforcement materials such as carbon fibers, steel wires and carbon nanotubes. It is therefore desirable to remove most of the defects by extracting cellulose at a nanoscale level and to use this as the building block for the next generations of cellulose-based composites.

Nanocellulose also displays nanoporosity in the solid state, and forms transparent dispersions and composite materials as well as porous fiber frameworks for functionalization. Potential applications based on these properties include drug carriers, additives for polymer reinforcement, transparent films, flexible displays, and supercapacitor electrodes.

1.2 Polypyrrole

Polymers are generally considered to be electronic insulators. However, the first work describing the synthesis of a conducting polymer was reported as early as the mid 19th century by Henry Letheby. Although many other reports followed Letheby’s discovery, it is the work by Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa in the late 1970s on doped polyacetylene that is considered by many to be the starting point for the research field of conducting polymers. This contribution resulted in their being awarded the Nobel Prize in Chemistry in 2000, which boosted activity in the field at the turn of the millennium.

Since then, polypyrrole (PPy), along with polyaniline and polythiophene, has become one of the most studied electronically conducting polymers. It can be synthesized either chemically, for instance using FeCl₃, or electrochemically. The commonly accepted polymerization route is shown in Fig. 3.
Figure 3. Polymerization mechanism of pyrrole.33, 36

In the first step of the polymerization, the pyrrole monomer is oxidized to a radical cation. Two of these subsequently dimerize at the α-position and release two protons. The dimer is then immediately oxidized, as the greater conjugation makes it more easily oxidized than the monomer,33 and it undergoes coupling with a new radical monomer or oligomer, again with the release of protons.

In electropolymerization, pyrrole monomers and an electrolyte salt are dissolved in a suitable solvent. As the working electrode is brought to high enough anodic potentials, a conducting PPy film is formed on the electrode. In contrast, in chemical polymerization, an oxidizing agent such as H2O2, K2S2O8 or FeCl337 is responsible for the oxidation of the monomers and the polymer that has already formed to their radical cation forms.

Because of the relative ease of oxidizing the polymer as it forms, compared to the free monomers, both synthesis methods will oxidize the polymer as it grows, with the inclusion of counterions, anions, to balance the excess positive polymer charge.33 These counterions come from either the polymerization solution or the oxidizing agent.

The charging and doping process for the resulting polymer can be seen as the oxidation of a number of monomer subunits, charge-balanced by an anion, see Fig. 4. Typical doping levels are 0.25–0.3 electrons per monomer.38, 39
Figure 4. Schematic illustration of p-doping of PPy from neutral PPy. The incorporation of anions (A⁻) is required to maintain charge neutrality.

PPy, in its neutral form, has a conjugated bond structure, alternating single and double bonds, with one electron for each of the carbon atoms building up the π-electron system. The orbitals of the π-electrons overlap, leading to delocalization of the electrons along the polymer chain, which forms the basis for the electronic conductivity of the polymer. However, due to the large gap between the (completely empty) conduction and the (completely filled) valence bands, the polymer is an insulator in the reduced state. With oxidative doping, the conductivity of the polymer is enhanced. This is achieved by chemically or electrochemically (through an applied voltage) moving the electrochemical potential (the Fermi level) into a region with a high density of electronic states (the valence band). The polymer is then oxidized, and additional positive charge carriers are introduced that can move within the π-electronic structure of the polymer or between different polymer chains.

The main advantages of chemical over electrochemical polymerization are that the polymer can be deposited on a variety of conductive or non-conductive substrates and bulk quantities of polymer can be produced for practical applications. The major disadvantages of chemical polymerization are that there is a limited choice of suitable oxidants and few available counterions, impurities are introduced with the oxidant, and it is difficult to control the oxidizing strength of the reaction solution, leading to poor control of the degree of chemical degradation during synthesis.

The movement of counterions during the oxidation and reduction of the polymer will also cause swelling and contraction of the material. This forms the basis for one of the applications of PPy: actuators. Other applications include batteries, supercapacitors, and materials for drug delivery.

1.3 Cellulose and polypyrrole composites

Composite materials, or composites, are multiphase materials obtained through the combination of various component materials in order to attain
properties that the individual components do not have.\textsuperscript{47} PPy can be chemically produced in bulk quantities and with good yields using $\text{FeCl}_3$ as oxidant. However, the product formed is generally a powder.\textsuperscript{48} As PPy is also insoluble and infusible,\textsuperscript{36} it is difficult to handle and process post-synthesis.

One way to achieve a cohesive electrode material is to mix the PPy powder with a binder such as PVDF and a conductive carbon additive in a process similar to that often used to prepare battery electrodes.\textsuperscript{49}

Another alternative for producing free-standing electrode materials is to polymerize PPy on a substrate\textsuperscript{50} or in the presence of fibers.\textsuperscript{51}

Cellulose is a material that combines widespread availability and low-cost manufacturing with high material strength, flexibility and an easily functionalized surface. Further, the idea of utilizing existing paper-making technologies and roll-to-roll processing for large-scale production of cellulose conducting polymer composites is intriguing. These properties of cellulose and its scalability have been a motivation for studying cellulose-PPy composites.

In the 1980s it was shown that a conductive paper could be formed by coating filter paper with PPy. This was achieved by soaking the paper in a $\text{FeCl}_3$ solution, followed by direct contact with liquid or vaporized pyrrole.\textsuperscript{52} Since then, numerous cellulose-PPy composites have been presented,\textsuperscript{53} and techniques such as ink-jet printing of PPy onto cellulose substrates\textsuperscript{54} and layer-by-layer deposition from dilute polymer solutions\textsuperscript{55, 56} have been developed.

Nanocellulose in the form of cellulose nanocrystals,\textsuperscript{57} bacterial nanocellulose fibers,\textsuperscript{58} nanocellulose extracted from algae (Papers I–III), and enzyme-treated (Paper IV) and TEMPO-oxidized (Paper V) wood-based nanocellulose has also been used to prepare composites with PPy.

The advantage of using nanocellulose as a matrix material for composites with PPy is that it produces a nanoporous material with a high surface area and high capacity for mass loading of PPy. This, in turn, allows the preparation of free-standing composites of millimeter thickness containing ~67 wt % PPy with high oxidation and reduction rates. The application of these composites as electrodes in energy-storage devices is investigated in the present thesis.

1.4 Electrical energy storage

Energy storage in a broad sense means storing energy in a device or in a physical medium for use at a later time. This could be gravitational potential energy stored in hydroelectric dams, thermal energy in the form of stored solar heat or mechanical energy stored in flywheels. The focus of this thesis is the storage of electric energy in electrochemical cells. To begin with, a brief historic overview of electric energy storage will be given and batteries and supercapacitors will be introduced.
A battery can consist of one or more electrochemical cells, each cell having three major components: a negative electrode, an electrolyte and a positive electrode. Electric charge is stored in the cell as an electrochemical oxidation-reduction (redox) reaction. When charging the cell, the negative electrode gets reduced, accepting electrons, and the positive electrode gets oxidized, giving up electrons. Reversing the reaction releases the stored chemical energy as electric energy and electrons flow in the reverse direction in the external circuit. The electrolyte provides the medium for charge transfer of ions inside the cell between the anode and cathode to maintain charge neutrality at the electrodes. Discharging a battery cell ideally occurs at constant cell potential, defined by the chemistry of the negative and positive electrodes.

Some of the major technological developments in the history of batteries are summarized in Table 1.

Table 1. Major technologies in battery development history.

<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Cell chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volta</td>
<td>1800</td>
<td>Galvanic cell: Zn/NaCl\textsubscript{aq}/Cu</td>
</tr>
<tr>
<td>Planté</td>
<td>1859</td>
<td>Rechargeable lead acid: Pb/H\textsubscript{2}SO\textsubscript{4}/PbO\textsubscript{2}</td>
</tr>
<tr>
<td>Leclanché</td>
<td>1864</td>
<td>Zn/NH\textsubscript{4}Cl/MnO\textsubscript{2}</td>
</tr>
<tr>
<td>Jungner</td>
<td>1899</td>
<td>Rechargeable nickel cadmium: Ni/KOH/Cd</td>
</tr>
<tr>
<td>Battelle-Geneva</td>
<td>1967</td>
<td>Nickel metal hydride battery: MH/KOH/NiOOH</td>
</tr>
<tr>
<td>Research Center</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rao</td>
<td>1968</td>
<td>Lithium sulfur battery: Li/organic electrolyte/S,C</td>
</tr>
<tr>
<td>Matsushita</td>
<td>1972</td>
<td>Lithium primary battery: Li/organic electrolyte/(CF)\textsubscript{n}</td>
</tr>
<tr>
<td>Whittingham</td>
<td>1977</td>
<td>Rechargeable lithium battery: Li/organic electrolyte/TiS\textsubscript{2}</td>
</tr>
<tr>
<td>Varta/BASF</td>
<td>1987</td>
<td>Rechargeable Li/PPy battery</td>
</tr>
<tr>
<td>Sony</td>
<td>1991</td>
<td>Commercial lithium ion battery: C/organic electrolyte/LiCoO\textsubscript{2}</td>
</tr>
<tr>
<td>Abraham</td>
<td>1996</td>
<td>Lithium air battery: Li/polymer electrolyte/O\textsubscript{2},C</td>
</tr>
</tbody>
</table>

In a traditional capacitor, energy is stored in the electric field between two oppositely charged plates separated by an insulator with a high dielectric constant. Supercapacitors, also called electrochemical capacitors or ultracapacitors, contain an electrolyte and the electric energy is stored in the electric double layer at the electrode/electrolyte interfaces.

Another type of supercapacitor stores its charge in the bulk of a redox material electrode, for instance manganese or ruthenium oxides or conducting polymers such as PPy. Although redox reactions take place as in batteries, the individual electrode potential varies with the degree of oxidation or reduction.
duction. During charge and discharge, the cell voltage of both of these supercapacitor types changes, ideally linearly, with the degree of charge. These systems thus behave as capacitors and are called pseudo-capacitors.60

Some of the major technological developments in the history of supercapacitors are summarized in Table 2.

Table 2. Major technologies in supercapacitor development history.66, 68

<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Cell type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Becker, General Electric</td>
<td>1957</td>
<td>Double-layer charging in porous carbon electrodes</td>
</tr>
<tr>
<td>SOHIO</td>
<td>1966</td>
<td>Double-layer charging in porous carbon electrodes, nonaqueous electrolyte, 3 V operation</td>
</tr>
<tr>
<td>Trasatti and Buzzanca</td>
<td>1971</td>
<td>Capacitor-like electrochemical charging in ruthenium dioxide films</td>
</tr>
<tr>
<td>NEC (under license from SOHIO)</td>
<td>1978</td>
<td>Based on SOHIO technology, first commercial product called “supercapacitor”</td>
</tr>
<tr>
<td>PRI</td>
<td>1982</td>
<td>First commercial metal oxide-based supercapacitor</td>
</tr>
<tr>
<td>Conway and Gottesfeld</td>
<td>1991</td>
<td>First conducting polymer-based supercapacitor</td>
</tr>
</tbody>
</table>

Conducting polymers were initially introduced as, primarily positive, electrode materials in batteries.44 Since the mid-1990s, however, research has been more focused on supercapacitor applications.69,71 Conducting polymer-based supercapacitors are usually divided into three categories:45

Type I (symmetrical): the same, usually p-dopable, polymer is used for both electrodes.
Type II (asymmetrical): different polymers, p- or n-dopable over different potential ranges, are used in the two electrodes.
Type III (symmetrical): the same, p- and n-dopable, polymer is used for both electrodes.

