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The Art of Cycling – Polymer Electrolytes at Extreme Conditions

ISABELL L. JOHANSSON



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Abstract

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With the rapid development of batteries for applications like electric vehicles and energy storage devices, it is essential to design and develop batteries with improved safety, long cycle life, and high energy density. To achieve this goal, the development and improvement of solid-state batteries, containing solid polymer electrolytes, is a promising solution.

The interest in polymer electrolytes is primarily owed to their proposed compatibility with high temperatures and reactive electrodes, such as metallic lithium, and their ability to withstand higher temperatures than traditional liquid electrolytes. Cycling polymer electrolytes at high temperature and with high-voltage cathodes, such as lithium-nickel-manganese-cobalt-oxide (NMC) involves a combination of high chemical, electrochemical, and mechanical stability, as well as the understanding of how to achieve these properties.

This thesis provides an overview of some challenges and possibilities of cycling batteries with polymer electrolytes at high temperatures and with high-voltage cathodes. With a focus on the stability of the polymer electrolyte, the effect of changing the polymer host material, the electrolyte salt, and the introduction of additives for enhanced mechanical stability or electrochemical stability, were all evaluated by both standard techniques and techniques developed for polymer electrolytes.

Long-term cycling at high temperature was achieved for a poly(ϵ -caprolactone-*co*-trimethylene carbonate) (PCL-PTMC) electrolyte by crosslinking additives that increase the mechanical stability of the polymer electrolyte; however, the cycling with high-voltage cathodes also required a high electrochemical stability of the polymer electrolyte. With the techniques developed herein, such as cut-off increase cell cycling, the electrochemical stability of PCL-PTMC was evaluated. By introducing zwitterionic additives to PCL-PTMC, the cycling performance with NMC was enhanced and the enhancement proved to stem from prevention of electrolyte salt decomposition. Finally, by changing the electrolyte salt, it was found that cycling with NMC was possible for PCL-PTMC below its oxidative degradation potential, as long as the electrolyte had an ionic conductivity that was high enough. By utilizing additives, the long-term stability and electrochemical stability toward NMC was also improved.

Overall, cycling solid polymer electrolytes at high temperatures and with high-voltage cathodes presents a unique set of challenges, which require that the electrochemical stability of the electrolyte is accurately described, and that the following properties are high: ionic conductivity, electrochemical and mechanical stability; all of which can be improved by utilizing additives in the polymer electrolyte.

Keywords: Solid polymer electrolytes, Lithium ion batteries, Electrochemical stability, Mechanical stability, Ionic conductivity, Additives, Polycarbonate, Polyester, Polyketone

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*Maturity, one discovers, has everything to do with the
acceptance of 'not knowing.'*

– Mark Z. Danielewski, House of Leaves

List of Papers

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

- I. Johansson, I. L., Brandell, D., and Mindemark, J. (2020) Mechanically Stable UV-crosslinked Polyester-Polycarbonate Solid Polymer Electrolyte for High-Temperature Batteries. *Batteries & Supercaps*, 3(6):527–533.
- II. Hernández, G., Johansson, I. L., Matthew, A., Sångeland, C., Brandell, D., and Mindemark, J. (2021) Going Beyond Sweep Voltammetry: Alternative Approaches in Searching of the Elusive Electrochemical Stability of Polymer Electrolytes. *Journal of the Electrochemical Society*, 168(10):100523.
- III. Johansson, I. L., Andersson, R., Shivakumar, K. I., Hernández, G., Inokuma, Y., Brandell, D., and Mindemark, J. Impossible combination? High Ionic Conductivity and Mechanical Stability in Highly Crystalline Polyketone Electrolytes. *In manuscript*.
- IV. Johansson, I. L., Sångeland, C., Uemiya, T., Iwasaki, F., Yoshizawa-Fujita, M., Brandell, D., and Mindemark, J. (2022) Improving the Electrochemical Stability of a Polyester-Polycarbonate Solid Polymer Electrolyte by Zwitterionic Additives. *ACS Applied Energy Materials*, 5(8):10002–10012.
- V. Johansson, I. L., Andersson, R., Erkers, J., Brandell, D., and Mindemark, J. The Electrolyte Salt – a Decisive Component for High-Voltage Cycling with Solid Polymer Electrolytes? *In manuscript*.

