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**Nafion-PolyBenzImidazole (PBI) Composite Membranes for DMFC Applications**

Research project

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Abbreviations:

BP – boiling point
DAB – diaminobenzidine (3,3’,4,4’-tetraaminobiphenyl)
DMF – dimethylformamide
DMFC – direct methanol fuel cell
DMSO – dimethyl sulfoxide
EtOH - ethanol
FC – fuel cell
IR – infra-red
MeOH - methanol
NMR – nuclear magnetic resonance
PBI – polybenzimidazole
PEM – polymer electrolyte membrane
PEMFC – polymer electrolyte membrane fuel cell
PPA – polyphosphoric acid
RT – room temperature
SOFC – solid oxide fuel cell
TGA – thermogravimetric analysis
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1. Introduction

1.1 Fuel cell history in brief

The beginnings of the fuel-cell saga date back to the first half of the 19th Century, when the British scientist Sir William Robert Grove, using his knowledge of electrolysis, proposed the possibility of a reversal reaction. His simple experiment with hydrogen and oxygen gases, platinum strips and dilute sulfuric acid as electrolyte led to the first “gas cell”, as he called the earliest ancestor of today’s fuel cell [1]. Much of the theoretical understanding of early fuel cells was generated by the Estonian scientist F.W. Ostwald, who struggled with the puzzle of Grove’s gas cell. Already at the end of 19th Century, he speculated that future energy production could rely on electrochemistry [2]. However, the practical importance of fuel cells remained hypothetical until the middle of 20th Century, when Dr. Francis Bacon at Cambridge University, England designed his first alkaline fuel cell. In 1958, after 27 years of improvements, Bacon’s machine was able to yield 5kW of power [1]. It was an essential milestone in fuel-cell history, attracting a lot of attention and generating new interest to the research field. Developments during the following decades led to new fuel cell concepts feasible for large-scale energy production, e.g., the phosphoric acid fuel cell power plant in Tokyo produces 11MW of electrical power. However, these types of fuel cell have yet to become important in today’s energy production technologies[2].

Another significant chapter in the fuel-cell story began in the 1960s, when Grubb and Niedrach from General Electric developed the sulfonated polysterene membrane fuel cell for the NASA Gemini spacecraft [4]. Although this fuel cell had a very short lifetime and low specific power, it marked the beginning of the era of polymer electrolyte membrane fuel cells (PEMFCs) [1]. Probably the most significant landmark in PEMFC history was the development by du Pont in the 1960’s of the novel ion-exchange membrane known as Nafion®. After more than two decades and numerous attempts to create alternative materials, Nafion still remains as the prime proton conducting polymer, through its superior combination of conductivity and stability. Nevertheless, Nafion is still not flawless; it is expensive, it has a low operating temperature limit, and a relatively high fuel permeation. These are factors which still limit its large scale use in the energy sector.
In the mid-1990s, growing ecological concerns and the almost disastrous energy situation in many over-populated regions of the World, as well as the increasing need for better energy sources for small devices like laptops and mobile phones, etc., have boosted more activity in the field of fuel cell science. This has resulted in the advent of the promising new technology in the direct methanol fuel cell (DMFC). The drive to improve the performance of both PEMFC and DMFC technologies for commercial applications has led to concerted international research effort to develop new fuel-cell components – including polymer membranes, electrode morphologies and catalysts.

1.2 The principle of a fuel cell

Our conventional way of energy production from chemical fuels exploits combustion engines, which means that the potential energy stored in molecular structures is converted to the kinetic energy of tumbling molecules (heat), and this heat flow is used to power engines. Unfortunately, this kind of device must follows the laws of thermodynamics, which do not permit high yields. However, this problem can be circumvented when the chemical energy is converted into electrical energy directly, without the thermal step. This kind of direct energy conversation is performed electrochemically in fuel cells and batteries.

![Fuel Cell Diagram](image)

**Figure 1.1** The fuel cell principle.

In principle, fuel cells are very similar to ordinary batteries. The only difference is that batteries store the energy inside the electrode materials, whereas fuel cells are supplied externally by gaseous or liquid fuels, which means that batteries must be re-
charged or replaced after depletion, while fuel cells can operate as long as fuel is provided. Like batteries, all fuel-cell types contain two electrodes, an anode and a cathode, and an electrolyte separating them (Figure 1.1). The anode and cathode are where the electrochemical reaction take place - fuel oxidation and oxygen reduction, respectively, while the electrolyte must be a selective medium preferentially facilitating transport of one type of charge carriers, thereby forcing the electrons to move through the external circuit and produce electric energy.

Figure 1.2 Examples of fuel-cell applications. (A) Motorola 1W miniature DMFC battery charging application IMPRES™ (Nafion membrane FC) [3a]. (B) Toshiba 100mW, the World’s smallest, (announced 2004) miniature DMFC for mobile phones and MP3-players (8.5g, fuel 99% MeOH) [3b]. (C) Ford Focus FC5, methanol fuel cell car, polymer electrolyte FC with methanol reformer [3c]. (D) Mercedes-Benz fuel cell bus [3d]. (E) General Motors 75kW stationary hydrogen FC unit (average energy for 50 average homes) [3e]. (F) Siemens SOFC 220kW. (Fuel is natural gas; 53% efficiency; for comparison, the efficiency of a diesel engine is 35%) [3f].
Table 1.1. Different types of fuel cell [2].

<table>
<thead>
<tr>
<th>Type</th>
<th>Electrolyte</th>
<th>T (°C)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline fuel cells</td>
<td>40-70% KOH solution</td>
<td>60-240</td>
<td>eg., used in US space shuttles</td>
</tr>
<tr>
<td>Medium-temperature phosphoric acid fuel cells</td>
<td>85-95% H₃PO₄ solution</td>
<td>180-200</td>
<td>Both autonomous energy sources (250kW) and power plants (up to 4MW)</td>
</tr>
<tr>
<td>High-temperature molten carbonate fuel cells</td>
<td>Mixture of sodium, potassium and lithium carbonates</td>
<td>~650</td>
<td>Power plants (up to 0.5MW)</td>
</tr>
<tr>
<td>High-temperature solid-oxide fuel cells</td>
<td>Zirconium dioxide doped with other metal oxides (like yttrium)</td>
<td>800-1000</td>
<td>Power plants (up to 100kW)</td>
</tr>
<tr>
<td>Proton-exchange membrane fuel cells</td>
<td>Polymer proton-exchange membrane</td>
<td>60-100</td>
<td>Autonomous applications</td>
</tr>
</tbody>
</table>

In addition to this more efficient and environmentally friendly energy production, fuel cells have also attracted attention because of their potential lightweight, low noise level and high energy density for autonomous devices - from mobile-phones to cars (Figure 1.2). Different demands have also led to the development of different type of fuel cell (Table 1.1) – high temperature fuel cells mostly for large-scale energy production and PEMFC for autonomous applications.