Hybrid supercapacitor systems also exist where, for example, a positive conducting polymer electrode is combined with a negative activated carbon electrode.72 The devices used in the present thesis, which were based on PPy electrodes, were of Type I.

Supercapacitors have specific energy densities that fall between those of capacitors and batteries, can be quickly charged, and are used, for example, in automotive and power tool applications and as backup energy storage.66, 73, 74 Batteries are an integral part of everyday life; they are used everywhere from consumer electronics to hybrid and electric vehicles and microchips.75
2. Aims of the thesis

The overall aim of the thesis was to evaluate the use of nanocellulose as a matrix material in composites of cellulose and polypyrrole, and the use of these composites in all-polymer paper-based energy storage devices.

The specific aims of the work were:

- To evaluate the possibility of utilizing a high surface area cellulose substrate from Cladophora algae coated with PPy as the electrodes in paper-based energy storage devices (Paper I).
- To study the galvanostatic cycling stability of these Cladophora cellulose-PPy composites when used in a symmetrical supercapacitor device and in a three-electrode electrochemical cell (Paper II).
- To evaluate the possibility of carrying out rapid potential step charging of Cladophora cellulose-PPy devices and to study the influence of the size of the device on the required charging time as a function of the cell resistance and resistor-capacitor (RC) time constant (Paper III).
- To investigate the use of wood nanocellulose as a matrix material for PPy-cellulose composites and to study the properties of these composites (Paper IV).
- To study the effects of various drying methods on the structural and electrochemical properties of TEMPO-oxidized nanofibrillated cellulose and PPy composites (Paper V).
3. Materials and Methods

3.1 Synthesis

Cladophora green algae were collected from the Baltic Sea. The nanocellulose used in the PPy composites in Papers I–III was extracted using grinding and acid hydrolysis.\(^5\) Nanofibrillated cellulose from wood, pre-treated with enzymes,\(^76\) was used for the PPy composites and the cellulose nanopaper in Paper IV. Wood-based cellulose pre-treated using a TEMPO-radical-mediated oxidation process\(^11\) was used for the PPy composites in Paper V.

Pyrrole, FeCl\(_3\), NaCl, Tween-80 and HCl were used as received from VWR or Sigma-Aldrich. Deionized water was used throughout the synthesis.

The composite syntheses in Papers I–V were performed by chemical polymerization of pyrrole onto cellulose nanofibers dispersed in water. The PPy-coated fibers were then washed and dried to form conductive paper sheets. Specific details of the syntheses are given below.

3.1.1 PPy-Cladophora cellulose composites (I–III)

In Paper I, 300 mg of Cladophora cellulose was dispersed in 50 mL of water using high-energy ultrasonication (VibraCell 750W, Sonics, USA). 3 mL of pyrrole (0.043 mol) and 1 drop of Tween-80 were dissolved in 100 mL of water, mixed with the cellulose dispersion, and dispersed for 1 minute using ultrasonication. The cellulose-pyrrole dispersion was allowed to stand for 30 minutes and was then collected on a filter paper, using a Büchner funnel. 8 g of FeCl\(_3\) (0.030 mol) was dissolved in 100 mL of water and poured into the funnel to initiate the polymerization. The polymerization reaction was allowed to proceed for 10 minutes, after which the PPy-cellulose dispersion was washed first with 100 mL of 0.1 M HCl and thereafter thoroughly with water. After washing, the PPy-cellulose dispersion was dispersed using ultrasonication, reintroduced into the funnel and collected on a filter paper, the filter paper was peeled off and the PPy-cellulose cake was dried under ambient conditions.

The synthesis conditions in Paper II were identical to those in Paper I except that no HCl was used in washing the PPy-cellulose dispersion.

In Paper III, 300 mg of cellulose powder was dispersed in 60 mL of water using high-energy ultrasonication. 1.5 mL of pyrrole (0.022 mol) was dissolved in 50 mL aqueous 0.5 M HCl solution, mixed with the cellulose
dispersion, and stirred for 5 minutes. 12.9 g of FeCl$_3$ (0.048 mol) was dissolved in 100 mL aqueous 0.5 M HCl solution and added to the cellulose-pyrrole dispersion to initiate oxidative polymerization. The polymerization reaction was allowed to proceed for 30 minutes, after which the PPy-cellulose dispersion was washed with 5 L of 0.5 M HCl, using a Büchner funnel, to remove iron residues originating from the FeCl$_3$ salt used as the oxidant. Subsequently, 1 L of 0.1 M NaCl was filtered through the dispersion before a final sonication for 2 minutes. The dispersion was then transferred back to the funnel and dried on a filter paper. The resultant PPy-cellulose cake was removed and dried in air under pressure (from a vice).

3.1.2 NFC paper (IV)

In Paper IV, NFC paper was obtained by diluting 12 g of thick 2 wt% NFC hydrogel (240 mg dry cellulose content) in 100 mL distilled water, after which the cellulose-water dispersion was collected on a filter paper in a Büchner funnel. The cellulose film was peeled off the filter paper while wet, and allowed to dry under ambient conditions.

3.1.3 PPy-wood cellulose composites (IV–V)

In Paper IV, the PPy-NFC composite was prepared by diluting 12 g of 2 wt% MFC hydrogel (240 mg dry cellulose content) in 100 mL water. The cellulose dispersion was then mixed with a solution of 3 mL pyrrole (0.043 mol) in 100 mL water. 8 g of FeCl$_3$ (0.030 mol) was dissolved in 100 mL water and added to the cellulose-pyrrole dispersion to initiate polymerization. Subsequently, 160 µL of 37% HCl was added to the reaction beaker. The polymerization was allowed to proceed for 15 minutes, after which the resulting PPy-coated cellulose fibers were washed thoroughly with water in a Büchner funnel, the filter paper was removed, and the PPy-NFC cake was dried to constant mass on a Petri dish in air.

In Paper V, the PPy-NFC composites were prepared by mixing 100 mL of 0.1 wt% cellulose hydrogel (100 mg dry cellulose content) with 100 mL of water to dilute the dispersion. 1 mL of pyrrole (0.014 mol) was dissolved in 50 mL aqueous 0.5 M HCl solution together with 1 drop of Tween-80. This solution was then mixed with the cellulose dispersion and stirred for 5 minutes. 9 g of FeCl$_3$ (0.033 mol) was dissolved in 50 mL aqueous 0.5 M HCl solution and added to the cellulose-pyrrole dispersion to initiate polymerization. The polymerization reaction was allowed to proceed for 30 minutes, after which the PPy-cellulose dispersion was washed with 5 L of 0.5 M HCl, using a Büchner funnel, to rinse away iron residues from the FeCl$_3$ salt. Subsequently, 1 L of 0.1 M NaCl was filtered through the dispersion before final sonication for 2 minutes, using the same settings as above. The PPy-cellulose dispersion was then transferred back to the funnel and dried on a
filter paper and the resultant PPy-cellulose cake was removed. Samples intended for mechanical testing and cellulose content estimation were dried under ambient conditions. In all other cases, the product was divided into 4 parts that were dried differently using the techniques described below.

3.1.4 Drying of TEMPO-NFC PPy composites (V)

The composites in Paper V were dried under ambient conditions, freeze-dried from water, freeze-dried from tert-butanol, or dried from liquid CO₂ using a critical-point technique.

3.1.4.1 Freeze-drying

The samples were placed in an aluminum cup and frozen from water or tert-butanol using liquid nitrogen (without direct contact between the sample and the liquid nitrogen). A thin layer of parafilm was put between the water samples and the bottom of the aluminum cups to protect the samples from aluminum corrosion products. Before freeze-drying from tert-butanol, the solvents used were ethanol 96% (24 h), then ethanol 99.9% (24 h) and finally tert-butanol at 28 ºC (24 h). The samples were quickly transferred to a Scanvac CoolSafe freeze-drier (Labogene, Denmark) where ice and tert-butanol sublimation took place under vacuum.

3.1.4.2 Critical-point CO₂ drying

Prior to drying, the solvents used were ethanol 96% (24 h) and then ethanol 99.9% (24 h). The samples were then placed with a small amount of ethanol into the critical-point drying machine (Autosamdi®-815, Tousimis, USA). Liquid CO₂ was injected at room temperature and a pressure of about 5 MPa. Over a purge time of 10 minutes, the ethanol was replaced by liquid CO₂. The sample chamber was then brought above the CO₂ critical point at ca 10 MPa and 36 ºC. The chamber was thereafter depressurized and the liquid CO₂ evaporated.

3.2 Supercapacitor cell assembly (I–III)

Symmetrical supercapacitor devices were assembled using two identical pieces of PPy-cellulose composite as the positive and negative electrodes, commercial filter paper as the separator and 2 M aqueous NaCl as the electrolyte, see Fig. 5.
Figure 5. Schematic image of the supercapacitor layout (left), reprinted from Paper I with permission from the publisher. Experimental setup in Paper II (right). The potential of each electrode was measured against a 3 M Ag/AgCl reference electrode, denoted R.E.

In **Paper I**, platinum foil was used to collect the current and glass slides were used to apply contact pressure between the electrode and the current collector and to stabilize the device. The cells were sealed in plastic-coated aluminum pouches. The typical dimensions of the electrodes used in the devices were 1.0 cm x 0.5 cm x 0.1 cm, which corresponded to a sample weight for each electrode of ~18.75 mg.

In **Paper II**, platinum foil was used to collect the current and the supercapacitor devices were assembled by placing two PPy-cellulose electrodes, separated by a filter paper, between two microscope glass slides. The assembled devices were left open, immersed in an electrolyte-filled crystallization dish, to allow the use of an external reference electrode for individual potential control of the electrodes, see Fig. 5. Each electrode weighed ~10 mg.

In **Paper III**, graphite foil (SIGRAFLEX, SGL Carbon, Germany) was used as a current collector for most cells, but a few had platinum foil current collectors for comparison. One open cell, of the same type as that used in Paper II, was also prepared. Symmetrical cells with increasing total amounts of electrode material (20–400 mg) were assembled and sealed in plastic-coated aluminum pouches.
3.3 Primary material characterization

3.3.1 Scanning electron microscopy (I–II, IV–V)

The surface morphology of PPy-cellulose composites was observed using Scanning Electron Microscopy (SEM).

In Paper I and Paper IV, the micrographs were taken with an environmental SEM instrument (FEI/Philips XL 30, the Netherlands) in high vacuum mode (3.5×10^{-6} mbar). The samples were mounted on aluminum stubs using double-sided adhesive tape. Prior to imaging, Au/Pt was sputtered on the samples to minimize charging.

In Paper II and Paper V, the micrographs were obtained with a LEO1550 field emission SEM instrument (Zeiss, Germany) operated at 1 kV. No sputtering was used prior to imaging and the in-lens detector was used to record the images.