Comments on my contributions to the papers:

- I. Planned and performed all experimental work. Interpreted data and results. Wrote the manuscript with input from co-authors.
- II. Took part in planning the study and sample preparation, and performed part of the experimental measurements. Wrote parts of the manuscript and participated in all discussions.
- III. Took part in planning the study and sample preparation, and performed part of the experimental measurements. Interpreted data and results, and wrote parts of the manuscript and participated in all discussions.
- IV. Planned and performed most of the experimental work. Interpreted data and results. Wrote the manuscript with input from co-authors.
- V. Planned and performed most of the experimental work. Interpreted data and results. Wrote the manuscript with input from co-authors.

Disclaimer: Parts of this thesis are based on my licentiate thesis titled *Mechanical and Electrochemical Stabilisation of Solid Polymer Electrolytes Through Additives* (Uppsala University, 2021).

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Abbreviations

BDA	1,4-Butanediol diacrylate
CICC	Cut-off increase cell cycling
CV	Cyclic voltammetry
DMPA	2,2-Dimethoxy-2-phenylacetophenone
DSC	Differential scanning calorimetry
EIS	Electrochemical impedance spectroscopy
LCO	Lithium cobalt oxide, LiCoO_2
LFP	Lithium iron phosphate, LiFePO_4
LMO	Lithium manganese oxides, LiMnO_2 or $\text{Li}_2\text{Mn}_2\text{O}_4$
LNO	Lithium nickel oxide, LiNiO_2
LNMO	Lithium nickel manganese oxide, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$
LSV	Linear sweep voltammetry
NMC	Lithium nickel cobalt manganese oxide, $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$
PEO	Poly(ethylene oxide)
PCL	Poly(ϵ -caprolactone)
PCL-PTMC	Poly(ϵ -caprolactone- <i>co</i> -trimethylene carbonate)
POHM	Poly(1-oxoheptamethylene)
PTMC	Poly(trimethylene carbonate)
SPE	Solid polymer electrolyte
SV	Staircase voltammetry
TMPTA	Trimethylolpropane triacrylate
VFT/VTF	Vogel–Fulcher–Tammann
XPS	X-ray photoelectron spectroscopy

1. Introduction

1.1 A Battery-Powered Future

Envisioning the future, judging from popular culture media, there are primarily three major ideas of what it will look like; a utopia of white buildings intermingling with greenery and airborne vehicles zooming around the buildings [1–3], no visible exhaust fumes or cables anywhere; cyberpunk megacities [4, 5], ruled by capitalism and overtaken by technology which not only is used as a means to facilitate everyday life, but is also incorporated with the human body; or an arid, burning wasteland because the advances of climate change were either unstoppable or ignored by humankind [6, 7], and although in a declining state, humanity is still utilizing electricity. Regardless of which version of the future you believe in, the advancement of energy storage technology is necessary, and the use of electricity and stored energy is essential.

In present-day modern society, there is one component we have to thank for allowing our electronic devices to be portable: the battery. Batteries power our devices, from small and simple entertainment gadgets like the Tamagotchi, to transport vehicles, and life-sustaining implantable medical devices like pacemakers. This range of applications is due to the different components of the batteries and the chemistries which are possible to use [8–11]. Some common battery cell formats are illustrated in **Figure 1**. Certain combinations of materials only offer a single use of the battery, while others allow the battery to be recharged and used again; these are called primary and secondary batteries, respectively.

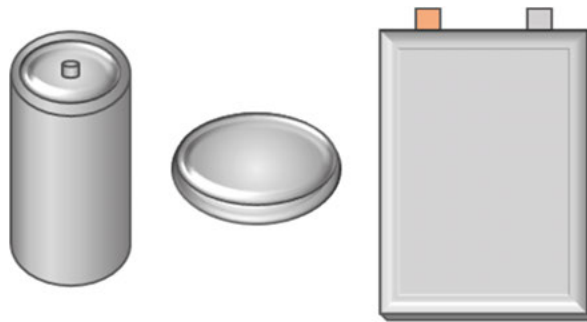


Figure 1. Schematic illustrations of some common battery cell formats, from left to right: cylindrical cell, coin cell or button cell, pouch/prismatic cell. Cylindrical cells are commonly seen in TV remote controls but are also used in Tesla cars. Coin cells can be found in wrist watches and Tamagotchi pocket devices. The rightmost cell is simply illustrated to show the general shape of both a pouch cell and a prismatic cell, the difference between the two is mainly the hard outer casing of a prismatic cell. They can both be found in laptops and modern electrical vehicles.