1.3 The Direct Methanol Fuel Cell (DMFC)

The Hydrogen Economy is one of the most significant goals of fuel-cell development. However, the handling of gaseous hydrogen is inconvenient, even for small-scale autonomous applications, and this has inspired the development of fuel cell concepts using liquid fuels. Unfortunately, fuels other than hydrogen are much more troublesome from an electrochemical point of view. Some technical solutions use reformers to convert hydrocarbons or alcohols into the more appropriate hydrogen, but reformers are not perfect and introduce inefficiencies in the form of incomplete chemical reactions and heat generation. Instead, direct fuel oxidation on at the fuel-cell electrode would increase efficiency, technical simplicity and allow miniaturization for devices like mobile-phones, etc. Anyhow, general methods for electrochemical fuel oxidation at moderate temperatures have unsolved problems. The most promising results have been achieved with methanol, that does not contain any carbon-carbon bonds which are difficult to break. The disadvantage of methanol is its harmful com-
bination of toxicity and volatility, which may well hamper future usage in everyday technologies. Nevertheless, methanol is still attractive because of its high energy content: 1 kg of methanol contains 6000Wh [5], which is approximately 10 times more than the theoretical maximum for state-of-art lithium-battery storage [6].

The typical DMFC is a polymer electrolyte fuel cell comprising an electrolyte membrane and two electrodes. Most of the technical solutions use hydrated Nafion as a membrane and Pt alloy catalysts (3-5nm particles) on a carbon-supported polymer matrix as electrodes [7]. The electrodes must be porous to have a sufficiently large active area to allow the fuel and oxygen diffusion, as well as being electronically conductive; whereas the membrane must be a good proton conductor but be an electronic insulator [4].

The electrochemical methanol oxidation occurs on the anode, where a Pt-Ru alloy is used as a catalyst. Eventhough the exact mechanism of this catalysis is unknown [5], it is reasonable to think about it as a binary mechanism (Figure 1.3), where methanol is absorbed on the Pt surface that facilitates cleavage of the C-H bonds, leading finally to the formation of carbon monoxide. Since CO absorption on Pt is exothermic, it reduces the active area of catalyst and thus diminishes the reaction rate. However, it has been found that the presence of ruthenium facilitates the reaction, which uses water oxygen for oxidizing CO to CO₂, liberating the catalyst and increasing activity. This mechanism is also in agreement with the findings from the realm of hydrogen fuel cells, where Ru additives improved catalyst activity, when used with technical hydrogen - containing CO. The net result of this catalytic cycle is that one molecule of methanol and water is converted to six protons and electrons.

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \rightarrow 6\text{H}^+ + 6\text{e}^- + \text{CO}_2 \text{ (anode)} \\
4\text{H}^+ + 4\text{e}^- + \text{O}_2 & \rightarrow 2\text{H}_2\text{O} \text{ (cathode)}
\end{align*}
\]
Figure 1.3. Methanol oxidation at the DMFC anode; and the catalytic cycle of the Pt-Ru catalyst. Many parallel pathways can exist, depending on which protons are removed first.

Figure 1.4. Example of alternative oxygen catalysts. A biologically inspired porphyrin catalyst. Oxygen bonding together two Fe ions (right)

On the cathode side, oxygen is reduced on the Pt catalyst, followed by combination with the protons, which finally results in water. Unfortunately, the protons are not the only moieties which can travel through membrane; some methanol leaks through
and, since Pt is active to methanol, absorption and electrochemical reactions can occur, which result in loss of fuel, reduction of active catalyst area, but also mixing of potentials, which reduces cell voltage. Putting this together, only small methanol permeation (known also as methanol crossover) can result in significant loss of DMFC efficiency. Many attempts have been made to overcome this problem. These include new and modified membrane materials (new polymers, as well various composites involving SiO₂ particles, polymer blends, etc.), but these materials are often either unstable or exhibit much lower conductivities. New oxygen catalysts insensitive to methanol are therefore of great interest (Figure 1.4) [8].

1.4 Polyelectrolyte membranes

As mentioned, the purpose of the membrane is to separate electronically the electrodes and the reactants, while facilitating transport of protons. With some exceptions, the majority of these membrane are gels, swollen in water, which basically limits their usage to under 100°C. Also, all of them carry strong sulfonic acid groups that donate their protons to the water phase, giving rise to hydronium (H₃O⁺) ions. Proton transport itself in these systems could be explained by two mechanisms; one is the so-called vehicular transport, while the other is Grotthus proton jumping. In principle, vehicular transport is the classical diffusion of a hydronium ion in a porous gel. Grotthus proton jumping is more specific: when an hydronium ion is inserted into the water, it can hand over its proton to another water molecule, which means that the hydronium ion can move without displacement of oxygen (Figure 1.5). However, rotational motion of the water molecules is needed to reestablish the initial situation and complete the cycle, which implies that excessively strong hydrogen bonding (hindered rotation) would not contribute to the proton transport.

![Figure 1.5. Grotthus proton transport](image)

In addition to the proton conductivity, fuel cell operation constitutes very demanding requirements for materials. The environment inside the membrane is aqueous, strongly acidic and holds a relatively high temperature. Furthermore, peroxides are formed as side products on the catalysts. This is fatal for all kinds of aliphatic
hydrocarbons, due to oxidative attack and chain-cutting. For example, sulfonated polystyrene membrane fuel cells first had very short lifetimes. Instead, fluorination makes aliphatic carbon chains very stable to oxidative degradation [4], which is the reason for the development of different fluorinated polymers for FCs (Figure 1.6 a,f). Nafion is unquestionably the most famous example of polytetrafluoroethylene backbone PEM materials. Another class of sufficiently stable polymers is the aromatic polymers with an aromatic backbone [4] (Figure 1.6 b,c,e); for example, poly(arylene ether) (Figure 1.6 e) and polybenzimidazoles [9] (Figure 1.6 b). More exotic are the silicates (Figure 1.6g) and phosphazenes (Figure 1.6 d).

