PTMC: A polycarbonate candidate for polymer electrolytes in sodium batteries?

A characterisation of the PTMC–NaFSI system

Ronnie Mogensen
Abstract

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The poly(trimethylene carbonate)--sodium bis(fluorosulfonylimide) system has been investigated as polymer electrolytes for sodium batteries. The properties of poly(trimethylene carbonate) with salt concentrations ranging from 8.7wt% to 67wt% have been measured by DSC, FTIR, and EIS. Half-cells based on both high-salt and low-salt electrolytes have been tested in order to determine their performance in a realistic environment. The tests reveal two distinct regions in salt concentration and the best-performing electrolytes show a conductivity of 50 µS/cm at 25 °C and 1mS/cm at 100 °C. The report presents cell data from sodium–prussian blue half-cells with only 10% capacity fade after 80 cycles at 60 °C and additional tests of high-salt cells capable of cycling at reduced temperature with good rate capability.
Sammanfattning på svenska

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**List of abbreviations**  
DSC Differential scanning calorimetry  
EIS Electrochemical impedance spectroscopy  
CPE Constant phase element  
FSI Bis(fluorosulfon)imide  
FTIR Fourier transform infrared spectroscopy  
GPC Gel permeation chromatography  
HMW High-molecular-weight  
NMR Nuclear magnetic resonance  
PB Prussian blue  
PDI Polydispersity index  
PEO Poly(ethylene oxide)  
PISE Polymer-in-salt electrolyte  
PTFE Poly(tetrafluoroethylene)  
PTMC Poly(trimethylene carbonate)  
SEM Scanning Electron Microscope  
SPE Solid polymer electrolyte  
TMC Trimethylene carbonate  
TFSI Bis(trifluoromethane)sulfonimide  
XRD X-ray diffraction
1. Introduction

1.1 Background
The world is in dire need of energy storage to enable the use of electrical vehicles and intermittent
energy sources such as solar and wind power. As the race to switch the energy supply from fossil hydrocarbons to renewable power intensifies, a pressing need to store electrical energy on a grand scale has emerged. The batteries currently available are either too expensive, unsafe, or environmentally hazardous to meet this rising demand. Batteries produced for portable electronics are less sensitive to high prices and the use of rare or toxic elements than batteries produced for grid storage. To provide enough capacity for grid storage, batteries used must be comprised of elements found in abundance at low cost and with low toxicity or other deleterious environmental effects. There is quite simply different demands placed on large-scale batteries; energy density and specific energy density (Wh/L and Wh/g) is not without importance but less important than the price, i.e. Wh/$. A significant part of the material costs in a typical lithium-ion battery is incurred by the separator, electrolyte, and current collectors. By switching from lithium-ion to sodium-ion chemistry as well as doing away with the separator by replacing the liquid electrolyte with a polymer electrolyte containing NaFSI salt, improvements in safety and decreases in cost and complexity are possible. By the use of sodium instead of lithium and an appropriate choice of salt, there is also a possibility to reduce the cost and weight of the current collector for the anode by using aluminium foil instead of the now prevailing copper foils. The use of polymer electrolytes can also help alleviate safety concerns by mitigating the problems associated with dendrite growth on the anode. There is a tendency to overstate the rarity of lithium when explaining why a non-lithium battery might be the best choice; the world-wide lithium reserves are as of yet not running out, but the price is expected to increase. The price a regular customer is willing to pay for a mobile phone with good battery performance far exceeds what utility companies are willing to pay for energy storage; the customers cannot save money by running their phones on natural gas or coal but the energy companies can and will. The main obstacles to realize the proposed grid storage batteries are price, safety and battery cycle life. While a battery for a laptop or mobile phone needs a lifetime of approximately 2 years, a grid storage battery needs more than 15 years of calendar life and should manage more than 4000 cycles. Focusing on lifetime, safety and price, instead of Wh/g, gives a different list of promising materials than those that would be attractive for portable electronics and should enable the development of batteries that are more suited for large-scale energy storage.

1.2 Batteries
Batteries are devices that can store electrical energy in the form of chemical energy and release this energy as electrical energy when required. The main components in a typical battery are the anode, the cathode, and the electrolyte, see Figure 1. The anode is the negative electrode where oxidation occurs during discharge. The cathode is the positive electrode where reduction takes place during discharge. The electrolyte is an ion-conducting medium that enables charges to move between the anode and the cathode without a direct electrical contact between the electrodes. The main requirements for the electrode materials are high capacity, suitable voltage, and good durability with high safety. The properties important for electrolytes are good ion-conduction, low electronic conductivity, and a good electrochemical stability.
In lithium-ion batteries the electrolyte is typically a mixture of organic solvents such as ethylene carbonate and propylene carbonate combined with a salt such as LiPF$_6$ in the case of lithium batteries. When using a liquid electrolyte there is also a separator that ensures that the anode and cathode do not come into physical contact, as this would lead to a short-circuit in the cell. A good separator should be both electrochemically inert and an electronic insulator that allows ions to pass through unimpeded. While there are some positive aspects of using organic solvents as the electrolyte, such as good ionic conductivity and a reasonable electrochemical stability, there are many drawbacks including safety concerns. The organic solvents are flammable and not particularly healthy and the liquid electrolyte can leak out of the cell or undergo unwanted electrochemical reactions.$^{6,7}$

In order to prepare the uninitiated reader for the data presented later in the report it will be necessary to explain some fundamentals of battery nomenclature. As the purpose of a battery is to store energy and to deliver the stored energy, it is very important to quantify the energy the cell can deliver. The energy a battery can deliver is usually described by the specific energy density with the unit Wh/kg or Wh/g while the amount of power available from a battery has the unit W/kg. Because the amount of energy a battery can deliver is dependent on how fast the cell is charged and discharged, the stated energy available is specified at a certain speed of charge/discharge. For this, a peculiar unit known as C-rate is used; if a battery is said to deliver 200 Wh at 1C it means that 200 Wh is available if the cell is fully discharged in one hour. If it is stated to deliver 200 Wh at 2C it can deliver that energy in 30 minutes while C/2 means it can deliver the stated energy only if it is fully discharged in 2 hours or more. A good battery should be capable of operating at high C-rates as this will reduce the time needed for recharge and improve the power available from the cell.