For example, the laptops on our desks and the mobile phones in our pockets, are all powered by a lithium-ion battery. The development of the lithium-ion battery is continually pushed by the users' request for higher power, lower mass, rechargeability, longer life time, and faster charge, and its initial developers received the Nobel Prize in 2019 for their contributions from the 1970s and onwards [12]. Although the technology is now more mature, there are still possibilities for improvements, as each separate component has yet to reach their full potential (in more ways than one), and challenges and issues are still present, with future directions pointing toward alternative chemistries [11, 13, 14].

If we are aiming for a non-dystopic future and to combat global climate change, reducing and eventually eliminating the use of fossil fuels is necessary. Replacing these energy sources is possible with renewable energy sources, and the combined use of renewable energy and rechargeable batteries, preferably containing environmentally friendly components, is a clear synergetic step in the right direction. It is also the desire of many large-scale European and global initiatives which aim for a more sustainable future.

The batteries which would be used in conjunction with renewable energy sources [15], like solar energy and wind energy, will not necessarily be portable, though. Stationary energy storage is another important aspect of an electrified future, and has slightly different requirements from the portable kind. In the stationary application, the weight of the battery will not be as important, but the safety, in case of fire, overheating, or damaging of the battery cell, is still of high importance. With an increase in global surface temperature a high operational temperature is also desirable, putting pressure on the already flammable components of commercial batteries [16–19].

1.2 The Lithium-Ion Battery

Batteries are just one type of energy storage devices, see **Figure 2a** for some examples, and the intended use of the device is what determines which type is the most fitting. With the energy storage devices that are available to us today, one can either have a high storage capacity (high energy), or fast energy delivery (high power). The reason why we specifically want batteries for applications like electric vehicles and stationary storage is the energy and power output they offer [15, 20, 21]. For example, while capacitors can deliver energy quickly, and therefore are suitable for load-leveilling applications, they cannot store enough power to run a vehicle for a very long time [22].

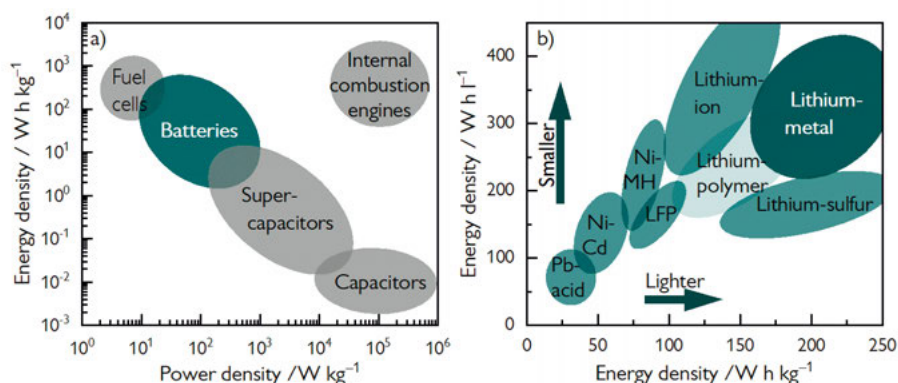
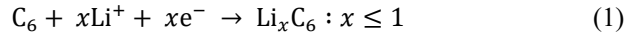


Figure 2. a) Comparison of the power density and energy density of different energy storage devices. b) Ragone plot showing the gravimetric and volumetric performance of some common and some potential chemistries for primary and secondary batteries. Note that a “lithium-polymer” battery as shown here does not contain a solid polymer electrolyte, only a liquid electrolyte within a non-conductive polymer matrix.