3.3.2 Transmission electron microscopy (I)

Transmission Electron Microscopy (TEM) was used to obtain information about the uniformity of the PPy coating and the diameters of single PPy-coated nanocellulose fibers. TEM images were recorded using a JEOL-3010 microscope, operating at 300 kV (Cs 0.6 mm, resolution 1.7 Å) with a CCD camera (Keen View, SIS analysis, size 1024 x 1024, pixel size 23.5 x 23.5 µm) at 150 000x magnification using low-dose conditions. A small piece of dry composite material was removed with a scalpel and ultrasonicated in ethanol. The suspension was allowed to settle and a small amount was transferred from the supernatant to a holey-carbon TEM grid using a pipette.

3.3.3 Electronic conductivity (I, III–IV)

The electronic conductivity of rectangular pieces of dry PPy-cellulose composite material was measured at room temperature using a semiconductor device analyzer (B1500A, Agilent Technologies USA) in Paper I. The voltage, \( U \), which was scanned between −1 and +1 V, was applied with titanium needle probes and the resulting dc current, \( I \), was measured. Prior to the measurements, silver paint was pasted on the ends of rectangular samples to ensure good contact with the needle probes.
The conductivity, \( \sigma \), was then calculated as: 
\[
\sigma = \frac{\Delta I}{\Delta U \cdot w \cdot d} 
\]
where \( \frac{\Delta I}{\Delta U} \) is the conductance of the sample obtained as the slope of the linear part of the current versus voltage curve, and \( L \) is the length, \( w \) is the width and \( d \) is the thickness of the samples.

In Paper III and Paper IV, the conductivity was measured using a multimeter (34401 A, Agilent Technologies, USA). Silver paint was applied on the ends of the samples to assure good electrical contact with the clip probes. The measured resistance was converted into conductivity using the same equation as above.

3.3.4 Specific surface area and pore volume (I, IV–V)

Nitrogen gas sorption isotherms were recorded with an ASAP 2020 (Micromeritics, USA) in Papers I, IV and V and the specific surface area was obtained according to the BET method.\(^{77}\)

Additionally, in Paper IV, argon gas sorption isotherms were recorded for the collapsed MFC paper. Nitrogen sorption is not feasible for materials with low surface areas (typically below \( \sim 1 \text{ m}^2/\text{g} \)). Since argon molecules have the same dimensions as nitrogen molecules but provide a 4-fold gain in sensitivity of measurement due to the lower saturation pressure,\(^{78}\) argon gas sorption was employed to analyze this low surface area material. Both measurements, nitrogen and argon gas sorption, were performed at liquid nitrogen temperatures, i.e. 77 K.

The pore volume of the samples was also measured, in Paper I, as the single point adsorption volume of pores with a diameter less than \( \sim 133 \) nm at a relative pressure of \( \sim 0.99 \).

3.3.5 Thermogravimetric analysis (I, IV–V)

Thermogravimetric analysis (TGA) was used to estimate the weight fraction of water, the weight fraction of PPy (in Paper IV) and the weight fraction of possible impurities left in PPy-cellulose composites after synthesis (in Paper V). The analysis was performed using a Mettler Toledo TGA/SDTA851 instrument. The samples were placed in an inert ceramic crucible and heated from 25 to 600 °C at a heating rate of 10 °C/min (in Papers I and IV). In Paper V, the temperature range was 25–800 °C and the heating rate was 5 °C/min.

In Paper I, a Cladophora cellulose-PPy composite (13 mg sample weight) and pure Cladophora cellulose (17 mg) were analyzed.

In Paper IV, an MFC-Ppy composite (7.5 mg), MFC paper (9.4 mg) and PPy powder (7.1 mg) were analyzed.
In Paper V, all of the different TEMPO-NFC composites were analyzed (sample weight ~3 mg).

3.3.6 Elemental analysis (I, V)
Elemental CHN analysis was used to determine the PPy content of the composites (Papers I and V). The PPy content was readily obtained from the measured nitrogen content in the CHN analysis, as PPy was the only nitrogen-containing substance in the composites. The analysis was performed by the company Eurofins MikroKemi AB, Uppsala, Sweden.

3.3.7 Viscosity measurements (V)
As a measure of nanocellulose degradation, the limiting viscosity was determined according to ISO standard 5351:2010. The method involved dissolving cellulose after the degradation experiments in a cupriethylenediamine (CED) solution and determining the limiting viscosity using an Ubbelohde viscometer.

3.3.8 Density and porosity measurements (V)
The true density, $\sigma_t$, of the composites was measured using helium pycnometry (AccuPyc 1340, Micromeritics, USA) and the porosity was estimated according to $\left(1 - \frac{\sigma_b}{\sigma_t}\right) \cdot 100\%$, where the bulk density, $\sigma_b$, was obtained from weighing the sample and measuring its dimensions with a caliper.

3.3.9 Tensile strength (V)
Tensile strength measurements were performed using an Instron 5944 equipped with a 50 N load cell. The samples were equilibrated at 23 ºC and 50% relative humidity and the test was performed under the same conditions. Rectangular strips 6 mm wide, 30 mm long, and ~0.7 mm thick were tested using a deformation rate of 0.003 mm/s.

3.4 Electrochemical characterization
Cyclic voltammetry, chronopotentiometry, chronoamperometry, and electrochemical impedance spectroscopy (EIS) were used to characterize cellulose-PPy composite electrodes and the symmetrical supercapacitor devices made with these composite electrodes.
3.4.1 Cyclic voltammetry (I, III–V)

Cyclic voltammetry (CV) was performed using a standard three-electrode electrochemical cell utilizing an Autolab/GPES interface (ECO Chemie, The Netherlands) with the sample as the working electrode, a platinum wire as the counter electrode and a 3 M NaCl-saturated Ag/AgCl electrode as the reference electrode. The reference electrode had a potential of 0.197 V vs the normal hydrogen electrode (NHE). In all experiments 2 M aqueous NaCl was used as electrolyte and a clip made from platinum wire was used to contact the sample.

In Paper I, cyclic voltammograms were recorded in the potential window of −0.9 to +0.9 V vs Ag/AgCl. Scan rates between 3 and 20 mV/s were used and the typical sample dimensions were 0.6 cm x 0.25 cm x (0.06–0.08) cm, which corresponded to a sample weight of ~2.5 mg.

In Paper III, the platinum counter electrode was placed in a separate compartment and the electrolyte was purged with nitrogen for at least 15 minutes prior to the measurements. A constant nitrogen flow was kept slightly above the solution surface during the measurements to prevent oxygen from re-dissolving. The cyclic voltammogram was recorded between −0.8 and +0.5 V vs Ag/AgCl at a scan rate of 5 mV/s and the sample weight was ~5.5 mg.

In Paper IV, CV was performed between −1.0 and +1.0 V vs Ag/AgCl at a scan rate of 5 mV/s. The sample weight was ~15 mg.

In Paper V, the electrolyte solution was purged with nitrogen for at least 15 minutes prior to the measurements and a constant nitrogen flow was kept slightly above the solution surface during measurements to prevent oxygen from re-dissolving. The counter electrode was placed in a separate compartment and the voltammograms were recorded using a cathodic turning potential of −0.8 V vs Ag/AgCl. The anodic turning potential was increased from +0.3 to +0.7 V vs Ag/AgCl with increased scan rates to include as much of the oxidation peak as possible without overoxidizing the material. Samples ranging from 1.4 to 2.9 mg in weight were first cycled through 3 scans at 5 mV/s to minimize break-in effects followed by a series of 3 cycles at 1, 5, 10, 25 and finally 50 mV/s.

3.4.2 Chronopotentiometry (I–III)

The electrolyte was 2 M aqueous NaCl in all measurements described below and an Autolab/GPES interface (Eco Chemie, The Netherlands) was used to control the chronopotentiometric measurements.

In Paper I, the supercapacitor cells were tested in experiments with charge-discharge currents between 10 and 320 mA. To test the long-term cycling stability of the cell, the charge-discharge measurements were continuously repeated for 100 cycles using a ±320 mA current, corresponding to...
a current density of 600 mA/cm² when normalized with the electrode cross section area.

In Paper II, a three-electrode setup with a coiled Pt auxiliary electrode (placed in a separate compartment) and a 3 M NaCl Ag/AgCl reference electrode was used. A current of 5 mA was employed and the potential cut-off limits were 0 and 0.6 V. Neutral and acidic (due to the addition of 0.01 M HCl) NaCl was used as the electrolyte.

In Paper III, all supercapacitor devices were pre-cycled using 30 constant-current charge-discharge cycles. The applied current was kept constant at 40 mA per gram total electrode weight, or 2 mA per cm² electrode area, and the cell potential limits were set to 0 and 0.8 V, respectively. A constant contact pressure of 25 kPa was kept over the cells in order to minimize variations in contact resistance.

3.4.2.1 Chronopotentiometry with an external reference electrode (II–III)
In these measurements, open supercapacitor cells were immersed in an electrolyte-filled crystallization dish. This allowed measurement of the individual electrode potential, in the supercapacitor device, vs a 3 M NaCl Ag/AgCl reference electrode (placed ~1 cm from the electrodes), see Fig. 5. Two multimeters (Agilent technologies 34401A, USA) monitored by a MatLab® script were used to record the potential of the individual device electrodes.

3.4.3 Chronoamperometry (III, V)
In Paper III, the supercapacitor cell voltage was switched between 0 and 0.8 V and the current transients were recorded for the equivalent of 10 RC time constants for the different cells. A constant contact pressure of 2.5 N/cm² was kept over the cells in order to minimize variations in contact resistance.

In Paper V, three-electrode measurements were performed in which the samples were first reduced at −0.8 V vs Ag/AgCl until the current reached the cut-off value (first positive value), indicating that the samples were fully reduced (as allowed by the applied voltage). This was immediately followed by oxidation at 0.3 V vs Ag/AgCl.

3.4.4 Electrochemical impedance spectroscopy (III)
The impedance spectroscopy measurements were carried out using a CH Instruments Electrochemical Workstation CHI660D (CH Instruments, USA). A three-electrode setup was used with 2 M aqueous NaCl (purged with nitrogen) as electrolyte, a 3 M NaCl Ag/AgCl reference electrode and a platinum wire counter electrode placed in a separate compartment. The sample, which was contacted with a coiled platinum wire, was allowed to equilibrate
for 100 s at each new potential as the steady-state potential was altered from the oxidized state (+0.5 V vs Ag/AgCl) stepwise, using a step size of 0.1 V, down to the reduced state (−0.5 V vs Ag/AgCl) and up to the oxidized state again. An ac signal amplitude of 5 mV was used and the frequency was scanned between 18 kHz and 1 Hz.
4. Results and Discussion

4.1 Energy storage devices with cellulose-based electrodes

4.1.1 Paper I

A conductive paper based on high surface area cellulose extracted from the green alga Cladophora coated with a 50 nm layer of the conducting polymer PPy, was presented and analyzed in a previous study. To produce this material, PPy was polymerized chemically, using FeCl₃ as oxidant, onto Cladophora cellulose fibers well dispersed in water. The coated fibers were washed thoroughly with water and dried under ambient conditions to form black conductive paper sheets that could be cut with scissors, see Fig. 6.