Battery researchers often use the term “capacity” with the unit Ah/kg or mAh/g. The capacity is simply the amount of charge a material can store, and to get the energy, the capacity must be combined with the potential. A good battery should thus possess as much capacity as possible at the highest potential possible to maximise the energy density. It should be noted that the mass used to calculate specific energy density in research is typically only the mass of the active material while for commercial batteries it is common to include the mass of all components. Another important factor for rechargeable batteries is the coulombic efficiency, which is the ratio of charge and discharge capacity for one cycle, i.e. the amount of charge delivered during discharge divided by the amount of charge put into the cell during charging. The coulombic efficiency should be as close to unity as possible. If
the coulombic efficiency is low, for example 50%, it means that half of the electrons used to charge the battery did not charge the cell but instead were consumed by side reactions. These side reactions are detrimental to energy efficiency and can consume electrolyte and destroy battery components; this in turn causes loss of capacity during cycling.8

1.3 Sodium batteries
Battery research is a huge field these days and a lot of this research is focused on lithium-based batteries. The two main reasons for this are (1) the small size and weight of the lithium ion and (2) the large negative electrode potential of lithium. These properties enable the lithium-based batteries to achieve superior performance in terms of both energy density and specific energy density.

After listing the excellent properties of lithium when used in batteries, the question of why anyone would spend time and money on sodium batteries arises. Sodium-based batteries look like an inferior choice, given that the sodium ion is larger, heavier, and has 0.3 V higher redox potential vs. 2H+/H2 than lithium, but there are some redeeming features. Firstly, the price and availability of sodium ensure that the raw material cost of the battery will be low and the global abundance ensures that no single nation or group of nations can control the supply.9 Secondly, the differences between lithium and sodium chemistry can enable the use of cathode materials that are not suitable for lithium.10 Sodium batteries are already commercially available in the form of sodium–sulphur11 and sodium–NiCl2 cells12; these cells however require operating temperatures of circa 300 °C and this makes them impractical for many applications. The high operating temperature is a result of using ceramic electrolytes and molten electrode materials; this adds complexity and gives rise to corrosion problems for manufacturers and operators of these cells.1,13

There is currently a great renaissance of research into sodium-ion batteries (SIB) and even though there are many differences between SIBs and LIBs the hope is to utilise some of the lessons learned from the extensive research on lithium batteries. The overlap between lithium and sodium research is large, especially in regard to electrolytes; polymer electrolytes would be equally beneficial with SIBs and LIBs as the problems they have with the toxicity and flammability of organic solvent electrolytes are similar. There is, however, a problem that has to be solved for sodium batteries; the sodium ion is too large to intercalate in many of the materials that are available for lithium batteries; most notable of these materials is graphite that serves as an anode material in many lithium-ion batteries. The work put into finding anode and cathode materials for lithium can therefore only be seen as a good place to start with no guarantee that the materials will work for sodium-ion batteries. There is also a big difference in melting temperature between sodium and lithium; lithium melts at 181 °C9 while sodium melts at 98 °C9. While the low melting point of sodium makes it a good choice for systems utilising molten electrodes, it also means that conventional sodium batteries are ill-suited to having a sodium metal anode.

1.4 Polymer electrolytes
There are some alternatives to organic solvents and among these are ceramic and polymer electrolytes. The ceramic electrolytes currently have conductivities that are acceptable15, but it is hard to make a practical ceramic electrolyte that is both thin enough to give good performance and durable enough to ensure safety during handling and operation. There is also an issue with contact between the electrodes and the electrolyte as the ceramic materials typically do not conform to the surface of the anode and cathode and they do not penetrate into the often porous electrodes.

The polymer-based electrolytes have their own set of challenges. Polymers with suitable properties can dissolve salts and thus become ion conductors while having all the fabrication advantages
associated with polymers. The primary obstacle to overcome for polymer electrolytes is their low ionic conductivities, especially at room temperature. There are many different types of polymer electrolytes and therefore an introduction to the field in general and to the most common varieties of polymer electrolytes will be given.

First we have the dry SPE or solid polymer electrolyte that consists of a polymer with polar segments or side groups that can dissolve salts; this polymer is combined with a salt that provides the charge carriers in the form of ions. The conduction mechanism of an SPE is mainly through segmental motion of the polymer\textsuperscript{16}, and this gives rise to the biggest challenge for SPEs namely the room temperature ionic conductivity. At room temperature the segmental motion of the polymer is often restricted and acceptable levels of conductivity is usually only attainable at 60 degrees or higher.\textsuperscript{17}

There are two subgroups of SPEs, and the difference between these is the amount of salt dissolved into the polymer. At low salt concentrations the SPE is labelled as a “salt-in-polymer” type and when the salt concentration reaches a certain amount the SPE can be denoted as a “polymer-in-salt electrolyte” instead, here abbreviated as “PISE”.

Secondly there are the gel polymer electrolytes. The gel consists of a polymer, a salt, and a solvent; the polymer acts as a porous matrix that can trap considerable amounts of solvent within it. The conductivity of gel electrolytes is generally quite good even at room temperature due to the high mobility of the ions in the solvent. The conduction mechanism is the same as in a liquid and while this solves the room temperature conduction issue it is detrimental to mechanical stability and only partially solves the problems associated with organic solvents.\textsuperscript{17}

Last but not least there are polymers that are salts themselves with the anion attached as a side group. The principal advantage of having the anion attached to the polymer backbone is that the transference number of the cation becomes close to unity. The transference number is simply the fraction of current that is transported by cations ($t_+$) or anions ($t_-$). The transference number $t_+$ is usually below 0.5 for the other polymer electrolyte types\textsuperscript{16} but the absence of anionic charge transfer in this type of polymer eliminates the polarisation effect that can occur if there is a build-up of negative charges at the anode.\textsuperscript{18} The single-ion conductors also struggle with low conductivity and are sometimes used as the polymer/salt matrix in gel electrolytes to avoid this shortcoming.\textsuperscript{17,19}