In very simplified terms, a battery is composed of two electrodes and an electrolyte. The electrodes, anode and cathode, can be made from many different materials and material combinations, as illustrated in **Figure 2b**. Although not very useful, a battery could be a potato with nails, made of two different metals, shoved into it.

The cathode in a lithium-ion battery is a composite electrode composed of an active material, a binder, and conductive carbon, the latter of which aids conduction electrons within the cathode. During discharge lithium ions are stored in the structure of the cathode, and during charge lithium ions are released from the cathode to allow the reaction at the anode site, the latter reaction is thermodynamically unfavorable. This redox reaction between the anode and the cathode dictates the operational voltage range of the battery, for state-of-the-art batteries the range is between 3.5 and 4.2 V, as determined by the potentials of the delithiated cathode against that of the anode. The electrodes are connected to current collectors which direct the electrons to the outer circuit, as illustrated in **Figure 3**.

Opposite the cathode is the anode. It should be a material which is able to either accommodate lithium ions within the structure, or chemically react with the lithium to form a new compound in order to store it, and the most commonly used material, graphite, is utilizing the former type of reaction. During charging lithium ions move into the structure of the graphite and form lithiated graphite, LiC_6



However, the optimal material to use as anode would be lithium metal (Li^0). The low negative electrochemical potential and high theoretical specific capacity are just two of the major advantages of using metallic lithium as anode, unfortunately there are many barriers preventing the commercial use of lithium metal batteries [23]. One is the reactivity of metallic lithium toward the other components in the battery cell, putting huge demands on the stability of the electrolyte which is in direct contact with the metallic lithium.

Another issue is the dendritic growth of lithium during repeated charging and discharging of batteries, giving a larger surface area to the reactive lithium resulting in more decomposition of the electrolyte; it could also lead to short-circuits of the cells or violent reactions that result in fire or explosions. This

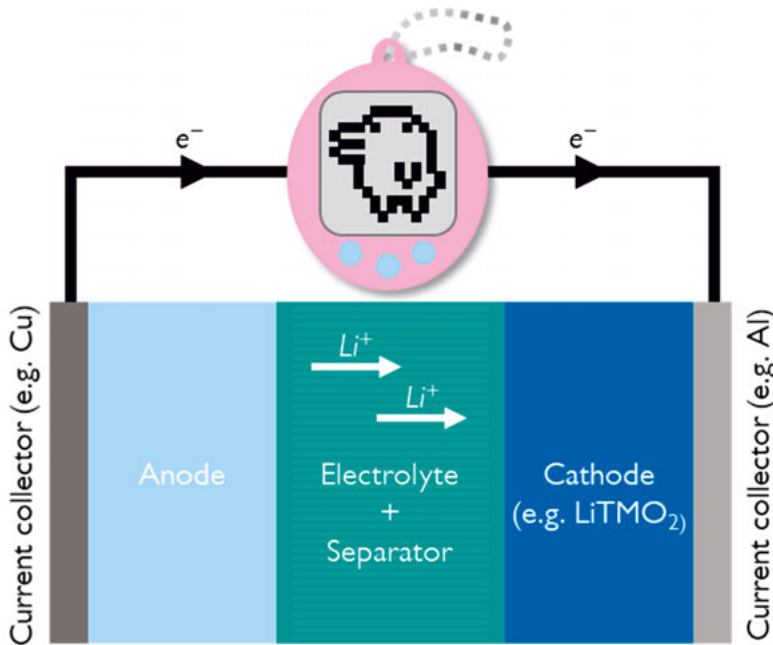


Figure 3. Schematic illustration of a lithium-ion battery during discharge; the current is drawn through the current collectors, while ions are moving through the electrolyte and separator in order to take part in redox reactions with the electrodes, powering a handheld entertainment gadget. (LiTMO_2 ; TM = transition metal such as Ni, Mn, Co, etc.)

leaves the lithium metal anode as a seldom used material in commercial batteries, until further research finds a way to prevent the mentioned safety hazards associated with this material.