![Figure 6. Photograph of the Cladophora cellulose-PPy composite paper sheet.](image)

The research carried out in Papers I–III was, apart from minor variations in the synthesis conditions (see section 3.1.1), based on the described material. Some of the composite's physical properties are summarized in Table 3.

Table 3. Physical properties of the Cladophora cellulose-PPy composite.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>~0.4 g/cm³</td>
</tr>
<tr>
<td>Porosity</td>
<td>~80%</td>
</tr>
<tr>
<td>Specific N₂ BET surface area</td>
<td>80 m²/g</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>1–6 S/cm</td>
</tr>
<tr>
<td>Mass fraction PPy (based on CHN analysis)</td>
<td>~67%</td>
</tr>
</tbody>
</table>
The objective of Paper I was to investigate the possibility of using this high surface area conductive paper as electrode material in symmetrical supercapacitor devices.

SEM revealed an open, highly porous, structure of intertwined PPy-coated cellulose nanofibers, see Fig. 7a. TEM was used to image single PPy-coated cellulose nanofibers. It can be seen in Fig. 7b that the diameter of individual fibers is around 100 nm. This can be compared to the diameter of pure Cladophora nanocellulose fibers of ~20 nm, leading to an approximate PPy layer thickness of 40–50 nm on the coated fibers.

Figure 7. Scanning electron micrograph (a) and transmission electron micrograph (b) of the Cladophora cellulose-PPy composite. Figure 7b was reprinted from Paper I with permission from the publisher.

To evaluate the electrochemical properties of the composites, CV was performed at a scan rate of 5 mV/s in 2 M NaCl, see Fig. 8 which shows the first five scans.

Figure 8. Three-electrode cyclic voltammogram obtained with the Cladophora cellulose-PPy composite at a scan rate of 5 mV/s.
The characteristic PPy oxidation and reduction peaks are seen along with the onset of a second oxidation peak, commonly referred to as the overoxidation peak, at potentials around +0.5 V vs Ag/AgCl.

To test the composite material as electrode material in an energy storage device, a symmetrical supercapacitor cell was assembled (see section 3.2). Galvanostatic charge and discharge experiments, with charging currents from 10 to 320 mA (corresponding to current densities of 20–600 mA/cm² or 0.27–8.5 A/g), show linear capacitor-like behavior, as seen in the inset of Fig. 9.

![Figure 9](image)

Figure 9. Charge capacities obtained at different charging currents. The corresponding charge-discharge curves are shown in the inset. Reprinted from Paper I with permission from the publisher.

Specific charge capacities were calculated from the charging curve by multiplying the charging current by the total charging time, i.e. over the whole presented cell voltage range, and normalizing with the total weight of both composite electrodes. Charge capacities between 25 and 33 mAh/g, or 38 to 50 mAh/g normalized by PPy weight, were found for the different charging currents used, see Fig. 9. The drop from the initial charge capacity of 33 mAh/g, at 10 mA, to 25 mAh/g at the highest charging current, 320 mA, corresponds to a 72% capacity retention when compensating for the increased IR drop at the higher charging currents. By increasing the charging current from 10 to 320 mA, the corresponding charging time decreases from 8 min to 11 s. Further, a 6% decrease in capacity was found as the cycling stability was investigated by performing 100 cycles at 320 mA charging current.

4.1.2 Paper II

The devices in Paper II were identical to those in Paper I but, instead of using pouch cells, they were left open; this allowed the use of an external 3
M Ag/AgCl reference electrode, against which the individual device electrode potentials could be measured (see section 3.4.2.1).

The objective of Paper II was to investigate the galvanostatic cycling stability of the Cladophora cellulose-PPy composite when used as the electrodes in a symmetrical supercapacitor device and in a three-electrode electrochemical cell, in greater detail than in Paper I.

Galvanostatic two-electrode measurements were carried out using a 10 mA charging current (corresponding to a current density of 30 mA/cm² or 0.48 A/g) and cell voltage cut-off limits of 0 and 0.8 V. The linear slope of the discharge curve was used to calculate the specific cell capacitance according to the following equation:

\[
C = \frac{I}{(\Delta V / \Delta t \cdot m)}
\]  

where \(I\) denotes the applied current and \(m\) is the total dry weight of both electrodes (20.8 mg). A maximum specific cell capacitance of 32.4 F/g was obtained, corresponding to a specific electrode capacitance of 129.6 F/g.\(^{83}\) After 4000 charge-discharge cycles, the two-electrode cell showed excellent cycling stability with only a 0.7% loss in capacitance, see Fig 10a.

Figure 10. (a) Two-electrode cell capacitance as a function of cycle number. (b) Specific electrode capacitance obtained from a three-electrode measurement in a neutral (triangles) or acidic (squares) 2 M NaCl electrolyte. Reprinted from Paper II with permission from the publisher.

SEM micrographs of the Cladophora cellulose-PPy composite electrodes before and after 4000 cycles revealed, in contrast to other research in the literature,\(^{84, 85}\) no change in morphology. This indicates very good adhesion of PPy to the cellulose substrate and also suggests that no fragments were lost during cycling due to the repeated swelling and contraction of the PPy layer.

In contrast, a rapid decrease in capacitance was seen in the three-electrode measurement when the electrode was cycled between 0 and 0.6 V vs Ag/AgCl using a 5 mA charging current, see Fig 10b (triangles).
Taking previously published results into consideration, it is reasonable to assume that this rapid degradation stems from a nucleophilic attack of OH\textsuperscript{-} (present in the neutral electrolyte) on PPy. This hypothesis is supported by the fact that the stability was drastically improved when the experiments were repeated in an electrolyte also containing 0.01 M HCl (pH ~ 2), see Fig. 10b (squares).

The two-electrode cell performed remarkably well compared to the three-electrode set-up using a neutral electrolyte. This can be explained by the partial degradation of the PPy coating on the positive electrode in the two-electrode cell resulting in the liberation of protons and degradation compounds including maleimide. This process would result in a local decrease in the pH within the two-electrode cell, as this was constructed in such a way, with glass microscope slides covering the entire electrode surface, that diffusion to and from the cell was limited. It is therefore reasonable to assume that a local acidic environment was created inside the two-electrode cell and that this protected the polymer against further degradation. In fact, a decrease in the pH of the bulk electrolyte was measured after the experiment.

The cycling stability of two-electrode cells was further investigated by pre-cycling a cell between 0 and 1.2 V using a 10 mA charging current. During this pre-cycling, the individual potential of the electrodes was stabilized at 0 V vs Ag/AgCl when the potential of the cell was 0 V. As no significant loss in capacitance was found in the experiment presented in Fig. 10a or in the voltage window 0 to 1.2 V, the upper cut-off in cell potential was increased to 1.8 V. Even at this high upper cell voltage no degradation was seen over 600 cycles or the equivalent of 20 hours' cycling time. The explanation for this behavior was found when looking at the individual electrode potentials vs Ag/AgCl, see Fig. 11.

![Figure 11](image-url)  
**Figure 11.** Potential windows, versus Ag/AgCl, of the positive and negative electrodes of a supercapacitor cell charged between 0 and 1.8 V. (a) Some of the charging and discharging cycles in more detail. (b) All of the 600 cycles. Reprinted from Paper II with permission from the publisher.

From these data, it is evident that the potential of the positive electrode never reaches more than +0.6 V vs Ag/AgCl and is therefore constantly moving in
a potential window where only minor degradation would be expected. Most of the potential at a cell voltage of 1.8 V is thus over the negative electrode which dropped as far as $-1.2$ V vs Ag/AgCl. This drop is explained by the increased resistance of the negative electrode as a result of the poorly conducting reduced PPy. It could therefore be concluded that this resistive feature of the system, which is based on the limiting capacity of the negative electrode, works as an inherent self-protection mechanism against overoxidation of the positive electrode.

4.1.3 Paper III

In Paper III, devices of the same type as those investigated in Papers I and II were used, except that graphite replaced platinum foil as the current collector. The objective of Paper III was to investigate the possibility of carrying out rapid potential step charging of Cladophora cellulose-PPy cells and to study the influence of the size of the cell on the required charging time as a function of the cell resistance and RC time constant.

Firstly, the charging efficiency of potential step charging was tested by charging a cell potentiostatically, immediately followed by a galvanostatic discharge. No detectable losses were found when comparing the charge stored in the cell with the amount of charge that could be extracted. This shows that potentiostatic charging is feasible in terms of charging efficiency, even though the charging currents are significantly larger than those typically used during galvanostatic charge and discharge.

Cells with Cladophora cellulose-PPy electrodes of identical size but with increasing total amounts of electroactive material (ranging from 20 to 400 mg total electrode weight) were then assembled and sealed as pouch cells. The cells were first galvanostatically pre-cycled for 30 cycles between 0 and 0.8 V cell voltage using a current density of 40 mA per gram total electrode weight. During the pre-cycling, the individual electrode potentials at 0 V cell voltage stabilized at $+0.09$ V vs Ag/AgCl, as evidenced in an open cell experiment of the same type (described in Paper II), where they remained during the subsequent potentiostatic experiments. During operation of the cell between 0 and $+0.8$ V cell voltage, the potential of the negative electrode spanned over the potential range of $+0.09$ to $-0.28$ V vs Ag/AgCl whereas the positive electrode moved through a potential window of $+0.09$ to $+0.52$ V vs Ag/AgCl.

The current vs time transients resulting from potentiostatic switching of the cell between 0 and 0.8 V are shown in Fig. 12.
As can be seen in the inset in Fig. 12, where a close-up of one of the current transients during a potential step to 0.8 V is shown, the charging current exhibited exponential decay, suggesting that the current was controlled by the RC time constant of the cell rather than by the mass transport rate of the counter ions or the kinetics of the electrode reactions. This behavior is in good agreement with that previously seen for the oxidation and reduction of thin films of conducting polymers. 88-90

A fit was therefore made using the following well-known equation for charging an RC circuit:

\[ i(t) = \frac{E}{R} \exp\left(-\frac{t}{RC}\right) + B \]  

(2)

where \( E \) denotes the applied cell voltage, \( R \) and \( C \) represent the cell resistance and cell capacitance, respectively, and \( B \) is a base line adjustment parameter. As can be seen in the inset to Fig. 12, the fit to the experimental data was generally very good, indicating that the charging process was indeed controlled by the RC time constant and that this fitting approach can henceforth be used to extract both the total cell resistance, \( R \), and the time constant, \( RC \), for the different devices.

The obtained RC time constants for the different devices were compared to the galvanostatic analogs (where the resistance was obtained from the IR drop and the capacitance from the discharge slope, see Eq. 1.), see Fig. 13a.
As can be seen in Fig. 13a, no significant difference was observed between the RC time constants obtained with the potential step and constant current approaches for a cell of a certain size. It can be estimated from RC circuit theory\(^9\) that 95% of full charge, from the current following a potential step, will occur within a time period of 3 RC time constants. This was therefore chosen as the equivalent of “full charge” of the cells. For the smallest cells, full charge was obtained in 10–15 s, in good agreement with the charging times found in Paper I for cells of similar size.