The conduction mechanism of ions in polymers is usually explained by movement of entire segments of the polymer backbone. The segmental motion naturally also moves the polar groups of the polymer, and given the attraction of ions to these sites along the backbone the ions move with the chain; during this motion the ions can move from one polar group to another.\textsuperscript{16} Because of the connection between segmental motion and ionic conduction, the temperature needed for activation of segmental motions becomes important too. This temperature is called the glass transition temperature and a polymer electrolyte will only be practical at temperatures above the $T_g$.\textsuperscript{16} It is common for polymers with polar groups to exhibit increased values for the $T_g$ when it is mixed with salts\textsuperscript{16}, this is due to a crosslinking effect that occurs when cations coordinate to several polar groups at once. The choice of anion can also affect the $T_g$; some anions are known to have a plasticising effect which means that they create free volume in the polymer, increased free volume lowers the $T_g$ because the space created between polymer chains enables them to move at lower activation energies. There is some discussion as to the conduction mechanism of the PISE type electrolytes. Often a percolation mechanism where ions can move between salt aggregates in loosely formed networks is suggested as a complementary mechanism to segmental motion.\textsuperscript{20,21,22}
The research in SPEs has historically been focused on poly(ethylene oxide) – PEO. PEO has a very low glass transition temperature of \(-58^\circ C\) but is semicrystalline at temperatures below \(57^\circ C\). The ether group in PEO is capable of dissolving various lithium and sodium salts and these dissolved salts enable the ionic conductivity of PEO. The conductivity of PEO at room temperature is far too low for practical applications but the conductivity increases with temperature due to the increased segmental motions of the polymer backbone. At \(57^\circ C\) the crystalline regions of PEO melt, giving an increase in conductivity. Research has shown that it is the amorphous phase in PEO that is responsible for ion conduction and that there is an optimal concentration of salt for good conductivity. There is some debate in the PEO literature regarding the matter of ion conduction in crystalline domains; some people claim that ionic conductivity does occur in crystalline domains while others claim that crystalline domains are not contributing to the ionic conductivity. Regardless of this, the fact that a marked increase in conductivity coincides with melting of crystalline domains suggest that the bulk of the ionic conduction occurs in the amorphous phase.

1.5 Poly(trimethylene carbonate)

Poly(trimethylene carbonate) – PTMC – is a polymer that is well known in the biomaterials research literature as it is biodegradable. Recently PTMC has been receiving attention as a polymer electrolyte host due to the work performed by Sun et al. The monomer trimethylene carbonate closely resembles the organic solvent ethylene carbonate which is used as a component of liquid electrolytes in commercial lithium-ion cells, see Figure 2.

![Figure 2. Comparison of the commonly used organic solvent ethylene carbonate and the PTMC monomer trimethylene carbonate (left). Repeating unit of PTMC (right)](image)

The properties of HMW PTMC that have drawn the interest of battery researchers are the polar carbonate groups and the fact that it is an amorphous polymer without crystalline domains, this fact means that there is no need for measures to prevent crystallisation in PTMC. Pure HMW PTMC is a transparent rubbery material that has a good mechanical stability. The glass transition temperature of PTMC is approximately \(-15^\circ C\) and the molecular weight of PTMC used in SPEs has been in the \(350,000\) to \(400,000\) g/mol range.

There are currently people working on developing other polymers that can overcome the limitations of PEO; examples include a close relative to PTMC, the polymer poly(ethylene carbonate) developed by Tominaga et al. and 2–hydroxyethyl methacrylate synthesised in an ionic-liquid by Noda and Watanabe. Electrolytes based on these polymers show high ionic conductivity but limitations in either mechanical or electrochemical stability remain.

1.6 Salt properties

The salts used in polymer electrolytes usually include the cation of interest, \(i.e.\) lithium or sodium and a bulky anion. The reason for the bulky anion is to restrict the amount of charge transferred by the...
negatively charged anion. The accumulation of anions at the anode when anions migrate does not contribute to the battery function and gives rise to polarisation within the cell.\textsuperscript{18,32} It is also common to use anions that have electron-withdrawing groups that delocalise the negative charge; the delocalisation of the negative charge leads to higher solubility as the dissociation energy of the ion pair decreases.\textsuperscript{17,33}

The work done with PTMC so far has been focused on lithium and the use of different salts such as LiPF\textsubscript{6}\textsuperscript{34} and LiClO\textsubscript{4}\textsuperscript{35} although the most promising salt so far has been LiTFSI\textsuperscript{27,29}. While the TFSI anion shows promising results, there is also interest in how the slightly smaller anion FSI performs in the PTMC system. The FSI and TFSI anions are similar with the biggest difference being their size (Figure 3) and melting points; 118 °C for NaFSI and 257 °C for NaTFSI.\textsuperscript{17}

![Figure 3. Illustration of the different anions FSI (left) and TFSI (right).](image)

1.7 Thesis scope and objectives

PTMC is a polymer that has shown promise for lithium batteries\textsuperscript{27} and NaFSI is a salt that is relatively unexplored compared to its close relative NaTFSI. The goal for this degree project has been to characterise the PTMC–NaFSI system and to produce a working sodium polymer cell using a PTMC–NaFSI electrolyte.

1.8 Strategy for characterisation

The strategy used to characterise the PTMC–NaFSI electrolytes will be explained so as not to confuse the reader as to the purpose of the conducted measurements. The synthesised polymer was characterised to obtain parameters such as molecular weight, polydispersity index and glass transition temperature. The molecular weight and polydispersity index were obtained by GPC where the polymer is dissolved and passed through a gel column that separates the polymer chains according to their size and detects the amount of each fraction. The $T_g$ was obtained through DSC where the difference in heat capacity above and below the $T_g$ is used to pinpoint the glass transition temperature. NMR was used to confirm the absence of significant levels of monomers in the polymer. The cathode material was characterised by XRD and SEM; powder XRD was used confirm the structure of the cathode material and SEM was used to determine the particle size. DSC, EIS and FT-IR were used to characterise the electrolytes, EIS measures the response of a sample to an alternating current at a range of frequencies and this gives information about the ionic conductivity. FT-IR utilises the response of chemical bonds to low-energy photons to give information about the chemical environment within the electrolyte. Cell cycling was performed to demonstrate the performance of the electrolyte in a practical application and gather information about capacity retention and coulombic efficiency. Furthermore, the cycling tests provide voltage profiles. The voltage profiles show at which potential the cell is working at the different stages of charge and discharge with discharge curves starting at a high potential going down and the opposite for charge cycles. By comparing the voltage for charge and discharge the amount of polarisation can be assessed; there are several causes for polarisation but as
this work is concerned with electrolytes, the polarisation is simply compared to a traditional electrolyte in an otherwise identical cell to isolate the influence of the polymer electrolyte.