For the electrons to be able to move to the outer circuit, ions must flow within the battery to balance and compensate for the generated electronic current. It is in the electrolyte ion conduction and charge compensation occurs. In commercial batteries, and in most cells prepared for research purposes, a liquid electrolyte is used. The liquid electrolyte must always be used in conjunction with a separator which separates the electrodes to prevent electrical contact between them. A separator is a chemically and electrochemically inert, porous membrane, which soaks up the electrolyte [24, 25]. It allows ionic flow between the electrodes but prevents electric contact, as this would result in a short-circuit of the battery. Separator materials are generally not ionically conductive, which is considered to be a disadvantage when attempting to design batteries with higher energy density. In high-performance lithium-ion batteries, the separators are generally made of polymers such as polyethylene and polypropylene. There are, however, moves within research to explore solid-state electrolytes, and in these cases the electrolyte itself will act as a separator. These solid-state electrolytes can be made of polymers, gels, ceramics, or composites of polymers and ceramics [26–30].

Commercial lithium-ion batteries utilize a liquid electrolyte which is composed of an organic solvent, salt, and additives. It is the organic and highly flammable solvent which is creating a hurdle when developing batteries that are capable of handling high temperatures, and batteries that are safe in case of fire, overheating, or damage of the battery cell; a hurdle which can be overcome if replacing the flammable solvent with a solid electrolyte [31]. This flammable component needs to be completely replaced in order to improve the safety of lithium batteries, either with alternative non-flammable solvents, or with solid electrolytes.

From this point on, the electrolyte and the electrodes directly in contact with the electrolyte (see **Figure 3**) will be discussed in more detail. Despite the solid polymer electrolyte, SPE, being the main topic of this thesis, it is a more niche topic when it comes to batteries, and the components found in non-solid state batteries will be discussed first.

i. Liquid Electrolyte Solvents

In commercial battery cells, liquid electrolytes are typically used. The main purpose is, as stated previously, to allow ion conduction within the battery, its components are one of the sources behind safety issues in commercial batteries. The flammability of the solvents used are the driving forces behind research for non-flammable electrolytes, the research on non-flammable liquid electrolytes is mostly focused on their ability to solvate inorganic salts and their electrochemical performance. Some common carbonate- and ether-based

solvents are depicted in **Figure 4**. The requirements of an electrolyte solvent¹ – aside from a chemical and electrochemical compatibility with the electrodes – includes the ability to solvate lithium ions. The number of solvent molecules coordinating to the lithium ion, and the structure of the resulting solvation shell, differs [32], but they have one thing in common: the carbonyl oxygen or ether oxygen is the functionality coordinating to the lithium ion.

When an electric field is applied to the battery cell, the ions move together with their coordinating solvent molecules through diffusion and migration. This mechanism of ion transport is called “vehicular transport”, which is different from the mechanism in solid electrolytes, as will be discussed in later sections.

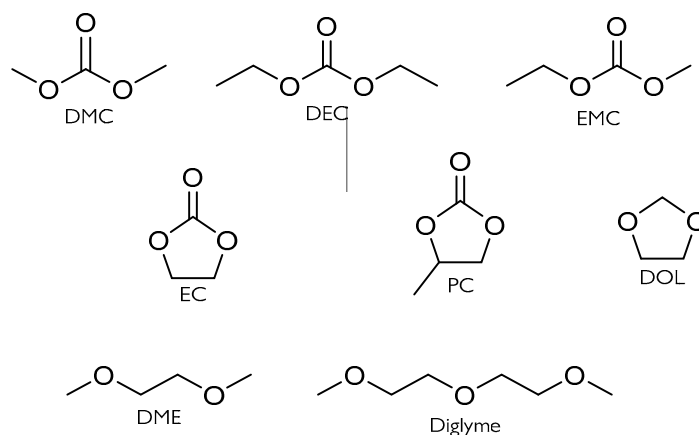


Figure 4. Molecular structures of common carbonate and ether solvents used in liquid electrolytes. The upper row shows linear carbonates, from left to right: dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC). The middle row shows cyclic solvents: ethylene carbonate (EC), propylene carbonate (PC), and dioxolane (DOL). The lowest row depicts the linear ethers dimethoxyethane (DME) and diglyme.