Besides chemical stability, materials must also be mechanically strong. In gels, the strength is dependent on the cross-linking, which can be either chemical or physical. Prevalently, these polymers are physically cross-linked by non-sulfonated regions in their chains, which are usually more hydrophobic and cause the formation of hydrophobic clusters. Thus, fine tuning of the molecular structures (number and distribution of sulfonic acid groups as well as chemical cross-linkers) is needed to achieve the best combination of proton transport, fuel impermeability and mechanical strength.

![Figure 1.6. Examples of chemical structures of different polyelectrolyte membrane materials.](image)

*Figure 1.6. Examples of chemical structures of different polyelectrolyte membrane materials.*
a) Nafion, b) sulfonated PBI, c) poly(1,4-phenylene), d) poly(phosphazene), e) poly(arylene ether), f) BAM, and g) a silicate.
1.5 Our aim to improve fuel-cell performance

The aim of the present work has been to improve membrane performance for DMFCs applications. We have attempted the design of sufficiently stable material that would exhibit a higher ratio of proton conductivity and methanol permeability. The well-known Nafion membrane has been used as starting material to modify and incorporate another polymer, polybenzimidazole (PBI), into its gel structure.

The idea of Nafion-PBI composite arose from considerations of proton transport mechanisms. The proton can travel in the pores using the two possible mechanisms. Regarding hydronium diffusion, it is hard to design a sufficiently selective material which would trap methanol but pass hydronium, since both are rather similar. However, the Grotthus mechanism could not facilitate methanol transport. The Grotthus mechanism does not need the displacement of water, but only rotational fluctuations, to pass on the protons. Nevertheless, it is difficult to immobilize water molecules in this way, but water is not the only substance that could facilitate the Grotthus proton transport; for instance, imidazoles also exhibit a very similar nature to water in this sense [10] (Figure 1.7). The drawback of using imidazoles as a proton conductive medium is their more hindered rotation, which decreases proton conductivity by roughly an order of magnitude at the same temperature, and needs a higher temperature to achieve the same conductivity as a water system. The advantage of the imidazole system is the easy way it can be immobilized by incorporating it into some polymer. These imidazole polymers maintain their rotational mobility, but are left without the freedom to diffuse far from their initial position. Also, acid-base interaction between the acidic Nafion and the basic PBI could show some interesting properties; PBI also possess very high thermal, hydrolytic and oxidative stability [9]. All these factors have inspired us in this research.
Figure 1.7. Grothuss type proton transport in the imidazole system; the important steps are proton jumps (A,B,C) and rotational tumbling (D), in order to restore the initial situation.
2. Results and discussion

2.1 Synthesis of polybenzimidazole (PBI)

PBI 3 is a fully aromatic polymer with basic character, due to the nitrogen-containing heterocycles. The PBI is usually synthesized by polycondensation of di-aminobenzidine 1 (DAB) and isophthalic acid 2, or its esters (Figure 2.1). Since the result is an aromatic structure, the product should be thermodynamically favorable and stable. Eventhough PBI can be synthesized in a one-step synthesis, this does not imply that the reaction is spontaneous and can proceed under any conditions.

The elementary reaction between two monomer units should occur as depicted in Figure 2.2. First, the acid-catalyzed step of polycondensation leads to the formation of the amide, which reacts further and forms imidazole ring. During the addition of one monomer unit two molecules of water are liberated. To facilitate the reaction, the medium should be acidic and contain some water-absorbing agent to avoid reversibility in intermediate steps. Once formed, the finally product is stable even in aqueous conditions. However, from the experimental results, we can conclude that the reaction has relatively high activation barrier, since elevated temperatures and long reaction times are needed.

![Figure 2.1. The synthesis and structure of PBI.](image)
We have compared and modified different synthetic procedures found in the literature (Table 2.1)

<table>
<thead>
<tr>
<th>Solvents and additives</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyphosphoric acid (PPA)</td>
<td>16-24</td>
<td>190-220</td>
<td>11</td>
</tr>
<tr>
<td>P₂O₅, CF₃SO₃H, CH₃SO₃H</td>
<td>0.5</td>
<td>150</td>
<td>12</td>
</tr>
<tr>
<td>Sulfolane</td>
<td>72</td>
<td>Reflux (285)</td>
<td>13</td>
</tr>
</tbody>
</table>

Under the described conditions, the polyphosphoric acid strategy yielded a dark brown polymer, which was later identified as being of good quality PBI. However, using the triflic and methanosulfonic acid strategy, we obtained materials which were found to be a starting material (isophthalic acid), according to its IR spectrum. One reason for this failure could be the low water absorption of P₂O₅. Instead, attempts with sulfolane resulted a black solid (116% yield), which was totally insoluble in both DMSO and DMF; neither did it show the characteristic peaks in the IR spectrum. One explanation could be sulfolane “cracking”, which leads to the formation of dark polymer and SO₂ at temperatures above 220°C [14]. Even at lower temperatures, we observed a similar problem. From a mechanistic point of view, all strategies contain a water absorbing agent and an acid catalyst, except the sulfolane strategy, which instead needs a much higher temperature and longer reaction time. We thus chose polyphosphoric acid as the most promising solvent for the larger scale synthesis of PBI.
However, different times and temperatures were also observed to affect the results with polyphosphoric acid (Table 2.2). Excessively long reaction times seem to lead to cross-linking.

**Table 2.2.** The influence of reaction conditions on the product. The second procedure resulted in material that was the most appropriate for the subsequent studies.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>210</td>
<td>Before quenching the reaction mixture was dark brown and very viscous and gummy. Product was only partially soluble in refluxing DMSO, some gel-like particles remained insoluble.</td>
</tr>
<tr>
<td>17</td>
<td>200</td>
<td>Before quenching the reaction mixture was dark red and viscous. Product (80%) was brown solid, which was soluble in DMSO.</td>
</tr>
</tbody>
</table>

The best synthesis procedure found was the following:

DAB, isophthalic acid, PPA, and ammonia solution were all purchased from Sigma-Aldrich and used as received; glassware was dried in an oven at T>100°C.