2. Experimental

2.1 Materials
SodiumFSI (Solvionic) was dried for 24 h at 80 °C and kept in a glove box before use. Acetonitrile (Acros 99.9+% extra dry) and TMC monomer was kept and handled in a glove box at all times. The synthesized PTMC and PTMC–NaFSI electrolytes were kept under inert atmosphere at all times with the exception of FTIR measurements.

All other chemicals used were obtained from commercial sources and used as received.

2.2 Synthesis of PTMC
The PTMC synthesis was executed in accordance with a method described in literature. For clarity the process will be described here. Synthesis was performed in a stainless steel reactor that was dried at 130°C before use. Under argon 10 g (0.1 mol) of trimethylene carbonate was added to the reactor and 0.02 mmol Sn(Oct)2 was added as a 20 µL 1 M dry toluene solution. The reactor was then sealed and placed in an oven at 130 °C. Mixing of the components was achieved by regular shaking of the reactor during the first couple of hours after the components had reached a liquid state. The reaction was then allowed to proceed for 3 days after which the reactor was cooled to room temperature and the transparent rubbery PTMC polymer was retrieved. The as-synthesised polymer was characterised using NMR and GPC to determine the molecular weight, and to confirm the absence of any significant levels of residual monomers in the product.

2.3 Gel permeation chromatography
To determine the molecular weight of the synthesised polymer, gel permeation chromatography was performed on a pure sample of PTMC. The sample was dissolved overnight in dimethylformamide containing LiBr at a concentration of 50 mM. Analysis was performed on an Agilent 1260 infinity instrument.

2.4 NMR
1H NMR analysis was performed on a JEOL Eclipse+ 400 MHz spectrometer at 25 °C. The PTMC sample was dissolved in CDCl3 and the residual solvent signal was used as the internal standard.

2.5 Differential scanning calorimetry
DSC was performed on TA instruments DSC Q2000 differential scanning calorimeter. The measurements were done between −70 °C and 80 °C with 5 °C/min ramp while cooling and 10 °C/min ramp while heating. All sample preparation was performed under inert atmosphere in a glove box. The samples were placed in hermetically sealed aluminium pans, and the glass transition temperature was found by using the “TA instruments Universal Analysis 2000” software. The software identifies the $T_g$ as the inflection point of the change in heat capacity.

2.6 Preparation of electrolyte films
Preparations of electrolyte films were performed in a glove box under argon atmosphere using a solvent casting technique. The PTMC polymer and the required amount of salt were dissolved in dry acetonitrile and left under magnetic stirring overnight. The PTMC–salt mixture was poured into a PTFE mould which was placed in a vacuum oven for 60 h; the vacuum oven was set to lower the
pressure from 200 mbar to full vacuum over a 20 h period at room temperature followed by 40 h at 60 °C under full vacuum. For cell construction the dissolved electrolyte was cast directly on cathodes to ensure infiltration of the electrolyte into the porous electrode; the cathode casting procedure is otherwise identical to the film preparation.

2.7 Electrochemical impedance spectroscopy
Electrochemical impedance spectroscopy was done using a Schlumberger impedance/Gain-Phase Analyzer SI 1260 instrument. The sample was placed between stainless steel electrodes in a Swagelok cell and the Swagelok cell was sealed under an inert atmosphere. A Swagelok cell is simply a sealable container that contains external electrical contacts to electrodes within the vessel, see Figure 4. Temperature control was achieved by placing the Swagelok cell into an oven and measuring the temperature with a thermocouple that was placed in close vicinity of the sample within the Swagelok cell. All samples were measured with 10 mV amplitude between 10–10^7 Hz with a total of 80 data points. The measurements were conducted while going down from 100 °C to 25 °C after annealing at 100 °C in order to ensure a good contact between the electrodes and electrolyte. The software used to analyse data was ZView 3.2b. The modified Debye equivalent circuit was used to obtain the conductivity from impedance data, see Figure 4. The constant phase elements in the circuit represent the capacitance originating from (1) the stainless steel electrodes and (2) the double layer capacitance of each electrode while the resistor is representative of the frequency independent resistance to the flow of ionic current through the electrolyte. The value of the resistor given by the data fitting can be used to obtain the conductivity through the relation showed in Eq. 1, where \( A \) and \( d \) represent the area and thickness of the film, respectively. The thickness of the cast electrolyte films was measured with a micrometer and the thickness ranged between 30–150 µm.

\[
\sigma = \frac{d}{R \times A} \tag{Eq. 1}
\]

Figure 4. Swagelok cell used for EIS and a stainless steel electrode (left). Modified Debye equivalent circuit used for fitting the electrochemical impedance results (right). The value obtained for the resistor is used to calculate conductivity.

2.8 FTIR spectroscopy
FTIR measurements were performed on a PerkinElmer Spectrum One FTIR Spectrometer. Scans were performed between 650 cm\(^{-1}\) and 4000 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\). The samples were briefly exposed to ambient conditions during the analysis although the samples were contained under inert
atmosphere up to the point of the measurements in order to minimise the exposure to ambient atmosphere.

2.9 Cathode synthesis
The Prussian blue cathode material was synthesised using the procedure described by You et al.\textsuperscript{36} The synthesis was performed by dissolving 2 mmol (0.968 g) of Na\textsubscript{4}Fe(CN)\textsubscript{6}•10H\textsubscript{2}O into 100 ml deionised water. The solution was subsequently heated to 60 °C and 1 ml 37% HCl was added under vigorous stirring. The solution was left stirring at 60 °C for 4 h forming a blue precipitate that was isolated and cleaned by repeated centrifugation in water and ethanol.