¹ When discussing electrolytes, it is important to be clear if the entire solution of ions, salts, additives, and co-solvents are the topic of interest, or only the separate components. To avoid confusion, the term electrolyte will, as much as possible, only be used when the entire system – that is, the electrolyte solvent and potential co-solvents, the electrolyte salt, and any potential additives – is concerned. In some cases, the solvent in a solid polymer electrolyte will be the topic of interest, that is the polymer host material; as opposed to the “polymer electrolyte” which relates to both the polymer host material and the salt that is solvated and coordinated by the polymer, and, once again, any potential additives. In order to be qualified as a solid electrolyte, the electrolyte which is used in the battery cell must be free of low-molecular weight solvent.

ii. Lithium Salts

Another important component of the electrolyte is the lithium salt. Only when dissociated does the lithium ion of the salt contribute to the ionic conductivity in the electrolyte; a good salt therefore is one that dissociates readily. The salts most frequently seen in electrolyte system differ depending on if the system is liquid or solid; in the former case lithium hexafluorophosphate (LiPF_6) is the most common [33, 34], and in the latter case lithium bis(trifluoromethanesulfonyl)imide (LiTFSI^2) is the most common salt.

During the development of rechargeable lithium-ion batteries, it was found that the combination of LiPF_6 with a solvent-mixture of ethylene carbonate and diethyl carbonate (EC-DEC), allowed stable and repeated charging and discharging with a graphite anode [35]. The finding that this specific salt and solvent combination gives a stable solid electrolyte interphase on graphite, is what allowed it to become the most commercially used electrolyte in lithium ion batteries, and it is what allowed LiPF_6 to ascend to the position of “the salt that is used in liquid electrolytes”. This feature, its ability to passivate aluminum, and its competitive pricing, are the reasons for the wide use of LiPF_6 in commercial cells. When it comes to other properties of this salt, it is comparatively not always the best salt in any area [31, 33, 34, 36]. While it does passivate the aluminum current collector, it does not have the highest ionic conductivity, it has poor stability toward water, and it has poor thermal stability [37, 38], limiting the cycling of commercial cells to below 55 °C [39–43]. The comparison of these properties and other important electrolyte properties of different salts are depicted in **Figure 5**.

Although LiPF_6 is commonly used in liquid electrolytes, it has mostly been abandoned for the use with solid polymer electrolytes. The reason for this is

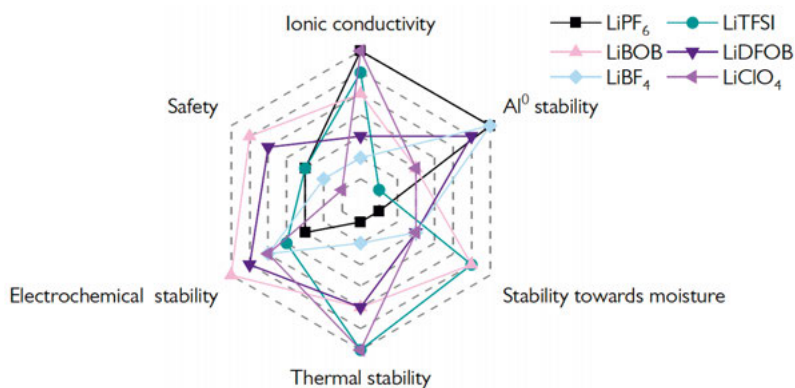


Figure 5. Properties of different salts when utilized in electrolytes for lithium-ion batteries. Adapted from [31, 33, 34, 36, 44, 45] and the material safety data sheet of each dry salt.

² Also commonly abbreviated as LiTFSA in certain parts of the World.

that the most widely used polymer is hygroscopic, and LiPF_6 decomposes into lithium fluoride (LiF) and PF_5 , especially at elevated temperature, PF_5 then reacts with even trace amounts of water to form HF , a highly reactive and dangerous compound that is also detrimental to the function and performance of the battery.