**Polybenzimidazole (PBI), 3.** All glassware was dried; 1g DAB, 776mg isophthalic acid and 20g PPA were weighed before mortaring and mixed thoroughly to obtain a homogeneous dispersion. This was loaded into a round-bottom flask fitted with a magnetic stirrer and septum. Slow N₂ flow was applied through needles. After stirring for 17h at 200°C, the reaction mixture turned dark red and became viscose. The reaction was quenched by pouring the hot solution into a large amount of cold water. The fibers formed were stirred for 48h in water and 7h in 300mL of a 10% NH₄OH solution, and then dried in oven at 100°C for 10h. The 80% product was obtained as a dark brown solid. The presence of PBI was proven, and some of its properties were characterized by NMR and FT-IR.

**PBI solution.** A round-bottomed flask was fitted with a magnetic stirrer and a reflux condenser. The flask was charged with DMSO and 1 wt. % (relative to DMSO) ground PBI. The mixture was refluxed until all PBI was dissolved (~1h); 1 wt. % PBI solution was obtained as an orange liquid.
2.2 NMR characterization of PBI

NMR spectra were recorded on a JEOL Eclipse+ 400 (\(^1\)H 400MHz; \(^{13}\)C 100MHz) in deuterated DMSO with the solvent proton as an internal standard. Because of the lack of a good reference for the NMR spectra of PBI, we decided to carry out a full peak assignment. To assist the assignment of the \(^1\)H spectrum, the COSY spectrum was also recorded, as well spectra of the starting materials. We also attempted to record the HSQC spectrum to assign the carbon peaks but, during a reasonable time, we were unable to achieve a sufficiently good signal-to-noise ratio. All labels in the following assignments are according to Figure 2.3.

Figure 2.3. Proton labels.

Starting materials:

**DAB, 1.** \(^1\)H NMR (400MHz, (CD\(_3\))\(_2\)SO) \(\delta\)\(_H\) 6.69 (d, \(J\approx 1.96\)Hz, 1H, H\(_{1a}\)), 6.55 (dd, \(J\approx 1.96\)Hz, 8.0Hz, 2H, H\(_{1b}\)), 6.50 (d, \(J\approx 8.0\)Hz, 2H, H\(_{1c}\)), 4.44 (s, 4H, -NH\(_2\)), 4.37 (s, 4H, -NH\(_2\)) \(\delta\)\(_C\) 112.8, 115.4, 131.5, 133.9, 135.6.

**Isophthalic acid, 2.** \(^1\)H NMR (400MHz, (CD\(_3\))\(_2\)SO) \(\delta\)\(_H\) 13.28 (s, 2H, -COOH), 8.48 (d, \(J\approx 1.65\)Hz, 1H, H\(_{2a}\)), 8.16 (dd, \(J\approx 1.65\)Hz, 7.64Hz, 2H, H\(_{2b}\)), 7.64 (t, \(J\approx 7.64\)Hz, 1H, H\(_{2c}\)) \(\delta\)\(_C\) 129.7, 130.5, 131.8, 134.0, 167.2.

The proton spectra (Figure 2.4) of PBI were interpreted as following: the very high chemical peak-shift (>13ppm) corresponds to the protons connected to the aromatic nitrogen. The next peaks can be identified by the COSY spectrum (Figure 2.6), where we can see a strong coupling between two pairs of protons, which should correspond to H\(_{3b}\), H\(_{3c}\) and H\(_{3e}\), H\(_{3f}\). However, knowing the integrals and the number of protons in the polymer repeat unit, we can separate them. Proton H\(_{3a}\) could also be identified by COSY. The remaining signals overlap and separation was aided by the mathematical procedure of *deconvolution* as performed by the spectrometer software;
peak 8.05ppm was found not to belong to the PBI structure. On the lower chemical-shift region of the spectrum, we can find small peaks similar to peaks found in the DAB spectrum. We therefore connected them to the end-groups and to remaining starting material. The comparison between integrals of end-groups and repeat units gave us approximate estimates of the average length of the polymer chains (so-called end-group analysis).

Figure 2.4. The $^1$H NMR spectrum of PBI.

Figure 2.5. The $^{13}$C NMR spectrum of PBI.

Figure 2.6. COSY spectrum of PBI.
**PBI, 3.** The proton chemical shifts, $^1$H NMR (400MHz, (CD$_3$)$_2$SO) $\delta_H$, are 13.28 (s, 2H/repeat unit, N-H), 9.16 (s, 1H/repeat unit, H$_{3a}$), 8.34 (m, 2H/repeat unit, H$_{3b}$), 7.84 (m, 2H/repeat unit, H$_{3c}$), 7.8 (m, 1H/repeat unit, H$_{3d}$), 7.69 (m, 2H/repeat unit, H$_{3d}$), 7.63 (m, 2H/repeat unit, H$_{3e}$), 7.41 (m, 2H/chain, H$_{3k}$), 6.68 (m, 2H/chain, H$_{3l}$). The ratio of peaks indicates that the average chain-length is approximately 40 repeat units. The traces of starting materials are negligible (less than 1%).

The carbon chemical shifts, $\delta_C$, are 110.1, 112.4, 117.6, 119.8, 122.5, 128.1, 130.3, 131.5, 136.9, 143.7, 145.2, 152.0, 155.0.

**2.3 Attempts to synthesize PBI in situ**

After succeeding to synthesize PBI, we attempted to create a method for the *in situ* synthesis in the Nafion pores. We used the following setup: a Nafion membrane was placed between two chambers, which were loaded with different solutions of monomers, one with DAB, another with isophthalic acid. The synthesis was performed under N$_2$. We varied the temperature from 150 to 210$^\circ$C and used a 65h reaction time. Reactions were quenched as earlier (2.1). At lower temperatures, we achieved a membrane that was very dark where it was in contact with the solutions. The solutions were both dark after removal, which could also indicate some permeation of components. Surprisingly, when higher temperatures were used, the resulting membrane was pale brown, and the solution on the isophthalic acid side was observed to be brownish-gray, indicating that DAB has not diffused through. On the DAB side, the solution was very viscose and dark, which can be result of isophthalic acid permeation and polymerization.