A cathode slurry was mixed using \textit{N}-methyl-2-pyrrolidone as the solvent and was comprised of Prussian blue, Ketjen black (EC-600) and PVDF (Kynar, Arkema) in a 70:20:10 ratio. The mixing was done by ball milling the slurry for 3 h at 150 rpm. The slurry was used to coat aluminium foil using a simple bar coating technique. After initial drying overnight in ambient conditions the cathodes were punched and vacuum-dried at 100 °C for 24 h before cell assembly.

2.10 X-ray diffraction
XRD analysis was performed using a Bruker TwinTwin instrument with a Lynxeye XE PSD detector and CuKα radiation source. Reference peaks were obtained from the \textit{Pauling File} database.

2.11 Scanning electron microscopy
SEM analysis was performed using a LEO 1550 Scanning Electron Microscope to determine the particle size of the synthesised cathode material.

2.12 Battery assembly
Both polymer batteries and conventional liquid electrolyte batteries were constructed; the liquid electrolyte cells are referred to as benchmark cells to reflect their use as a reference when evaluating the polymer cells. The assembly of batteries was conducted in a glove box under inert argon atmosphere. The cathode, electrolyte and anode were placed in a pouch cell consisting of aluminium foil coated with an insulating polymer. After placing the electrode stack between aluminium current collectors the pouch cells were vacuum sealed at 30 mbar for the benchmark cells and 5 mbar for the polymer cells. For benchmark cells a separator (Solupor) was used while for the polymer cells the polymer was used both as electrolyte and separator.

2.13 Battery cycling
Battery cycling was performed using a \textit{Digatron BTS–600} battery test system. The cells were cycled using constant current for both charging and discharging. Cycling was performed between potentials of 4.2 V and 2.0 V relative Na\textsuperscript{+}/Na. Temperature control was achieved by cycling the cells within an oven.

3 Results and discussion

3.1 PTMC synthesis and electrolyte preparation
The first step in the process of investigating the PTMC–NaFSI system was to synthesise the PTMC. This was done through a ring-opening polymerisation reaction of the TMC monomer catalysed by Sn(Oct)\textsubscript{2}. The resulting PTMC product was transparent with a hard rubbery consistency and good mechanical properties. The synthesised PTMC was analysed with GPC and the results of the analysis show that the synthesised polymer had a number average molecular weight of 334 000 g/mol and a
PDI of 1.9. The PTMC was also analysed by NMR to measure the amount of residual monomer and the relative amount of TMC monomer was determined to be 6 ‰. The relative amount of Sn(Oct)₂ in the synthesised PTMC is calculated to be < 0.9 ‰ by weight.

The PTMC polymer and the NaFSI salt were dissolved in acetonitrile in order to produce the electrolyte by solvent casting. For convenience the notation PTMCₙNaFSI will be used instead of wt% while discussing the different electrolytes in this work. With this notation the subscript n is replaced with a number indicating the molar amount of TMC monomer for each mole NaFSI. The conversion between notations is shown in Table 1.

<table>
<thead>
<tr>
<th>PTMCₙNaFSI:</th>
<th>wt% NaFSI</th>
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<tbody>
<tr>
<td>n = 21</td>
<td>8.7</td>
</tr>
<tr>
<td>n = 13</td>
<td>13</td>
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<td>n = 8</td>
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<tr>
<td>n = 2</td>
<td>50</td>
</tr>
<tr>
<td>n = 1</td>
<td>67</td>
</tr>
</tbody>
</table>

Table 1. Conversion between PTMCₙNaFSI notation and wt% NaFSI in the electrolyte.

PTMCₙNaFSI electrolytes with n = 1, 2, 3, 5, 8, 13, 21, were prepared for use in electrochemical impedance measurements. The films were easily handled and showed good mechanical properties, being elastic and tough. The electrolyte films remained transparent at all salt concentrations.

3.2 Sodium ion conduction in PTMC

The main parameter for a polymer electrolyte is the ionic conductivity. To determine the conductivity of PTMCₙNaFSI, electrolyte films were measured by electrochemical impedance spectroscopy at temperatures from 25–100 °C (Figure 5). The change in conductivity of polymer electrolytes when the Li-salt is replaced with the equivalent Na-salt was expected to be small based on the literature from PEO systems.¹⁷ The conductivity of PTMCₙNaFSI is comparable to the PTMCₙLiTFSI system²⁹ at salt concentrations below n = 2, but some notable differences appear as the salt concentration increases.
Figure 5. Ionic conductivity for PTMC$_n$NaFSI as a function of salt concentration obtained using electrochemical impedance spectroscopy. The x-axis shows the concentration $n$ according to the PTMC$_n$NaFSI notation.

The conductivity of PTMC$_n$NaFSI is almost monotonically increasing with salt concentration only displaying a very slight decrease from $n = 5$ to $n = 3$. In contrast, the best-performing concentration for PTMC–LiTFSI is shown to be at $n = 8$ after which the conductivity starts to decrease without any sign of increased conduction at higher salt concentrations. The conductivity of PTMC$_n$NaFSI shows some similarity to the PEC$_n$LiFSI system investigated by Tominaga et al. where there appears to be a similar concentration dependence of conductivity. The monotonic increase with salt concentration cannot be attributed to the FSI anion alone as LiFSI in PEO does not show the same behaviour and LiTFSI in PEC also shows a monotonic increase of conductivity between 40 and 80 wt% salt. Compared to the PEC$_n$LiFSI and PEC$_n$LiTFSI systems the PTMC$_n$NaFSI system achieves comparable or better conductivity at lower concentrations of salt. This is an advantage over the PEC electrolytes because the PTMC$_n$NaFSI electrolytes are still mechanically robust enough to yield free-standing films at these concentrations.

The results of conductivity measurements performed on electrolyte films show that there is a local maximum at PTMC$_5$NaFSI but also that the conductivity rises sharply as the salt concentration surpasses that of PTMC$_3$NaFSI. The local maximum at $n = 5$ also coincides with the highest $T_g$ in the measured concentration range (Figure 6), and this shows that when increasing the concentration of salt from $n = 21$ to $n = 5$, the increase in available charge carriers is enough to increase the conductivity despite the concomitant increase of the $T_g$. The increase in conductivity that occurs at salt concentrations higher than $n = 3$ suggests either a complementary mechanism such as percolation of ions along salt aggregates, or it might simply be an effect of reduced $T_g$ in high-salt samples as described by Tominaga et al.
Figure 6. Glass transition temperature as a function of salt concentration in PTMC$_n$NaFSI determined by DSC measurements (left). Ionic conductivity measured by electrochemical impedance spectroscopy for PTMC$_n$NaFSI between 25°C and 100°C (right). The annotated numbers refer to the concentration of salt according to the PTMC$_n$NaFSI notation.