The capacitance was found to increase linearly with increasing cell size, which simply reflects the increasing amounts of electroactive material in the cells. From a linear fit to these values, the specific cell capacitance was evaluated as 38.3 F/g using the composite weight of both electrodes or or 2.1 F/cm\(^2\) using the cross section area of the electrodes.

It can also be seen in Fig. 13a that the RC constant increases linearly with increasing cell size for cells containing 100 mg or more of electrode material. In order for the time constant, and thereby the minimum charging time, to be independent of the cell size, the resistance needs to decrease as the capacitance of the cells increases.

In Fig. 13b, the total cell resistance was plotted as a function of the electrode area (as the thickness of the electrodes is constant, a change in the area directly translates to a change in the electrode weight). The total cell resistance is a sum of the resistance of the current collectors, the electrolyte resistance across the separator, and the resistances of the electrode material itself, the electrolyte within the pores of the electrodes, and the contacts. The resistance of the carbon current collectors was estimated, using end-to-end resistance measurements of the individual current collectors, as 1.5 Ω.
This value was used as a constant in equation 3, which was used to fit the data in Fig. 13b:

\[ R = \frac{x}{A} + 1.5 \, \Omega \]  

(3)

where \( A \) denotes the electrode cross-section area and \( x \) is the area-specific resistance obtained in the fitting process. The resistance of the electrode material and the resistance across the separator can be estimated from the resistivity of the electrode material (0.17 \( \Omega \) cm) and the electrolyte (11.63 \( \Omega \) cm) by taking the geometry of the electrodes into account, see Table 4.

Table 4. Total resistance, electrode resistance and the resistance across the separator for cells with increasing total amounts of electrode material.

<table>
<thead>
<tr>
<th>Electrode weight [mg]</th>
<th>Electrode area [cm(^2)]</th>
<th>Total cell resistance [( \Omega )]</th>
<th>Single electrode resistance [( \Omega )](^a)</th>
<th>Resistance across separator [( \Omega )](^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.9</td>
<td>0.49</td>
<td>5.9</td>
<td>0.024</td>
<td>0.324</td>
</tr>
<tr>
<td>40.5</td>
<td>0.64</td>
<td>3.6</td>
<td>0.018</td>
<td>0.245</td>
</tr>
<tr>
<td>100.7</td>
<td>1.96</td>
<td>1.9</td>
<td>0.006</td>
<td>0.080</td>
</tr>
<tr>
<td>199.6</td>
<td>3.76</td>
<td>1.7</td>
<td>0.003</td>
<td>0.042</td>
</tr>
<tr>
<td>400.1</td>
<td>7.16</td>
<td>1.8</td>
<td>0.002</td>
<td>0.022</td>
</tr>
</tbody>
</table>

\(^a\): An average electrode thickness of 0.067 cm was used.

\(^b\): An average separator thickness of 0.0135 cm was used.

The presented results indicate that the cell resistance was controlled by the contact resistance and/or the electrolyte resistance. In a simplified effort to estimate the contribution from the electrolyte resistance to the measured cell resistance, half of the cell volume (including both of the porous electrodes and the separator) was considered the mean ionic diffusion volume. Combining this value with the electrolyte resistivity, 11.63 \( \Omega \) cm, a resistance of about 1.8 \( \Omega \) and 1.4 \( \Omega \) was found for the smallest and second smallest cells in this study respectively. From this estimation it is clear that the resistivity of the electrolyte had a large influence on the total resistance for the smaller cells but also, when comparing to the total resistance values in Table 4 and subtracting the current collector resistance of ~1.5 ohm, that a significant part resulted from contact resistances. The fact that the cell resistance was found to decrease when pressure was applied on the electrodes supports the contributions of contact resistance to the smaller cells.

Experiments were also performed with platinum foil current collectors which have significantly lower resistance than graphite foil current collectors. These cells, however, had resistances in the order of 14.7 \( \Omega \) (Paper I), 8.5 \( \Omega \) (Paper II) and 10.4 \( \Omega \) (Paper III) for small devices of 20–40 mg total
electrode weight, which are considerably higher than the values found when using graphite foils, see Table 4. The differences were ascribed to a higher contact resistance between the platinum foil and the Cladophora cellulose-PPy composite than between the graphite foil and the same composite electrodes.

As PPy is well known to change conductivity with different degrees of oxidation and as the electrode resistance contributions estimated in Table 4 were based on as-synthesized and partially oxidized material, an attempt was made to estimate the increase in resistance of the reduced electrode in the cell. For this purpose, three-electrode EIS was performed on the Cladophora cellulose-PPy electrode in 2 M NaCl at different potentials, in the frequency range of 1 Hz to 18 kHz. As is seen in the Nyquist plot of the recorded data shown in Fig. 14a, the use of more cathodic potentials results in a widening of the semi-circle. Interpretation of these results based on the Randles equivalent circuit indicates that the charge transfer resistance increased as the PPy sample was reduced.

![Figure 14](image)

Figure 14. (a) Nyquist plot of impedance data recorded at different steady-state potentials, the dashed arrows highlight the broadening of the semi-circle as the steady-state potential is reduced. (b) Charge transfer resistance obtained from fitting the data to the semi-circles in panel (a), as a function of steady-state potential during reduction (open circle) and directly followed by oxidation (filled circles). Reprinted from paper III.

In Fig. 14b, the charge transfer resistances obtained from the curves in Fig. 14a have been plotted as a function of steady-state potential when the potential was first stepped cathodically (open circles) and then anodically (filled circles). However, as these experiments were performed with a three-electrode configuration and the PPy composite sample was contacted using a platinum wire, the experimental values obtained from these EIS experiments should not be compared with those for the supercapacitor cells presented in Table 4. In the potential interval of interest in this study (i.e. +0.5 V to −0.3 V vs Ag/AgCl corresponding to electrode potentials during cell operation), the charge transfer resistance increased from 1.7 to 3.1 Ω as a result of the reduction of the composite. Thus, it can be estimated that the maximum in-
crease in resistance of the reduced electrode would be two-fold. This corresponds to an increased resistance contribution to the total cell resistance of 2 to 24 mΩ depending on the size of the electrode, as seen in Table 4.

Consequently, it did not appear that the conductivity of the electrode material limited the total resistance of the cells. Instead it was concluded that, for small cells, the cell resistance was determined to a large extent by the electrolyte resistance and contact resistances, whereas the resistance of the current collectors dominated the total resistance of the cell for larger cells.

To prove that the current collector resistance was indeed the limiting factor for larger cells, one large cell with platinum current collectors was assembled. This cell had a total resistance of 0.6 Ω and an RC time constant of 7.5 s, see the squares in Fig. 13a. It could therefore be concluded that short charging times below 22 s could be obtained for all the cells in the study.

Finally, long-term potentiostatic cycling of devices (100 mg cells) demonstrated that 80–90% of the original cell capacity was retained after 10 000 potential step cycles between 0 and 0.8 V.

4.1.4 Discussion of Papers I–III

The use of algae-based cellulose nanofibers in composites with chemically polymerized PPy allowed free-standing electrodes of millimeter thickness to be produced. In these, the cellulose matrix serves the dual purpose of providing mechanical reinforcement and a 3D network of high porosity. The high porosity ensures good availability of electrolyte and short counterion transport distances during electrochemical operation. On the other hand, the porosity also adds volume and dead weight to the device when the pores are filled with excess electrolyte.

In the original version of Paper I, the devices were named paper batteries, a terminology based on the faradaic charge storage mechanisms in PPy. However, as may be seen in the Ragone plot (Fig. 15), these devices actually fall in the area of electrochemical capacitors. This classification is also in agreement with the linear capacitor type charging and discharging curves seen in Fig. 9 and in the literature.45, 69-71 A more appropriate terminology for the devices is therefore electrochemical capacitors or supercapacitors.
In Paper I, the full potential window of both electrodes was used and the cell was cycled from negative to positive cell voltage. This is unrealistic in practical terms, but shows the true reversibility of the electrodes in that the positive and negative electrodes are constantly switching from a fully reduced to a fully oxidized state.

As the polarity of the cell is switched during charging and discharging, only half of the reported charge capacity is practically available, i.e. 15 mAh/g in a symmetrical device. Also, the method or unit used to report the charge capacity, mAh/g, was found to be very sensitive to changes in IR drop. This meant that an apparent capacity fade during cycling of the cell might in fact have been an increase in IR drop due to changes in the equilibrium potential of the electrodes or worsened contact between electrode and current collector.

Capacitance, used in Papers II–III, was a better measure of performance and provided the natural unit, given the capacitive behavior of the devices. The reported capacitance was 32.4 F/g in Paper II and 38.3 F/g in Paper III, normalized by the total dry weight of electrode material in the devices.

Both specific charge capacity and capacitance have been used in the literature to quantify the amount of charge that can be stored in devices. The reported charge capacities in Paper I (25–33 mAh/g) can be compared to 15 mAh/g found for a redox PPy battery, 22 mAh/g for an all-polymer PPy battery, and 10 mAh/g for a flexible polymer fiber PPy-based battery. The reported capacitances in Papers II–III can be compared to 305 F/g for PPy nanowires normalized by single electrode PPy weight (the corresponding values are 193 F/g in Paper II and 230 F/g in Paper III) or 70 F/g for a
PPy hydrogel electrode measured from symmetrical two-electrode CV (the corresponding value is 120 F/g in Paper II).

It is hard to make any direct comparisons, as the experimental setups and the methods used to calculate the capacity or capacitance greatly influence the obtained values. However, it seems that the capacities and capacitances presented in the thesis can be considered to be of the same order of magnitude as the previously reported values. The use of cellulose in the composites does not seem to limit the utilization of PPy.

Poor cycling stability is considered to be one of the main limitations of the use of conducting polymers in energy storage devices. Much work has been done and some progress has recently been made in this field, however, results vary between a 9% and a 50% loss in capacitance over 1000 cycles in aqueous electrolytes. In this respect, the 0.7% loss in capacitance over 4000 galvanostatic cycles in Paper II or the 10–20% loss over 10 000 potentiostatic cycles in Paper III must be considered good. This indicates excellent adhesion of PPy to the cellulose substrate and further that the cellulose fibers are capable of swelling and contraction to account for the volume changes in PPy during electrochemical operation.

The stability of PPy also depends on the pH of the electrolyte as was verified by the galvanostatic three-electrode experiment in Paper II (see Fig. 10b). Although the electrodes used in this study were very porous, the whole of the electrode area was covered with a glass slide in the device. Thus, diffusion was limited and it is reasonable to believe that the local acidic environment was maintained in the cell.

The external reference electrode used in Paper II allowed for better control over the individual electrode potentials and also highlighted the resistive feature of the system, which was found to protect the positive electrode against overoxidation. The stability at extended cell voltages is in conflict with results for carbon nanotube substrates covered with PPy. The differences in stability between the two systems could be related to the high conductivity and capacitance of the CNT substrate. For a conductive high capacitance substrate, a less rapid change in potential than seen with PPy on a cellulose substrate would be expected, since the capacitance of the substrate would be significant even when the polymer was fully reduced. The slower decrease of the potential over the negative electrode in the PPy CNT case would lead to the positive electrode reaching a higher voltage and thereby undergoing more severe degradation.