Due to the moisture sensitivity of this salt, and its poor thermal stability, it is incompatible for use with most solid electrolytes. The use of LiTFSI in solid electrolytes started in 1983 after Armand and El Kadiri Cherkaoui el Moursli [46] suggested its use in polymer electrolytes due to its compatibility with this class of electrolytes, and its many advantages over the commonly used salts at the time [34]. The thermal stability of both lithium bis(fluorosulfonyl)imide (LiFSI) and LiTFSI [38] is excellent compared to LiPF_6 . The ability to passivate aluminum is an important property for lithium salts because it is used as a current collector for the cathode; this is something that is lacking for both LiTFSI and LiFSI . Of the two, LiFSI is slightly better at suppressing aluminum corrosion [47–49], despite this LiTFSI is the salt commonly used with solid polymer electrolytes. The preference for LiTFSI stems from an apparent tendency to easily dissociate into its respective ions; it also reduces the crystallinity of semi-crystalline polymer materials due to the structural flexibility of the anion.

There are alternative salts that are less frequently used in both liquid and solid electrolytes. To start with, lithium hexafluoroarsenate and lithium perchlorate are both deemed unfit for use in rechargeable batteries due to their toxicity and dramatic side-reactions [50].

On the other hand, we have salts that can be used in rechargeable lithium batteries, but are not due to other issues. For the borate-containing salts like lithium tetrafluoroborate (LiBF_4), lithium bis(oxalato)borate (LiBOB), and lithium difluoro(oxalato)borate (LiDFOB), the fault lies in their poor solubility in most organic solvents that are used in liquid electrolytes. LiBF_4 is also inefficient at forming stable films at the electrode–electrolyte interfaces [51]. LiBOB and LiDFOB are, however, known for their excellent film forming abilities [52, 53]. LiBOB also has the added bonus of being fluorine-free, which makes it more benign than the other salts discussed thus far.

Overall, LiTFSI is seen as an excellent choice in solid electrolytes, as the issue with aluminum corrosion is less pronounced, or even non-existent, in solid-state battery cells [54, 55], perhaps because most of these cells are cycled at lower voltages where aluminum corrosion does not occur, or because of the poor dissolution of aluminum complexes in these solid electrolytes. Corrosion of aluminum can be suppressed by additives or salts [56].

iii. Additives and Electrolyte–Electrode Interphases

Electrolyte additives are a quick, simple, and affordable way to improve the performance of lithium-ion batteries. To be considered an additive, the added amount should be small, and an arbitrary threshold is usually set as “maximum 5% of the content”, whether this is in weight percent, volume percent, or molar percent varies between authors.

Additives can target different components and different events in the battery [17, 57–60], some of these events are depicted in **Figure 6**. The performance of the battery can be improved by an additive that

- 1) assists in the formation of an effective, smooth, and stable electrolyte interphase on either the anode or the cathode;
- 2) enhances the electrochemical or thermal stability of the electrolyte;
- 3) protects the cathode material from dissolution or overcharge;
- 4) improves the properties of the electrolyte; or
- 5) improves the battery’s overall safety.

Additives for battery safety are traditionally flame-retarding agents, since the liquid electrolytes in lithium-ion batteries contain flammable organic solvents. There are more ways in which an additive can improve the performance of a battery than the ones listed above, and there are some additives that enhance the performance in several ways. An example of this is LiBOB, which was introduced in the previous section as a conductive salt in the electrolyte. LiBOB can also be used as an additive to: inhibit aluminum corrosion, increase the thermal stability of the electrolyte, and protect the cathode from overcharge. Generally, borate salts, such as the ones mentioned in the previous section, can protect the cathode from unwanted reactions. Many additives are