The lowering of glass transition temperature in high-salt samples is one possible explanation to the large increase in ionic conductivity when the salt concentration goes above 40 wt%. As can be seen in Figure 6 the $T_g$ of the electrolytes rises steadily as the salt concentration increases until a breaking point is reached at $n = 5$ where the $T_g$ starts to decrease. This breaking point is often held as the point at which the SPE becomes a PISE.$^{21,22}$ The initial increase of the glass transition temperature as salt is added can be explained by crosslinking of electronegative groups by the sodium ions.$^{39}$ The $T_g$ decrease at higher concentrations is however harder to explain as the plasticising effect of the FSI anion does not appear to be large enough to be solely responsible; PEO–LiFSI for example has the opposite $T_g$ response to increasing LiFSI concentration and the same is true for the PTMC–LiTFSI system where the $T_g$ increases with addition of LiTFSI from 36 to 74 wt% salt.$^{29,30}$

Why variation in the salt concentration causes the $T_g$ to rise and fall is not entirely clear, but a mix of effects from (1) interactions of sodium ions with the polar carbonyl groups, (2) formation of salt aggregates and (3) the plasticising properties of the FSI anion could cause this behaviour. The impact on $T_g$ from salt aggregates is twofold as the formation of aggregates affects the amount of sodium ions that interact with carbonyl groups and might have plasticising effects by themselves.$^{21}$

The amount of coordination between sodium ions and carbonyl groups should be detectable as a shift in the carbonyl peak in FTIR spectroscopy at 1737 cm$^{-1}$. The peak from the carbonyl group can be seen between 1800 cm$^{-1}$ and 1670 cm$^{-1}$ (Figure 7).
Figure 7. Normalised FTIR absorption spectra of PTMC$_n$NaFSI with different NaFSI concentrations.

The carbonyl peak displays a slight shift to lower wavenumbers when it is coordinating with a sodium ion. By separating these peaks and making certain assumptions it is possible to roughly estimate the ratio of coordinated to uncoordinated carbonyl groups. The assumptions are (1) that the extinction coefficient of the IR absorption remains the same for coordinated and uncoordinated C=O groups, and (2) that the signals in the 1800–1670 cm$^{-1}$ region exclusively originate from uncoordinated or coordinated C=O groups.

This free-interacting carbonyl ratio can be compared between different films to see if increasing the salt concentration actually increases the amount of coordination between sodium ions and carbonyl groups. The deconvoluted peaks are presented in Figure 8. The calculated ratios resulting from deconvolution in Table 2 are approximate as there is quite a bit of uncertainty introduced when deconvoluting peaks; the results are however good enough to provide an indicator of the environment around the carbonyl groups. The method used for deconvolution is not applicable to the high-salt concentrations of $n = 2$ and $n = 1$ as there is an additional signal of unknown origin appearing at 1760 cm$^{-1}$ for these concentrations.
Figure 8. Deconvoluted FTIR peaks corresponding to the carbonyl group for the PTMC–NaFSI electrolytes.

<table>
<thead>
<tr>
<th>Composition:</th>
<th>Interacting C=O : Free C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 21</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>n = 13</td>
<td>0.28</td>
</tr>
<tr>
<td>n = 8</td>
<td>0.38</td>
</tr>
<tr>
<td>n = 5</td>
<td>0.61</td>
</tr>
<tr>
<td>n = 3</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Table 2. Composition of electrolytes and the corresponding ratio of interacting:free carbonyl groups.

The increasing coordination of sodium ions to carbonyl groups follows the trend in $T_g$ up to $n = 3$ where the glass transition temperature is slightly lower than for $n = 5$ despite indication of greater coordination of sodium to the carbonyl groups. For the electrolytes with greater concentration than $n = 5$ the reduced $T_g$ can be explained either by plasticising effects of the anion or by formation of salt aggregates between the polymer chains that increase the free volume as postulated by Forsyth et al.\textsuperscript{21} If the effect of decreasing $T_g$ is caused by formation of ion-pairs and aggregates it would indicate that the solubility limit for NaFSI in PTMC lies in the region between $n = 5$ (29 wt%) and $n = 3$ (40 wt%) in the sense that NaFSI is not dissociated to discrete ions at higher concentrations.

The formation of salt aggregates is usually detrimental to conductivity due to a decrease of dissociated sodium ions; however it seems that formation of these salt aggregates might enable the PTMC$_n$NaFSI material to achieve conductivity levels that are several orders of magnitude larger than the low-salt mixtures that are unlikely to contain aggregates. Despite the fact that a lower $T_g$ is playing a role in the increase of conductivity one might argue that the difference in $T_g$ between the $n = 1$ and $n = 2$ electrolyte is quite small while the conductivity increase is so large that it indicates a different conduction regime than segmental motion alone.

One hypothesis is that the conduction in high-salt polymers includes a complementary mechanism to segmental motion. This mechanism might be percolation and is the effect when the ion clusters and aggregates become so prevalent that the small distance between them enables the cations to move from cluster to cluster. The percolation mechanism is dependent on a certain critical concentration called the percolation threshold. When this threshold is reached, the ion clusters go from being dispersed and out of contact with each other to being so prevalent that a chaotic network is formed which provides a diffusion path through the polymer.\textsuperscript{21,22}
3.3 Cathode performance

Conductivity measurements of the electrolytes provide a convenient screening method for good electrolyte candidates, but the performance in an actual application is not obtained by these measurements. One issue is that the conductivity obtained from electrochemical impedance spectroscopy is the total of both anionic and cationic charge transport and another issue is that the mechanical and electrochemical stability is not tested in their intended working environment. To provide relevant appraisal of the electrolytes, half-cell cycling tests are required. The term “half-cell” is used to differentiate between cells consisting of at least one electrode of pure sodium (half-cell) from cells that are composed of an anode and a cathode that are not made from pure sodium (full cell). The construction of a half-cell requires a cathode capable of reversible cycling against sodium metal; because no commercial sources of such cathodes were available, it was decided to construct cathodes as part of the degree project. Prussian blue was chosen as the active material for the cathode based on the easy synthesis and good performance. Prussian blue (Fe[Fe(CN)₆]) has a simple cubic structure with large interstitial sites that enables easy insertion and removal of sodium ions, it has a theoretical capacity of 170 mAh/g as well as good rate capability and capacity retention. The synthesis is a facile precipitation reaction where the single precursor, sodium ferrocyanide, is decomposed in the presence of hydrochloric acid to form the product. After synthesis the structure of the active material for the cathode was verified by XRD and the results show a good fit with the database information for Prussian blue (Figure 9).