The characterization of the result product turned out to be troublesome. At first, we tried to compare different parts of the membrane with ATR-IR spectroscopy. But areas suspected to be with and without PBI exhibited almost identical spectra, the only difference was slightly shifted SO$_3$ symmetrical-stretching in Nafion (1056cm$^{-1}$ and 1054cm$^{-1}$ without and with additive, respectively). The spectral region associated with the H$_3$O$^+$ ion (around 1700 cm$^{-1}$) also exhibited some differences (Figure 2.7), which could indicate different water states. Additional subtle features were found at 2854 and 2924 cm$^{-1}$, where Nafion not treated with the solutions but quenched like rest of the membrane exhibited some small peaks. However, treated Nafion as well as the untreated one did not exhibit these peaks, which most resembled the CH$_3$ stretching
vibrations. However, the presence of CH$_3$ is hard to explain in the context of the synthesis performed. NH$_4^+$ - which could be a much better candidate - has usually absorption bands at slightly higher frequencies.

Another method used to study the materials was thermogravimetric analysis (TGA) performed on a TA Instruments Q500 (temperature ramp-rate: 20°C/min; maximum temperature: 900°C). The results for pure Nafion (Figure 2.8) and pure PBI (Figure 2.9) were comparable with previous findings by Samms et al. [15,16]. Decomposition of Nafion started slightly above 300°C and, before 600°C, all material had degraded. PBI showed slight degradation around 600°C. However, around 80% of the mass still remained at 900°C.

When the composite was burnt in the TGA experiment, the degradation pattern resembled that of Nafion, but after reaching the point (600°C) where pure Nafion had vapourized completely, 4.3 wt % of the original composite still remained. The remains were ground, dispersed in KBr, and studied by IR spectroscopy. The residuals of pure PBI after thermal treatment gave a spectrum similar to that of untreated PBI, but the spectrum of the residuals of the composite resembled neither PBI nor Nafion. We could therefore not make any certain analysis of the composition of the material, which was also one of the reasons for discarding the idea of in-situ synthesis and trying alternative ones. Also, our set-up did not permit the production of membranes large enough for further characterization of performance.
Figure 2.7. IR spectra of Nafion, with the interpretation according to Tan et al.\cite{17}. Processed and unprocessed Nafion correspond to the parts of membrane that have and have not been in contact with reagents, respectively.

Figure 2.8. Nafion degradation in TGA

Figure 2.9. PBI degradation in TGA
2.4 Casting the Nafion-PBI blend

Recasting from DMSO was tested at 175°C (slightly below the BP of DMSO) for 15h. When the glass plate carrying the film was immersed in water, the membrane could be easily removed. After a simple chemical cleaning procedure (as in 2.5), the recast membrane resembled the as received Nafion membrane: transparent, pliable, strong and stable in water. However, since we lacked hot-pressing equipment, we were unable to achieve a homogeneous thickness, and therefore could not characterize the membrane performance in terms of MeOH crossover and proton conduction.

Another method to create polymer composites is by casting a mixture of their solutions. This necessitates that we have both polymers in solution phase. PBI was dissolved as described above (2.1). However, dissolving Nafion is not as straightforward a process as dissolving PBI - we used a method developed by Martin et al. [18]: a glass tube equipped with a magnetic stirrer was charged with 300mg of purified as received Nafion, and 30mL of a 50:50 ethanol:water mixture was added. The tube was placed to a high-pressure reactor (a steel vessel with an inert Teflon® interior). The reactor was sealed, the top was covered with insulating layer, and placed on a laboratory hot plate (at 260°C). After stirring for 4h, the reactor was left to cool. The derived solution (average concentration c ≈ 10mg/mL ≈ 1%) had a strong smell of diethyl ether.

The obtained solution was tested in a simple casting experiment. The solvent was evaporated at 100°C, after which we attempted to remove the film from the glass plate by immersing it in water. However, the dipping process caused the membrane to lose its mechanical integrity - and fell into pieces. This same behaviour was also observed by Moore III et al. [19,20], who found that the mechanical properties are related to the existence of small crystalline domains in the Teflon backbone [21]. To form the crystalline part, the membrane must be cast at elevated temperature (around 200°C) or annealed. We therefore attempted to cast from DMSO instead. A Nafion-DMSO solution was prepared as follows: a distillation apparatus was loaded with equal amounts of DMSO and a Nafion EtOH:water solution, and stirred with a magnetic stirrer. The bath temperature was set to 140°C, and distillation was complete when the temperature of the vapour began to decrease.
We were also interested in studying the properties of the composite membranes. However, difficulties were experienced when attempting to mix the DMSO solutions of Nafion and PBI: since one of them is basic and the other acidic, the strong acid-base interaction caused the polymer chains to cross-link (Figure 2.10) - appearing as gel particles in the flask, which remained insoluble even on continuous DMSO reflux.

![Figure 2.10. Acid-base interaction (left) and cross-linking of polymer chains (right).](image)

However, this was overcome by screening the acidic sites of Nafion. When the Nafion solution was pretreated with diethyl amine, the solutions mixed without difficulty. The stronger diethyl amine base blocks the -SO₃ groups to PBI, so that the polymers no longer cross-link.

### 2.5 Composites by dipping Nafion into PBI solutions

Further approaches to assemble a Nafion-PBI polymer composite (following in situ synthesis and recasting) were: the infusion of solution-phase PBI into pores of solid Nafion; and the creation of laminate structures in which Nafion and PBI layers are deposited on the surface of an original Nafion membrane. We here used pre-cleaned Nafion 117 membranes and DMSO solutions of PBI. Nafion was cleaned using procedure by Ludvigsson et al [22] in which the membrane was boiled for 1h in 10% H₂O₂, then 1h in water, followed by 1h in 0.2M H₂SO₄ and finally 1h in water. Prior to testing, the membranes were dried for at least 24h at 105°C to remove all free water from the Nafion.