The influence of the cell resistance is also readily seen in the high current experiments in Paper I, where increasingly large IR drops resulted from increasing the charging current. The cell voltage window was also adjusted at each new current density used for the constant current cycling in order to compensate for the IR drop. With this method, 72% of the capacity was retained with increasing charging currents. If, instead, the capacitance from the
slope of the discharge curve is considered, the same trend is seen and 78% of the initial capacitance is maintained at the highest current density.

A better way to achieve fast charging and to diminish the effects of IR drop is to use constant potential charging, as was demonstrated in Paper III. The lowest reported charging times in Paper I were also reproduced by potentiostatic charging in Paper III.

In Paper III, the minimum charging time was controlled by the RC time constant of the cell. The RC-controlled behavior was not unexpected given the porous structure of the composite electrode (which facilitates mass transport within the electrode) and the previous finding that the inherent redox processes of conducting polymers are sufficiently fast to be controlled by the RC time constant of the cell.

As the capacitance increased linearly with increasing cell size, the resistance of the cell set the limit for the minimum charging time. The resistance of the cell was, in turn, partially controlled by the contact resistance between the electrode and the current collector for smaller cells. Carbon-coated or PPy-coated metal foil current collectors should reduce contact resistance.

For larger cells, the contact resistance was negligible and the resistance was instead dominated by the resistance of the current collector itself. Metal current collectors, such as the platinum foil used in Papers I–II, of course, have a low internal resistance and, for large enough cells, the contact resistance can be minimized. For non-metal-based current collectors, various types of carbon could be an alternative. The graphite foil used in Paper III was, however, too resistive. CNT ink pasted on a paper substrate has been suggested as a current collector, with the claimed advantage of reducing the dead weight of devices by replacing traditional metallic current collectors. The reported sheet resistances of CNT paper current collectors are 10–20 Ω per square. Given a typical paper thickness of 100 µm, resistivity will be 0.1–0.2 Ω cm. This, in turn, is around 2 orders of magnitude higher than the resistivity of the graphite foils (Sigraflex, grade Z, 0.15 mm) used in Paper III and is therefore not an alternative.

The electronic resistance of the composite material itself was found not to limit the cell resistance in Paper III. This conclusion was based on estimations of the electrode resistance from resistivity measurements of as-synthesized material and the only slight increase in charge transfer resistance found in the interval +0.5 to −0.3 V vs Ag/AgCl. As these are only relative estimations of the resistance drop of the electrode, an in situ electrode conductivity measurement during cycling would have been preferred. Such measurements, however, also show only small variations in PPy conductivity in the same potential range. It was further noted that the IR drop during the constant current pre-cycling at 0.8 V compared to 0 V increased only by a factor of 2–4% for the different cells. This strongly suggests that the resistance of the individual electrodes does not change very much in the potential window used by the device.
Although not shown in Fig. 14 above, impedance spectra were recorded at potentials down to -0.8 V vs Ag/AgCl. At potentials more cathodic than -0.5 V vs Ag/AgCl, the charge transfer resistance increased significantly. This behavior is in good agreement with previously published findings, including the results obtained at extended cell voltages in Paper II.

It can also be noted that, on returning PPy from the fully reduced state to the oxidized state, the original Nyquist plot and charge transfer resistance were recovered (see Fig. 14b). This clearly shows that the properties of the material were retained in these experiments, indicating that the material can indeed be reversibly reduced and oxidized, in good agreement with our previous findings in Papers I–II.

4.2 Electroactive composites from wood cellulose

4.2.1 Paper IV

In Paper IV, wood-based nanocellulose was used instead of Cladophora nanocellulose to prepare cellulose-PPy composites. The objective was to investigate whether composites with similar properties to those of the Cladophora cellulose-PPy composites described in Papers I–III could be obtained with this form of cellulose.

The cellulose used was enzymatically pre-treated wood-based nanocellulose made from wood pulp from pine (40%) and spruce (60%) trees. The diameter of the nanofibers ranged from 5 to 20 nm. The nanofibers were coated with PPy using a similar process to that described for the composites used in Papers I–III (see section 3.1.3). The resulting composite material was hard but brittle, was about 1.5 mm thick, and had an electric conductivity of 1.5 S/cm.

Drying cellulose fiber materials directly from water dispersion usually results in the structure collapsing. This is ascribed to the attractive capillary forces that water exerts on the hydrophilic cellulose fibers and, later in the drying process, to the strong cooperative hydrogen bonding between the hydroxyl groups on the nanocellulose surfaces. Thus, upon complete removal of liquid, the neighboring nanofibers are drawn into intimate proximity and bond through numerous hydrogen bonds. The collapsed morphology of nanocellulose paper dried directly from a water dispersion under ambient conditions can be seen in the SEM micrograph in Fig. 16a.
Individual nanofibers can be seen on the surface of larger (micrometer) regions of cellulose fiber material. After polymerization of PPy onto the fibers, the morphology became more porous (Fig. 16b) with a network of coated nanofibers that were separated to a much higher degree than in Fig. 16a, despite the same drying conditions being employed. It is believed that by covering the individual cellulose nanofibers with a continuous layer of PPy, the contact angle between water and the composite nanofibers increases, resulting in weaker capillary forces during drying. PPy is also thought to block hydrogen bonding between the individual nanofibers during drying. This should lead to a less collapsed structure in the dry state. It was also found that the degree of loss of surface area upon drying decreased with increasing PPy content in the composite.

A nitrogen BET surface area of 90 m$^2$/g was found for the NFC-PPy composite, whereas the surface area of the NFC paper was below the detection limit of the instrument for nitrogen adsorption. Using argon instead, which is more sensitive due to its lower saturation pressure, an argon BET surface area of 1.5 m$^2$/g was found.

Thermogravimetric analysis estimated the PPy mass fraction in the composite as \(~0.7\).

Finally, the specific charge capacity of the NFC-PPy composite was evaluated by integrating the positive current in the cyclic voltammogram, seen in Fig 17, performed in 2 M NaCl at a scan rate of 5 mV/s. A charge capacity of 289 C/g or 80 mAh/g was found when normalizing with respect to the total weight of the composite electrode.
Figure 17. Cyclic voltammograms of the NFC-PPy composite in 2 M NaCl at a scan rate of 5 mV/s. Reprinted from Paper IV with permission from the publisher.

4.2.2 Paper V

In Paper V, composites of PPy with nanofibrillated cellulose prepared from wood pulp by TEMPO-mediated oxidation and mechanical shearing were synthesized using FeCl₃ and dried under ambient conditions, or using freeze-drying or supercritical CO₂ drying. It is important to note here that despite the differences in drying methods, all the samples were from the same synthesis batch. This allowed direct comparison of the effects of the different drying techniques on the structural and electrochemical properties of the composites, which was the objective of Paper V.

The degrading effects of HCl and FeCl₃ on the fibers were investigated by measuring the limiting viscosity value of the nanocellulose after various periods in a solution similar to that later used in the polymerization of composites. A small but statistically significant amount of degradation was found for all samples, irrespective of the degradation period. Based on these results, only minor degradation of the nanocellulose fibers is to be expected during composite synthesis, especially since the polymerization of pyrrole onto the nanofibers is rapid and also since a layer of PPy on the fibers should protect them against degradation, as PPy is known to be insoluble in common solvents.³⁶

SEM micrographs of the composites after polymerization of PPy onto cellulose nanofibers and drying using ambient conditions (Comp_Air), freeze-drying from water (Comp_Water), freeze-drying from tert-butanol (Comp_t-But), and supercritical CO₂ drying (Comp_CO₂) are shown in Fig. 18.
Figure 18. SEM micrographs of Comp_Air (a and b), Comp_Water (c and d), Comp_t-But (e and f) and Comp_CO₂ (g and h). Scale bars correspond to 5 µm (a, c, e and g) and 200 nm (b, d, f and h). Reprinted from Paper V.

Nanofiber structures can be seen in all the samples, with single fiber diameters of ~25–40 nm, as revealed in the high magnification micrographs. Drying under ambient conditions results in a compact structure as the fibrils, to a high extent, aggregate as a result of attractive capillary forces between the fibrils when water leaves the sample, see Fig. 18a,b. The other drying techniques resulted in more porous morphologies with increasingly open pore volumes, as seen in the high resolution micrographs (compare Fig. 18f and 18h).
The difference in porosity between the Comp_Air sample and the three porous samples was also confirmed by the estimated porosities, see Table 5. However, there were no significant differences between Comp_Water, Comp_t-But, and Comp_CO₂ in terms of estimated porosity. This is explained by the limitations imposed by the employed method of porosity estimation, where no exact measurement of the volume of the irregularly sized samples could be made.

Table 5. BET surface area and estimated porosity of NFC-PPy composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Drying method</th>
<th>Estimated porosity (%)</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp_Air</td>
<td>Ambient drying</td>
<td>30–35</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Comp_Water</td>
<td>Freeze-drying from water</td>
<td>95–96</td>
<td>37–106</td>
</tr>
<tr>
<td>Comp_t-But</td>
<td>Freeze-drying from tert-Butanol</td>
<td>97–98</td>
<td>147–162</td>
</tr>
<tr>
<td>Comp_CO₂</td>
<td>Supercritical CO₂ drying</td>
<td>92–98</td>
<td>170–246</td>
</tr>
</tbody>
</table>

*Data represent values from two separate batches.

Table 5 also summarizes nitrogen BET surface areas, which ranged from <1 for the sample dried under ambient conditions to 246 m²/g for the sample dried with supercritical CO₂. The variations between the two batches can be explained by variations in the extent of drying, in the compactions prior to the drying step, and in the drying protocols that had not yet been optimized. The BET surface areas are also in agreement with the gradually increasing pore volumes and lower degrees of fiber aggregation seen in the high resolution micrographs of Fig. 18.

Similar structures to those seen in Fig. 18 were found when drying pure cellulose hydrogels by freeze-drying and supercritical CO₂ drying. This suggests that the properties of the cellulose fibers greatly influence the properties of the composite material. It should also be noted that about half of the maximum specific surface area for uncoated TEMPO-NFC aerogels, 482 m²/g, was maintained after coating the fibers with PPy and drying the composite with supercritical CO₂.

The mean PPy content of the composites, determined by CHN analysis, ranged from 67.9 to 71.7 wt % for the different drying procedures. No statistically significant differences between the samples were observed and it can be concluded that PPy is not removed to a significant extent during any of the drying procedures (or that PPy is removed to an equal extent in all samples) and specifically not during solvent exchange. The cellulose content in the composites was estimated as 9.0 wt % by drying and weighing a complete synthesis batch while adjusting for the weight contribution from the remaining solvent in the material after drying.

Tensile tests of the ambient-conditions samples (Comp_Air) showed an average Young’s modulus of 0.51 GPa (standard deviation ± 0.12 GPa, n=4),
an average maximum stress at break of 10.93 MPa (standard deviation ± 0.70 MPa, n=4), and a strain-to-failure of about 2.5%.