![Figure 9](image_url)

Figure 9. Background-corrected XRD pattern of the Prussian blue material used for the cathodes. Black peaks are from the synthesised material and the red lines indicate where peaks are expected according to a database fit of Prussian blue.

From the fact that all significant peaks belongs to the Prussian blue material combined with a very low background (not shown in Figure 9) there is no reason to suspect that there are any crystalline or amorphous impurities in the synthesised material. The well-defined and sharp peaks also suggest a high degree of crystallinity. The size of the synthesised crystals was determined by SEM and the crystal-sizes ranged between 150 nm and 1.5 µm with the bulk of the crystals being between 400 and 700 nm (Figure 10).
Next a slurry consisting of Prussian blue, Ketjen black, and PVDF, was produced and coated on aluminium foil to produce the cathodes. The cathodes were tested in benchmark-cells using a 1:1 EC:DMC 0.5 M NaFSI electrolyte to better be able to assess the performance of the polymer electrolytes. As can be seen in Figure 11 the cathode shows an acceptable capacity and rate capability while having quite stable performance after some initial capacity fading that occurs during the first 20 cycles.
The benchmark cell also maintains a coulombic efficiency above 99% from cycle 10 to 100 which indicates that there are no significant side reactions taking place. The benchmark cells cycled at room temperature show that the cathode can deliver cycling performance with capacity above 95 mAh/g at C/5 for at least 100 cycles. The performance of the benchmark cell also shows that the cathode can cycle at rates close to 1C and therefore it is a reasonable assumption that the cathode should not be the rate-limiting step when cycling polymer cells.

### 3.4 Polymer battery performance

After the initial screening of electrolyte compositions through electrochemical impedance measurements, it was decided to test the most promising salt concentrations; $n = 1$ and $n = 5$. The reasoning behind this choice was that previous experience with high-salt systems indicated that there might be issues with ageing effects and mechanical stability in these systems. The issues with high-salt systems and the opportunity to compare high-salt electrolytes (PISE) and low-salt electrolytes (SPE) dictated that $n = 5$ should be included in cycling tests as it is the best-performing composition before the onset of decreasing $T_g$. The $n = 5$ and $n = 1$ electrolytes were cast directly on cathodes, and these cathodes were used for construction of half-cells that were used to represent the low- and high-salt systems, respectively. The PTMC$_5$NaFSI electrolyte was cycled exclusively at 60 °C due to the poor conductivity at lower temperatures. Figure 12 shows the cycling data and coulombic efficiency for a cell containing PTMC$_5$NaFSI; the capacity is slightly reduced compared to the benchmark cell and this is probably an effect of higher electrolyte resistance causing polarisation. While the number of cycles achieved is encouraging, there are some obvious problems that require solving; 1) the low coulombic efficiency is bothersome and would affect the capacity of a full cell relatively quickly; 2) the fact that the cell abruptly failed after 82 cycles and shows some strange behaviour around cycle 60 suggests that the cell suffers from instability due to reactions of either the PTMC polymer or NaFSI salt.

![Figure 12. Performance data for a half-cell using PTMC$_5$NaFSI at 60 °C cycled at C/5. Voltage profiles (left), discharge capacity and coulombic efficiency (right).](image-url)
By looking at the conductivity data from electrochemical impedance measurements one might suspect that the high-salt electrolyte PTMC$_1$NaFSI would outperform the low-salt electrolyte PTMC$_5$NaFSI. This is also initially the case; the data from cycling of a PTMC$_1$NaFSI cell presented in Figure 13 shows excellent rate performance at 40 °C where the low-salt electrolytes would have a hard time cycling at C/20.

![Figure 13](image.png)

**Figure 13.** Cycling data for a half-cell using PTMC$_1$NaFSI electrolyte at 40 °C cycled at C/5. Voltage profiles showing the increasing polarisation (left), Discharge capacity and coulombic efficiency (right).

There is however some critical drawbacks that show their impact after 30 cycles, where the increase in the polarisation implies a reduction of conductivity, that not only deteriorate the cell function, but in some cases also degrade the performance to the point of cell failure. Cycling data shows an increase of capacity followed by degradation of capacity after cycle 5; this cell achieved a coulombic efficiency that was consistently close to 100%, so it seems that the degradation is not primarily caused by side reactions. The degradation in the cell is likely due to precipitation of salt from the polymer as described in the AN-co-BuA–LiTFSI system by Łasińska et al.$^{39}$ The most convincing evidence for this is the increasing polarisation during cycling, seen as an increased split between charge and discharge voltage plateau in Figure 13. The cell gave consistent results for 30 cycles after which the polarisation had increased so much that cycling was ended. The increase in capacity from cycle 2 to cycle 5 is likely explained by improved contact between the polymer and electrodes with time as seen in other publications.$^{27}$ Although the coulombic efficiency was high (between 99% and 102%) it was consistently higher than 100% after the first cycle; this is evidence that the stability of the cell is not sufficient to avoid side reactions completely. In order to test the stability of the high-salt electrolyte at 60 °C, a cell utilising the n = 1 electrolyte was constructed and cycled at various C-rates, see Figure 14.
The results from this cell show that a significant capacity reduction takes place during the initial cycles at C/5 followed by what looks like stable cycling until the cell suddenly ceases to function. A closer look at the coulombic efficiency shows that the cause of battery failure probably started close to cycle 30 where the amount of charge put into the battery is quite large compared to what is returned during discharge. There must be a reaction occurring within the cell that is unwanted and detrimental. Due to the rather unpredictable behaviour of the cycle data it is hard to draw any solid conclusion as to what actually happened within the cell, but the most probable cause is decomposition of either the salt or the aluminium current collector.