Eight different membranes were prepared at room temperature (M1 to M8 in Table 2.3) using different solution concentrations, drying and annealing procedures. Some membranes were also formed in acid and some in an acid-base complex.
Table 2.3. Preparation of the membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Preparation procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>Original Nafion</td>
</tr>
<tr>
<td>M2</td>
<td>Membrane dipped for 15 min into a 0.1% PBI solution, after which it was dried with a heating gun at ca. 300°C. The procedure was repeated 4 times, after which the membrane was annealed at 200°C for 1 h.</td>
</tr>
<tr>
<td>M3</td>
<td>Membrane immersed in a solution of diethyl amine (~50% at DMSO) for 4h, followed by a 1% PBI solution for 2.5h. Finally, the membrane was dried at 100°C for 2h.</td>
</tr>
<tr>
<td>M4</td>
<td>Membrane dipped for 15 min into a 0.1% PBI solution, after which it was dried at 200°C for 5 min, followed by immersion in a 1% Nafion solution (in DMSO) for 5min, after which the membrane was dried at 200°C for 5min. The entire cycle was repeated 4 times before annealing at 200°C for 1 h.</td>
</tr>
<tr>
<td>M5</td>
<td>Membrane was dipped for 60 min into a 0.1% PBI solution, after which it was dried with a heating gun at ca. 300°C. This was repeated 4 times, after which the membrane was annealed at 200°C for 1 h.</td>
</tr>
<tr>
<td>M6</td>
<td>Membrane immersed into a solution of diethyl amine (~50% at DMSO) for 5h, followed by a 0.1% PBI solution for 1.5h. Finally, the membrane was dried at 100°C for 20h.</td>
</tr>
<tr>
<td>M7</td>
<td>Membrane immersed in a mixture of solutions of PBI, Nafion and diethyl amine (5mL 1% Nafion solution, 5.5mL diethyl amine, 5mL 0.1% PBI solution) for 15 min. It was then dried at 100°C for 3h and annealed at 200°C for 1h.</td>
</tr>
<tr>
<td>M8</td>
<td>Membrane dipped for a 15 min into 1% PBI solution, after which it was dried at 100°C for 5h.</td>
</tr>
</tbody>
</table>

After preparation, the membranes were cleaned as described above. All membranes except M4 maintained their appearance during the cleaning procedure (Table 2.4). During boiling in the oxidizer, M4 excreted small narrow particles into the solution, indicating that the laminate structure of PBI-Nafion was not sufficiently stable.
Table 2.4. Appearance of membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>Transparent, colourless</td>
</tr>
<tr>
<td>M2</td>
<td>Surface inhomogeneous, yellow colour, slightly resembling mother-of-pearl, semi-opaque</td>
</tr>
<tr>
<td>M3</td>
<td>Transparent, mainly colourless</td>
</tr>
<tr>
<td>M4</td>
<td>Similar to M2</td>
</tr>
<tr>
<td>M5</td>
<td>Similar to M2</td>
</tr>
<tr>
<td>M6</td>
<td>Homogeneous, yellow, no mother-of-pearl appearance</td>
</tr>
<tr>
<td>M7</td>
<td>Colourless, transparent</td>
</tr>
<tr>
<td>M8</td>
<td>Slightly yellowish, transparent, strong mother-of-pearl appearance</td>
</tr>
</tbody>
</table>

2.6 IR spectroscopy

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer with an ATR module. The spectral range was 650-4000 cm\(^{-1}\), with resolution 4 cm\(^{-1}\). Membranes were in a fully hydrated state for these spectroscopic studies. The spectrum of PBI was also recorded as a reference (Figure 2.10).
Spectra of the membranes exhibited the general character of Nafion (Figure 2.11), with only minor differences from membrane to membrane.

Some spectra exhibit stronger peaks at 2850 and 2920 cm$^{-1}$ that could indicate the presence of CH$_3$ groups – possible residues of MeOH or diethyl amine. This feature was found to be strongest for membranes M4, M5, M7 and M8, and weaker for
membranes M1, M2, M3 and M6 (Figure 2.12). Other spectral peculiarities that can be useful are found in the region around 1450cm\(^{-1}\) which should reflect strong uptake of PBI (Figure 2.13). M1, M4 did not show this peak, and it was strongest for M8; other membranes had peaks of intermediate strength. Another interesting observation was that the M2, M5 and M8 peaks had slightly lower frequencies than those of M3, M6 and M7.

![Figure 2.12. IR spectra of membranes (2800-3000cm\(^{-1}\))](image)

![Figure 2.13. IR spectra of membranes (1380-1500cm\(^{-1}\))](image)

Even less substantial differences were noted in the region around 1560cm\(^{-1}\) (Figure 2.14) corresponding to Nafion –SO\(_3\) stretching. Pure Nafion (M1) had an absorption band at a slightly higher frequency (1057cm\(^{-1}\)) than the other membranes, which had a maximum as much as 1cm\(^{-1}\) lower in resonance frequency. The last traces of PBI were observed around 802cm\(^{-1}\), which is a strong PBI absorption band (Figure 2.15). In this range, M8 was strongest; M6 and M5 average; and M1-M4 and M7 had negligible absorption peaks.

![Figure 2.14. IR spectra of membranes (1040-1070cm\(^{-1}\))](image)

![Figure 2.15. IR spectra of membranes (780-830cm\(^{-1}\))](image)
2.7 Conductivity measurements

Membrane conductivities were characterized in two current directions: in-plane and through-plane. Since protons permeate through the membrane in real fuel-cell operation, the through-plane method is the most appropriate. However, the Nafion membrane is highly conductive, causing a very low resistance in the bulk membrane compared to at the interface. Consequently, it is very difficult to achieve reliable and reproducible through-plane results so that, in practice, in-plane conductivity measurements are more common. Both techniques are described briefly here.

2.7.1 In-plane conductivity measurements

Membrane conductivities were characterized using a Solartron impedance spectrometer, an analytical Impedance/Gain-Phase Analyzer 1260, and a simple homemade four-point probe (Figure 2.16) made from four stainless-steel strips which were glued to an insulating plastic plate. The outer stripes were the current source and sink, while the inner ones were used for the voltage measurements. To ensure good contact between the membrane and the strips, the membrane was pressed onto the probe using a rubber insulator and a heavy load.