Electrochemical characterization in the form of cyclic voltammograms of the compact Comp_Air and the porous Comp_CO₂ samples at scan rates of 1, 5 and 50 mV/s is shown in Fig. 19.

Figure 19. Cyclic voltammograms of Comp_Air and Comp_CO₂ at scan rate 1 (a), 5 (b) and 50 (c) mV/s. In (d) the specific charge capacities as a function of scan rate are seen for all composites. Reprinted from Paper V.

Distinct faradaic oxidation and reduction peaks are seen in the voltammograms for Comp_CO₂ whereas Comp_Air does not display clear peaks at any scan rate. Specifically, for Comp_Air, the oxidation peak appears as a current plateau at 1 mV/s, which diminishes relative to the Comp_CO₂ peak as the scan rate increases. The contrasting voltammetric behavior can be interpreted as differences in the mobility of the counterions needed to establish charge neutrality during oxidation and reduction, in the compact and porous composites.

In the case of Comp_Air, it is envisioned that the bulk of the PPy is inaccessible for ions at the start of oxidation and that oxidation is initiated at easily accessible PPy/solution interfaces, in line with previous work.\textsuperscript{112-114} The material is thought to then gradually undergo conformational changes and open up, making more PPy available so that the oxidation can slowly continue.\textsuperscript{113-115}
In contrast, Comp_CO\(_2\) has a porous structure from the beginning, with thin PPy layers that allow faster mass transport of counterions and thus rapid oxidation of the entire material, resulting in much more pronounced oxidation peaks. As the scan rates are increased, the requirement for fast mass transport increases, which Comp_CO\(_2\) can facilitate, although the shifting and widening of the peak suggests some minor limitations in the mass transport capacity. Comp_Air, however, cannot facilitate this increasing requirement for fast mass transport of counterions, as seen in the CV experiment as decreasing oxidation and reduction currents relative to Comp_CO\(_2\).

This drop in oxidation current for Comp_Air at increasing scan rates was also seen in the specific charge capacities calculated from the oxidation CV sweeps, which are plotted in Fig. 19d for all samples. Only about 40% of the capacity reached at 1 mV/s was retained at 50 mV/s. For the porous samples, the capacity was maintained at all scan rates. The slight increase seen in the charge capacity as the scan rate increased is a result of inclusion of part of the overoxidation peak at higher scan rates, rather than an actual increase in capacity. It is also interesting to note that, at 1 mV/s, there was no statistical difference in charge capacity between the samples, with mean values of 212–226 C/g. These results support the interpretation of the voltammetric data and illustrate that the porous samples allow fast transport of ions throughout the entire material whereas, in the compact sample, only a fraction of the electroactive material is used unless the oxidation is allowed to proceed slow enough for the complete transport of charge-balancing counterions to occur.

The experimentally obtained charge capacities, 212–226 C/g, can be compared to recently estimated theoretical values of 252–266 C/g based on a 25% doping level,\(^{38}\) see Table 6. The discrepancy could be the result of the experimental values not being corrected for solvent remaining in the samples, the full reversible potential window not being employed, and/or the uncertainty in the estimate of the 25% level of doping.

Table 6. Mean nitrogen content derived from CHN analysis used to estimate PPy content and theoretical charge capacities in NFC-PPy composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nitrogen(^a) (wt %)</th>
<th>PPy(^b) (mmol/g)</th>
<th>PPy(^a) (wt %)</th>
<th>Theoretical charge capacity(^c) (C/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp_Air</td>
<td>14.6±0.3</td>
<td>10.4±0.2</td>
<td>67.9±1.3</td>
<td>252±5</td>
</tr>
<tr>
<td>Comp_Water</td>
<td>14.9±0.3</td>
<td>10.6±0.2</td>
<td>69.0±1.3</td>
<td>256±5</td>
</tr>
<tr>
<td>Comp_t-But</td>
<td>15.1±0.3</td>
<td>10.8±0.2</td>
<td>70.1±1.3</td>
<td>260±5</td>
</tr>
<tr>
<td>Comp_CO(_2)</td>
<td>15.4±0.3</td>
<td>11.0±0.2</td>
<td>71.7±1.3</td>
<td>266±5</td>
</tr>
</tbody>
</table>

\(^a\) Values have been compensated for weight contributions from solvents and, in Comp_Water, also for impurities; see Paper V for further details. Values are expressed as means ± pooled standard deviations (n=10).

\(^b\) PPy content per gram composite.

\(^c\) Based on 25% doping level of PPy.\(^{38}\)
4.2.3 Discussion of Papers IV–V

In Papers IV–V, it was demonstrated that dispersed wood-based nanocellulose could replace the algae-based counterpart to produce cellulose-PPy composites with similar properties to those of the materials studied in Papers I–III. An alternative approach would be to produce the PPy composites using pre-formed paper sheets as substrates. In a related study, the approach used in this thesis (preparation of composites by chemically polymerizing PPy onto dispersed fibers) was compared with dip-coating polymerization, where Cladophora and commercial filter paper sheets were used as substrates. These substrates were first dipped in an aqueous solution containing pyrrole monomer and subsequently dipped in an aqueous solution containing FeCl₃, where polymerization onto the substrate occurred. In Fig. 20, the available charge capacity calculated from CV for these different materials are plotted against their PPy content calculated from elemental CHN analysis.

![Figure 20](image)

Figure 20. Specific charge capacity (total composite weight), calculated from CV at a 5 mV/s scan rate, as a function of the weight fraction of PPy in the composite, calculated from CHN analysis. The composites prepared from paper sheets are represented by squares and those prepared from dispersed fibers are represented by triangles. Dip-coated composites (squares in the figure) resulted in lower PPy concentrations and consequently lower specific capacities than dispersed fiber-based composites (triangles). Despite repeating the dip-coating process up to three times, the PPy weight fraction was still significantly lower than in the standard Cladophora composite (Clad_fibers-1). The approximately linear dependency of the specific capacity on the weight fraction of PPy for both polymerization methods suggests that the achieved conducting polymer was relatively insensitive to the polymerization method. It also suggests that the same fraction of the material was available for charge storage, most likely
close to 100%. This further indicates that there were no PPy regions in the composite electrodes that were inaccessible to counterions.

In an effort to increase the PPy mass loading of the standard Cladophora composite, syntheses were performed with double the amount of reactants, in one step (Clad_fibers-double) and by two consecutive polymerizations (Clad_fibers-2). As can be seen in Fig. 20, this had only a marginal effect on the PPy mass fraction of the composites. It therefore seems that there is an upper limit for PPy loading in the composites and that the material used in Papers I–III had a somewhat maximized PPy content (~67 wt %).

The PPy mass fraction in the composite in Paper IV was estimated as 0.7 by TGA. This method is, however, rather uncertain because of the simultaneous thermal decomposition of cellulose and PPy. However, 0.7 is still likely to be correct, based on the similarity of the synthesis conditions used in Paper I (see section 3.1.1 and 3.1.3). In Paper V, the more solid method of elemental CHN analysis was used to estimate the PPy weight fraction as 67.9–71.7 wt % for the different composites.

The PPy mass fractions reflect the available specific charge capacities in the composites, as can be seen in Fig. 20. The reported capacity, calculated from CV, in Paper IV was 289 C/g, whereas the corresponding values in Paper V were 212–226 C/g. This difference can be explained by the larger potential window considered in Paper IV, where the charge from the second (overoxidation) peak was included in the total charge.

Although numerous previous publications dealing with PPy on cellulose substrates exist,52, 54, 56, 57, 117-119 with a few of these reporting CV data,57, 118, 119 no specific charge capacities have been reported. However, the charge capacities found for the composites in Papers IV–V for wood-based cellulose fibers correspond well with those found in Papers I–III for Cladophora cellulose-based fibers.

The degradation experiments in Paper V showed that only minor degradation of the cellulose fibers occurred during composite synthesis. This indicates that the impaired mechanical integrity of the presented composite, compared to the standard Cladophora cellulose-PPy material discussed in Paper IV, is most likely not due to degradation of the cellulose fibers. It was found during the work with the synthesis conditions in Paper V that a low concentration of thoroughly dispersed (ultrasonicated) nanofibers was critical for achieving a continuous composite after drying.

During drying of the composites under ambient conditions in Papers IV–V, the structure collapsed, but to a varying extent. In Paper IV, a nitrogen BET surface area of 90 m²/g was found whereas, in Paper V, the surface area was below the detection limit for nitrogen adsorption for the ambient-conditions sample. The reason for this difference is not known but could possibly be related to differences in the cellulose fibers that were used in the two studies. It is also not known what caused the large surface area to be maintained in Cladophora cellulose-PPy composites dried under ambient
conditions (Papers I–III). It is possible that the larger dimensions of the Cladophora and the enzyme-treated cellulose fibers made these stiffer than the thinner TEMPO-NFC fibers, and that this influenced the morphology and ability to maintain porosity after drying.

The cellulose nanofibers, apart from providing a porous 3D scaffold, also served the purpose of mechanically reinforcing the brittle PPy. Although the composites dried under ambient conditions in Paper IV were not characterized mechanically, they were considered mechanically stable but brittle. In Paper V, tensile strength measurements of the samples dried under ambient conditions showed an average Young’s modulus of 0.51 GPa, an average maximum stress at break of 10.93 MPa and a strain-to-failure of about 2.5%. This is of the same order of magnitude as previously published results of cellulose-PPy composites with 55.5 wt % and 71.4 wt % cellulose, whereas the weight percentage of cellulose in the current study was significantly lower (9.0 wt %). Since chemically polymerized PPy forms a powder and therefore cannot, in itself, bear any load, the obtained mechanical properties are surprisingly good considering the low weight and volume fraction of reinforcing NFC.

The different drying techniques used in Paper V, previously applied to dry pure cellulose dispersions, were found to have a great influence on the morphologies of the obtained composites. The surface area of the supercritically dried CO₂ sample of 246 m²/g was the highest reported for cellulose conducting polymer composites. Drastically different surface areas and porosities were obtained for the samples dried under ambient conditions and those dried with CO₂. Differences were also observed in specific charge capacities from CV at different scan rates, where a drop in capacity was found for the compact (ambient conditions) sample but not for the porous (CO₂) sample. As the same charge capacity was observed at the lowest scan rate, the surface area of these composites, as expected, only influenced the oxidation and reduction rates, or the power density of energy storage devices utilizing these electrodes.

From a fundamental science point of view, these composites with different porosities can be used to study ion transport and assist in the interpretation of voltammograms. The shapes of the voltammetric peaks of conducting polymers are thought to be caused by the distribution of overlapping redox states as a result of different chain lengths. Additionally, the results presented in Paper V show that the shapes of the voltammetric peaks, especially the oxidation peak, are highly influenced by the mass transport of ions and their access to the PPy-layer.