In regards to the degradation and failure of the high-salt cells, there are several different likely causes of degradation. Firstly, salt precipitation; as mentioned earlier the high-salt polymer might simply be metastable when exposed to heat or left to age. It is likely that the salt leaves solution and forms nano-size salt crystals but XRD measurements of cycled or aged cells are required to prove or disprove this degradation mechanism. Salt precipitation should however not cause cell failure by electrochemical instability, instead one might expect that the $T_g$ would start to rise and the conductivity decrease until the salt concentration is reduced to a level where it can be maintained in solution. This mechanism looks probable in the case of the cell cycled at 40 °C (Figure 13). Secondly there is a possibility that the SEI formation between the electrodes and electrolyte changes character depending on temperature and salt concentration. If the SEI forms products that are themselves soluble or electrochemically active as redox shuttles it might start to consume salt while also lowering the coulombic efficiency of the cell. There is of course the possibility of failure due to inadequate mechanical stability, where problems such as dendritic growth can cause a short-circuit in the cell. This failure mode seems unlikely, as a failure through short-circuiting should be clearly visible as a sudden voltage drop. The

Figure 14. Cycling data for a half-cell cycled at 60 °C at various C-rates. Voltage profiles (left), discharge capacity and coulombic efficiency (right).
fact that the benchmark cell did not fail even after 100 cycles is also indicating that dendritic growth is not the cause of failure in the polymer cells. While there is a lot of research into SEI formation in liquid electrolytes, there are few articles devoted to SEI formation in polymer electrolytes. The two main sources found on related systems deal with PEO and PTMC combined with the salt LiTFSI. Although the articles investigate different salts than NaFSI, and the concentrations used in this work are higher than in the articles, there are enough similarities to use the articles as evidence that SEI formation does occur in cells with polymer electrolytes. The issue of electrochemical stability of the electrolyte seems to be the main cause of cell failure and poor coulombic efficiency. Whether the stability issues stem from corrosion of aluminium or from the formation of an unstable SEI on electrodes remains to be investigated, but the use of high salt concentrations seems to aggravate the problems. The problems associated with bad SEI formation seems likely for the high-salt cell cycled at 60 °C and therefore a closer study of the SEI by ESCA/XPS should be undertaken for a high-salt cell although such a study would be hard due to the difficulty in separating the infiltrated electrolyte from the electrodes.

The apparent instability of FSI could be attributed to both aluminium corrosion and bad SEI formation on the cathode but a closer look at the literature gives some insight into this issue. Numerous articles have studied LiFSI and its compatibility with aluminium; Han et al. shows that LiFSI is compatible with aluminium if the electrolyte is devoid of chloride impurities, if however there are chloride impurities the corrosion of aluminium by LiFSI becomes quite severe. In other publications it is asserted that LiFSI corrosion of aluminium is occurring even at chloride concentrations of less than 6 ppm. The case of aluminium corrosion without any mention of chloride is also described for electrolytes in organic solvents by Otaegui et al., where it is concluded that both the temperature and choice of solvent has a noticeable impact on the aluminium corrosion and SEI formation with NaFSI. It is difficult to assess whether aluminium corrosion is the cause of electrochemical instability for the cells in this study with the data currently available. The data needed to elucidate this matter could be obtained by testing the stability of a cell constructed with current collectors of a different metal such as nickel.

Beyond the electrochemical stability issues there are indications that the high-salt electrolytes suffer from aging effects that affect the conductivity of the electrolyte in a negative manner. Doeff et al. show that the precipitation of salt is accelerated by the concentration gradients that form during cycling. The results from cell cycling published by Tominaga et al. show that the electrolyte interfacial resistance increases over time without cycling, and even when this ageing is reduced by the addition of an ionic liquid, the cycling results show insufficient capacity retention even at low discharge current (C/15) and the elevated temperature of 75 °C. The lack of publications that show high-salt cells with more than 10 cycles is in itself a grim reminder of the severity of the problems associated with high-salt mixtures. The results shown in this work were obtained at lower temperatures – 40 °C and 60 °C – and, although a step in the right direction in terms of rate capability and number of cycles completed, these results also add to the evidence of instability in high-salt polymer electrolytes. In contrast, the low-salt electrolyte cell presented here outperforms most of the high-salt cells in terms of capacity retention and durability even when operating at 60°C against a cathode with inferior voltage and capacity as compared to LiFePO₄.

The PTMC–NaFSI system maintains a good mechanical stability even at high salt concentrations and the polymer cell data presented are from cells where PTMC–NaFSI acts as both electrolyte and separator. The mechanical stability deteriorates somewhat at higher concentrations, but even at 67 wt% salt concentration the films are flexible and easy to handle. Even though the mechanical stability and conductivity of high-salt PTMC shows promise, the degradation of cells during cycling shows that
a lot of problems remain to be solved before the PTMC–NaFSI PISE is useful in practical applications. For low-salt-concentration SPEs the stability is better and the cycling data is indicates that practical cells might be possible if a suitable anode can be found.

4. Conclusion
The goal of this project was to investigate the PTMC–NaFSI system and construct a working cell. This was achieved by the successful cycling of half-cells that show promising performance. The PTMC–NaFSI electrolyte can provide excellent stability when a low salt loading is used but to obtain high ionic conductivity the use of high salt loadings is necessary, and the higher conductivity comes at the cost of stability. There is however still a lot to investigate, especially in the high-salt system and successful cycling of full cells remains to be realised. The experiments performed as a part of this degree project indicate that polymer electrolytes with high salt concentrations should be tested thoroughly in cell cycling because electrochemical impedance and transport number measurements do not show the drawbacks of high-salt electrolytes. And in closing, the answer to the question in the title is: Yes, PTMC is certainly a candidate for sodium polymer batteries, if the stability issues can be resolved. PTMC displays excellent mechanical characteristics, even when mixed with salt at high concentrations and is a good platform for further development of polymer electrolytes.

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