In the low frequency range, Nafion acts as an insulator because of its low electronic conductivity. At higher frequencies, the result from the measurements are easily processed; the imaginary part of the impedance is approximately zero; the relatively frequency independent real part can be considered as a resistance (Figure 2.17-2.18). Typical measurement were performed on the frequency range 1kHz-1MHz (50 point, with logarithmic distribution), with a sine wave of amplitude 200mV; saved
data points were averaged. Important geometrical characteristics of the membrane, like width and thickness, were measured with a normal ruler and a Mitutoyo Absolute micrometer, respectively. To ensure reproducibility, all measurements were carried out at least 4 times and the results were averaged.

\[ \text{Conductivity} \ (K) \text{ of the membrane sample, where } R \text{ is the resistance of the membrane:} \]
\[ K = \frac{1}{R} \]

Specific conductivity of the material, where \( L \) is the distance between the voltage measurements electrodes, and \( w \) is width of sample and \( a \) is thickness of membrane.
\[ \sigma = \frac{K \cdot L}{w \cdot a} \]

The results of the measurements are shown in Table 2.5.
Table 2.5. Thickness and calculated specific conductivity of the membrane.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness (μm)</th>
<th>Specific conductivity (S/m)</th>
<th>Relative uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>201.8(76)</td>
<td>7.15(38)</td>
<td>5.34</td>
</tr>
<tr>
<td>M2</td>
<td>232.5(36)</td>
<td>7.56(22)</td>
<td>2.86</td>
</tr>
<tr>
<td>M3</td>
<td>204.8(11)</td>
<td>3.004(92)</td>
<td>3.06</td>
</tr>
<tr>
<td>M4</td>
<td>238(24)</td>
<td>6.54(68)</td>
<td>10.3</td>
</tr>
<tr>
<td>M5</td>
<td>227.3(44)</td>
<td>6.56(20)</td>
<td>3.07</td>
</tr>
<tr>
<td>M6</td>
<td>209.0(22)</td>
<td>3.953(81)</td>
<td>2.04</td>
</tr>
<tr>
<td>M7</td>
<td>216.8(25)</td>
<td>2.77(13)</td>
<td>4.83</td>
</tr>
<tr>
<td>M8</td>
<td>211.8(19)</td>
<td>8.37(16)</td>
<td>1.96</td>
</tr>
</tbody>
</table>

2.7.2 Through-plane conductivity measurements

Through-plane type conductivity measurements were attempted with the same impedance spectrometer and metal electrode system, which also permitted temperature control when coupled to a thermostat (Figure 2.19).

Figure 2.19 Conductivity measurements.

A simple electrical equivalent circuits can be used to model impedance spectra (Figure 2.20). The simplest model contains $R_M$ to describe the bulk resistance of the membrane, and $R_I$ and capacitor $C_I$ to represent the interfacial properties. Since conduction mechanisms are different in electrode (electron) and membrane (proton), the interface should act as an insulator, which implies that $R_I$ is high (Figure 2.20, left) (Eq. 1). However, this model can be inadequate in the low frequency region as a result of diffusion processes, and a special mathematical element (the Wartburg element) is
incorporated into the scheme (Figure 2.20, right). The impedance of the Wartburg element is described by Eq. 2, where $A$ is the Wartburg parameter [25].

\[
Z = \frac{1}{R_i} + \frac{1}{R_M} + i\omega C + R_M = \frac{R_i}{1 + \omega^2 C_i^2 R_i^2} + R_M - i \frac{\omega C_i R_i^2}{1 + \omega^2 C_i^2 R_i^2}
\] (1)

\[
\text{Re}(Z) = \frac{R_i}{1 + \omega^2 C_i^2 R_i^2} + R_M
\]

\[
-\text{Im}(Z) = -\frac{\omega C_i R_i^2}{1 + \omega^2 C_i^2 R_i^2}
\]

\[
Z_W = \frac{A}{\sqrt{\omega}} - i \frac{A}{\sqrt{\omega}}
\] (2)
Experimentally measured spectra were similar to those shown in Figures 2.21, 2.22 and 2.23. Modelling over an extended frequency range proved completely impossible; it was even difficult to achieve sufficient stability in the high frequency region. The spectra were severely dependent on the wetness of the membrane surface and the applied pressure. Deviations were of the order of 20-100%. Neither was any systematic temperature dependence observed over the temperature range 40 to 90°C. The impedance method was therefore not consider to be sufficiently precise for materials characterization.

2.8 Methanol diffusion measurements

The passive methanol permeability was measured using a diffusion cell and a Raman spectrometer; the spectroscopy was used to assess the methanol concentration in a water solution. The simple diffusion cell was constructed by pressing together two cavities with the membrane sample separating them. Both cavities were loaded with equal amounts of solutions – the feed side with the methanol solution and the permeate side with pure water. Stirring was applied on both sides to ensure a homogeneous concentration within the cavities. At given time intervals samples were taken from the permeate side and their Raman spectra recorded using a green argon laser (514nm) on a Renishaw Ramascope coupled to a Leica microscope (Figure 2.25).
The Raman spectra of the methanol-water mixtures contain signals which are convenient to use in this quantitative characterization of the solution (Figure 2.26). In the spectral range from 2400 to 4200 cm\(^{-1}\), signals corresponding to methanol C-H stretching and water OH stretching vibrations can be found. Methanol C-H stretching have narrow asymmetric (2945 cm\(^{-1}\)) and symmetric (2836 cm\(^{-1}\)) vibrations peaks, whereas water OH stretching exhibits a very broad peak around 3400 cm\(^{-1}\) due to the hydrogen bonding. The spectral analysis contained three simple steps: baseline correction, assessment and subtraction of OH peak, summation of intensities of the methanol peaks (Figure 2.26).
Figure 2.26 Methanol-water spectra. Methanol solution with different concentrations (left); data processing of the spectra (right).

Figure 2.27 Relation between peak ratio $X$ and methanol concentration.

$$ X = \frac{I_{CH_{2}} + I_{CH_{3}}}{I_{OH}} \quad (3) $$

$$ c(X) = -0.6695X^2 + 5.4351X - 0.0205 \quad (4) $$

The relation between peak-ratio $X$ (Eq. 3) obtained from spectral analysis and methanol concentration was calibrated (Figure 2.27) and fitted to a second-order polynomial (Eq. 4).