It should be noted that, as the actual synthesis conditions were identical (the samples originated from the same synthesis batch, which was divided into four differently dried parts), it seems unlikely that the properties of the PPy chains themselves, such as length and degree of crosslinking, would differ significantly between the samples. Thus, for studies relating to mass
transport in conducting polymers, these composites with variable porosities and surface areas would complement electrochemically synthesized polymers, where the synthesis conditions are altered in terms of, for example, polymerization charge\textsuperscript{123-126} or choice of counterions\textsuperscript{127} to generate films of varying thickness and porosity. In particular, it can be difficult to electrosynthesize films with identical structural and electrochemical properties for repeated measurements,\textsuperscript{33} while the cellulose-PPy composites can be easily made in bulk quantities.
5. Future work

The presented concept of nanocellulose- and PPy-based energy storage with aqueous electrolytes is simple, environmentally friendly and cost effective. Synthesis processes resemble those used in cellulose and paper-making industries and should therefore be up-scalable. The rapid progress made in the field of organic solar cells, in terms of efficiency, stability and technical production, is also inspiring. In principle, conducting, polymer-based, energy-storage electrode materials could be printed in roll-to-roll processes similar to those used commercially for organic solar cells. There is, however, still a lot of work that needs to be done. A few key areas with respect to the results of this thesis are discussed below.

Energy density. The devices studied in this thesis are symmetrical, with PPy in both of the electrodes. This means that only half of the available charge in each electrode is utilized. An asymmetrical setup would lead to better utilization of the available charge capacity in the electrodes and would also offer the possibility of extending the voltage window to increase the energy density of the devices. Fundamentally, however, the degree of doping for common conducting polymers used for energy storage is too low, resulting in low energy density electrodes and devices, both volumetric and gravimetric. Work needs to be directed at increasing the energy density of PPy or exploring other polymers or organic compounds.

Stability. The literature on the performance limitations of conducting polymers is primarily based on empirical observations and not on a detailed scientific understanding. Though not presented in the thesis, efforts were made in our laboratory to study the degradation and self-discharge mechanisms of PPy. From in-situ ultraviolet/visible spectroscopy measurements, PPy is known to chemically degrade in aqueous electrolytes, even at low charging potentials, resulting in chain cleavage and degradation products such as maleimide. Although degradation is probably responsible for some of the lost charge on open circuit, it cannot account for all of the charge lost during the self-discharge process. Initial experiments with organic electrolytes did not improve the self-discharge of the positive electrode. If devices are to be made commercially available, the stability must be improved. The stable operation of light-emitting electrochemical cells, which in principle operate
in the same manner as the devices in this thesis, albeit with different applications, provides some promise.

**Electrode porosity.** The rapid transport of counter ions during oxidation and reduction associated with conducting polymers enables the use of high charging currents and results in devices that can be quickly charged. This was generally found to hold true for all the samples in this thesis. Real mass transport limitations were only discovered for the most compact sample in *Paper V*. The results of *Paper V* are encouraging in that they show that the porosity of the composites can be controlled. This means that an optimal porosity, one that allows good access to the electrolyte but with no excess free volume in the electrode, can be found. The porosity, or amount of free volume, of the Cladophora-PPy electrode material in *Papers I–III* was considered too large, potentially leading to an unnecessary build-up of volume and dead weight (water) in the electrodes and devices. Work directed towards finding the optimal electrode porosity and the preparation techniques needed to achieve this would be valuable for practical applications.

**Cell design/current collectors.** The graphite foils used in *Paper III* were found too resistive for practical application. If metal-free, carbon-based, environmentally friendly and fast-charging energy storage is desired, further work on cell design and new current collector materials are required.
6. Summary

Composites of cellulose nanofibers coated with the conducting polymer PPy by chemical polymerization of pyrrole in the form of a hydrogel are presented for application in electrical energy storage. The characteristic features of these composites are a high specific surface area, moderate bulk conductivity, a low weight proportion of the cellulose reinforcement material, rapid oxidation and reduction rates, and a high degree of utilization of the available PPy material.

Symmetrical energy storage devices with aqueous electrolytes were assembled. These showed capacitor-like behavior and specific electrode charge capacities and capacitances similar to literature values on other PPy-based energy-storage systems. The performance of laboratory-scale devices, un-optimized in terms of reducing dead weight, placed them in the region of electrochemical capacitors in the Ragone plot. The devices appeared stable compared to similar devices with aqueous electrolytes in the literature, during both galvanostatic and potentiostatic repeated charging and discharging. The self-discharge of devices left at open circuit was, however, rapid.

The main advantages of the presented electrical energy storage devices based on nanocellulose and PPy are the simple, up-scalable and potentially cost-effective production process; the safe, metal-free and environmentally friendly system; and the mechanical strength, controllable porosity and moldability offered by the cellulose matrix material.

Principal findings

• The concept of nanocellulose-based conducting polymer composites as electrodes in electrical energy-storage devices was introduced and functional devices were presented.

• Galvanostatic charging and discharging of the devices was relatively insensitive to the positive cell potential cutoff. This was traced back to the loss of conductivity of the fully reduced negative electrode. Most of the cell potential was, thus, over the negative electrode and the positive electrode potential was thereby limited to values below critically degrading potentials.
• Potentiostatic charging and discharging of the devices was demonstrated. Charging was very efficient; the minimum charging time of the devices was controlled by the RC time constant of the cells.

• The devices were charged very quickly at the smallest lab scale, while larger lab scale devices highlighted the need for more sophisticated cell designs to reduce the total cell resistance and, subsequently, the charging times.

• There were no indications that the resistance of the devices studied in this thesis was limited by the insulating nature of the cellulose matrix material.

• The first wood-based nanocellulose and PPy composite was demonstrated. This had properties similar to those of the algae-based nanocellulose-PPy composites used as electrodes in the energy storage devices.

• TEMPO-oxidized wood-based nanocellulose fibers showed only marginal reductions in viscosity after acid and oxidant treatment. This indicates that there was only marginal degradation of the cellulose nanofibers and, in turn, that the polymerization conditions used during composite synthesis should not be critically detrimental to the cellulose fibers.

• The first attempt to produce nanocellulose and PPy composites with tunable structural and electrochemical properties was reported. By varying the methods of drying PPy-coated nanocellulose fibers from the hydrogel it was possible to control the surface area and porosity of the conducting polymer-nanocellulose composite material.

• The highest specific surface area (i.e. 246 m$^2$/g) for a cellulose and conducting polymer composite reported to date was achieved by changing the PPy-coated nanocellulose hydrogel solvent to ethanol followed by supercritical CO$_2$ drying.

• Cyclic voltammetry of samples from the same synthesis batch but with different porosities provided information about the influence of porosity on the cyclic voltammetry peaks. The results suggested that the shape of the oxidation peak is strongly influenced by the mass transport of counterions and their access to the PPy layer.

• Nanocellulose-PPy composites that had been dried under ambient conditions had similar tensile strengths to those of samples with significantly higher reinforcing cellulose weight fractions in the literature. Thus, our
samples, normalized by cellulose weight, are the strongest cellulose-PPy composites produced to date.

År 2000 tilldelades Alan J. Heeger, Alan G. MacDiarmid och Hideki Shirakawa nobelpriset i kemi för deras arbete med ledande polymerer.


Syftet med den här avhandlingen har varit att studera kompositer av nanocellulosa och PPy och dessas användning som elektrodmaterial för elektrisk lagring av energi. Nanocellulosan har extraherats från grönligen Cla-

För de träbaserade PPy-nanokompositerna erhölls liknande egenskaper som för de algbaserade kompositerna. Detta är ett viktigt tekniskt resultat eftersom trä utgör den huvudsakliga råvaran för dagens cellulosaframställning. Fördelen med att använda fria nanocellulosafibrer, för beläggning av den ledande polymeren, jämfört med ett redan format pappersark är att processen med de fria nanofibrerna i vattenlösning möjliggör att erhålla en högre viktsprocent ledande polymer i det färdiga kompositmaterialet. Detta är viktigt i exempelvis batterisammanhang då en högre viktsprocent ledande polymer innebär att en större mängd laddning per vikt kan lagras i batteriet.

Generellt sett kan man säga att de elektriska egenskaperna och mängden laddning som kan lagras i kompositen styrs av den ledande polymeren medan strukturen och de mekaniska egenskaperna styrs av nanocellulosan. I ett av delarbetena i avhandling visar vi att det, genom att variera sättet som de träbaserade PPy-nanokompositerna torkas på, går att påverka porositeten (volymandelen av materialet som utgörs av tomrum) och areaen av den mångd mikroskopiska ytan. För de kompakta proverna ser vi då begränsningar i hur snabbt det går att ladda upp och ur materialet. Detta betyder att cellululosan i det här fallet faktiskt påverkar den tillgängliga laddningsmängden vid en given laddningshastighet. De kompakta materialen visar, å andra sidan, på en hög dragstyrka vid en förhållandevis liten viktsprocent förstärkande nanocellulosafibrer. Genom kontrollerad torkning tillverkades också högporösa ledande kompositer där endast 5% av den totala volymen utgjordes av fast material.
8. Acknowledgements

I would like to thank everyone who has supported me throughout this study and especially:

Professor Maria Strømme, Department of Engineering Sciences, my supervisor, for introducing me to the exciting field of nanotechnology, for your inspiring positive attitude and work ethics, and for your warm, generous support.

Professor Leif Nyholm, Department of Materials Chemistry, my co-supervisor, for introducing me to the field of electrochemistry, for always taking the time to discuss results, and for your serious yet lighthearted approach to research.

Associate Professor Albert Mihranyan, Department of Engineering Sciences, for introducing me to the field of cellulose research, and for your innovative thinking towards materials research.

Dr. Martin Sjödin, Department of Engineering sciences for showing great interest in this study, and for fruitful scientific discussions and sound advice.

Professor Lars Berglund, Department of Fiber and Polymer Technology, Royal Institute of Technology, for showing interest in my work, for helpful collaboration, and for allowing me to work in your laboratory.

Associate Professor Qi Zhou, School of Biotechnology, Royal Institute of Technology, for valuable discussions and help with the studies of cellulose degradation.

My other coauthors Mr. Daniel O. Carlsson, Department of Engineering Sciences, Professor Tom Lindström, Innventia AB, Mr. Henrik Olsson, Department of Engineering Sciences, and Dr. Aamir Razaq, Department of Physics, COMSATS Institute of Information Technology, for your contributions to this study.
Dr. Alfonso E. Garcia Bennett, Department of Engineering Sciences, for generously investing your time, and for guiding and helping me with the TEM work on our materials.

Mrs. Maria Melin, Mrs. Maria Skoglund, Mrs. Ingrid Ringård, Mr. Jonatan Bagge and Mr. Enrique Carrasco at the Department of Engineering Sciences for help and support in various ways.

Mrs. Antona J. Wagstaff, for revising the English text.

Colleagues at the Nanotechnology and Functional Materials Division, Department for Engineering Sciences, for creating a great working atmosphere.

My family for your love and support.

The studies were supported by grants from the Swedish Foundation for Strategic Research (SSF) (grant RMA08-0025), the Swedish Science Council (VR), the Bo Rydin Foundation and the Nordic Innovation Centre (contract number 10014).
9. References


Acta Universitatis Upsaliensis

Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology 898

Editor: The Dean of the Faculty of Science and Technology

A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology.

Distribution: publications.uu.se
urn:nbn:se:uu:diva-168664