Fick’s first law of diffusion (Eq. 5) was used for calculating methanol permeation. We assume that the volume of liquid on either side of the membrane remains constant during the experiment (Eq. 6), although the osmotic processes and the sampling affect this assumption slightly. The concentrations on the feed and permeate
side can be denoted by $c_1$ and $c_2$, respectively. The time-concentration dependence (Eq. 7) on the permeate side can be obtained after solving a simple differential equation. Since all experimental parameters were kept unchanged over all measurements, the rate constant $k$ is a suitable parameter to characterise membrane performance:

$$\frac{dn}{dt} = -D \frac{dc}{dx} \quad (5)$$

$$V_1 = V_2 = V = \text{const} \quad (6)$$

$$c_1 V_1 + c_2 V_2 = \text{const} \Rightarrow c_1 + c_2 = c_{i_0} = \text{const}$$

$$\frac{c_1 - c_2}{l} DS dt = dn_2 = V dc_2 = \frac{c_{i_0} - 2c_2}{l} DS dt$$

$$\int DS IV dt = \frac{dc_2}{c_{i_0} - 2c_2} \quad \text{or} \quad \int DS IV t = -\frac{1}{2} \ln \left( \frac{c_{i_0} - 2c_2}{c_{i_0}} \right) \rightarrow 1 - \frac{2c_2}{c_{i_0}} = e^{-\frac{2DS}{IV}} \rightarrow c_2 = c_{i_0} \left( 1 - e^{-\frac{2DS}{IV}} \right)$$

$$c(t) = c_\infty \left( 1 - e^{-kt} \right) \quad (7)$$

Where the rate constant is $k = \frac{2DS}{IV}$, and $c_\infty = \frac{c_{i_0}}{2}$ is final equilibrium concentration.

$D$ is the diffusion coefficient, $S$ the diffusion area, $l$ the membrane thickness, and $V$ the volume of solution in the cavity.

**Table 2.6 Parameters of the experimental set-up**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experimental value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{i_0}$</td>
<td>10M</td>
</tr>
<tr>
<td>$V$</td>
<td>55mL</td>
</tr>
<tr>
<td>$S$</td>
<td>1000mm$^2$</td>
</tr>
</tbody>
</table>

Typically, 10 samples were taken over 5h during the methanol diffusion experiment. The results were fitted to Eq. 7, which yielded the characteristic rate constant $k$ (Figures 2.28a-h).
2.9 Relative performance

The membrane performance was evaluated as a ratio between conductivity and methanol permeability. The results indicate ultimate performance increases by up to 50% (Table 2.7). ALL PBI treatments resulted in lower methanol permeation. However, most treatments also resulted in lower conductivity. An especially poor result was seen from treatment with diethyl amine (M3, M6 and M7). Although the membrane was re-purified and IR spectra showed no significant CH₃ peaks (the existing peaks could not be correlated to the diethyl amine treatment), some of these molecules could still remain and affect the conductivity. Despite the fact that different techniques were used here, similar results were obtained compare to previous work with PBI/Nafion membranes [26]. The resulting performance was even higher and even an unexpected conductivity increase was observed in some cases. According to IR (which showed characteristic PBI peaks around 1450cm⁻¹), PBI content should be highest in membrane M8, and also high in membranes M2 and M5. At slightly higher frequencies (1460cm⁻¹), membranes M3, M6 and M7 show very small peaks after treatment with diethyl amine, but these peaks can also belong to C-H deformation vibrations in the –CH₂ groups of diethyl amine. In the other characteristic region near 805cm⁻¹, membranes M5, M6 and M8 show larger peaks. All membranes showing the characteristic peaks of PBI also exhibit better performance. It would appear that we can divide the membranes into two groups: M2, M5 and especially M8 exhibit a more
laminar structure, and M6 exhibits a more homogeneous structure (yellowish in colour, but with no interference).

Even though the quantitative composition of the composites are unknown, as well as the structures and mechanisms associated with them, there are indications from IR which suggest presence of PBI in Nafion. The amount of PBI also seems correlated to the improvement of the performance in terms of the requirements of DMFC applications; namely, higher conductivity and lower methanol permeability.

<table>
<thead>
<tr>
<th>Table 2.7.</th>
<th>Experimental results and comparison with Nafion. Estimated uncertainties of performance values remained into range 2-8%, except M4, that had significantly higher 15%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conductivity (S/m)</strong></td>
<td><strong>MeOH permeation (relative units)</strong></td>
</tr>
<tr>
<td>M1</td>
<td>7.15</td>
</tr>
<tr>
<td>M2</td>
<td>7.56</td>
</tr>
<tr>
<td>M3</td>
<td>3.00</td>
</tr>
<tr>
<td>M4</td>
<td>6.54</td>
</tr>
<tr>
<td>M5</td>
<td>6.56</td>
</tr>
<tr>
<td>M6</td>
<td>3.95</td>
</tr>
<tr>
<td>M7</td>
<td>2.77</td>
</tr>
<tr>
<td>M8</td>
<td>8.36</td>
</tr>
</tbody>
</table>

3. Conclusions

Different strategies for producing the PBI/Nafion membrane were attempted. The only successful technique was the immersion of the Nafion membrane in a PBI solution. Improvements were seen both in conductivity and MeOH diffusion; the best membranes exhibited performances up to 50% better that Nafion. Still further research in a real fuel-cell situation can show whether these potentially interesting materials have any practical value in applications. In addition, it is important to ascertain the variation of PBI content across the membrane, and structural relationship between Nafion and PBI; our efforts to use Raman spectroscopy failed because the high levels of fluoroscence. If the membrane does not behave well in a real DMFC fuel-cell environment, it will be necessary to find out why this is!
4. Acknowledgements

I would like to express my gratitude to all the people who have contributed to this work, or have helped me in any other way during my year in Uppsala. First, I would like to acknowledge Prof. Josh Thomas for providing me with an interesting research topic, and my supervisor Dr. Daniel Brandell for all his attentive assistance. Also, I wish to thank Prof. Michel Armand for his many ingenious and interesting suggestions. My special thanks go to Docent Torbjörn Gustafsson for helping me in all kinds of ways with experimental and laboratory problems. I would also like to thank Prof. Jan Lindgren and people in the Polymer Chemistry Group for teaching me the principles and use of the various instruments I have needed in this work. I must also thank Anders Lund for helping to design a new instrument for conductivity measurements. Also, I am very grateful to my new friends in Uppsala, especially Elena, Emilie and others for our many nice times together.

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No less important is the encouragement and support I feel from my family in Estonia.

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5. References


6. Kokkuvõte


Appendix

Alar Ainla, Daniel Brandell; *Solid State Ionics*. 2007, **178**, 581-585