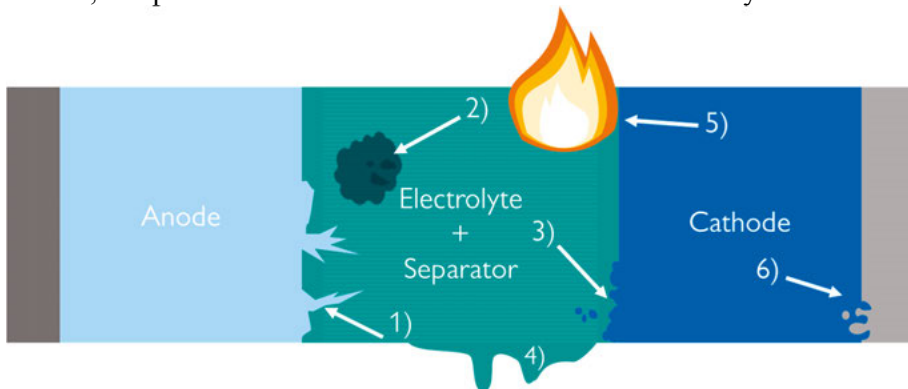


Figure 6. Examples of unwanted battery reactions or events that degrade the performance of the battery cell. 1) Uneven or dendritic growth on the anode, caused by the growth of a solid electrolyte interphase or by lithium plating; 2) decomposition of the electrolyte; 3) dissolution of the cathode or undesired reactions with the cathode; 4) poor physical properties of the electrolyte, such as high viscosity or poor wetting of the separator or electrodes; 5) dramatic events caused by fire or causing fire to start; 6) dissolution of the aluminum current collector.

sacrificial, and are intended to be consumed during the initial charge–discharge cycles of the battery, or when certain conditions are met in the battery cell. Additives are well used in commercial electrolytes, which often contain a mixture of several additives at their optimal concentration in order to get the ideal battery performance, **Figure 7** shows the molecular structures of several additives that can be used in electrolytes [17, 57–59].

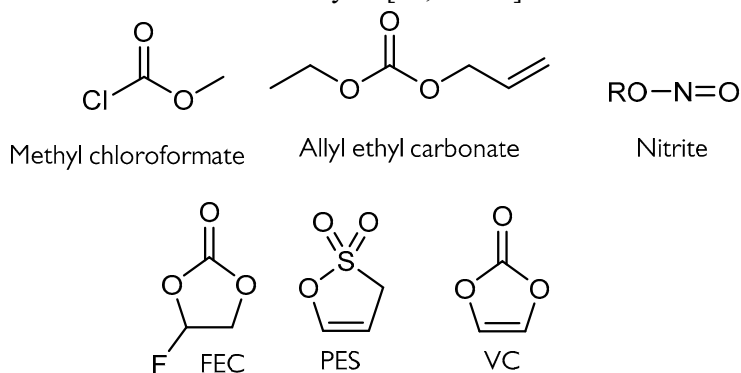


Figure 7. Electrolyte additives used in liquid electrolytes; the abbreviated compounds on the bottom row are: fluoroethylene carbonate (FEC), prop-1-ene-1,3-sultone (PES), and vinylene carbonate (VC).

Since commercial electrolytes contain LiPF_6 salt, for safety reasons, there are additives for scavenging water and HF, such as lithium 2-trifluoromethyl-4,5-dicyanoimidazole and heptamethyldisilazane [61]. But the specifics on the composition is commonly kept a secret. Meanwhile, on the research level, the focus of additives is mostly on discovering and designing potential electrolyte additives by utilizing one additive at a time and unraveling its function.

An example of when an additive has a sacrificial purpose is when, during the initial charging of a battery, a protective film is formed between the electrolyte and the electrode(s). This is because the electrolyte is generally not thermodynamically stable in contact with the electrode(s), and a kinetically stabilizing layer needs to be formed between them in order to stop the continuous decomposition of the electrolyte during charging and discharging. The protective film is called the solid electrolyte interphase when formed on the anode, and the cathode electrolyte interphase when formed on the cathode, abbreviated as SEI and CEI, respectively. There are a number of old and new high-voltage cathodes – these will be discussed in the following section – which require the formation of passivating electrode interphases for stable cycling.

The composition of the electrolyte interphases is still something of a mystery, but it is known that the mechanical properties and the stability toward dissolution of these interphases are important properties for successful and long-term cycling [57, 62]. Dissolution of the interphases, and when cracking of the film occurs due to volume change in the electrode particles, results in a

steady consumption of the electrolyte to form a new passivating film during cycling. One of the reasons for exploring solid electrolytes as an alternative to liquid electrolytes, is the assumption that solid electrolytes are more electrochemically stable. While not as much work has been performed on characterizing the electrolyte interphases in solid-state cells, due to the material properties of solid electrolytes, there should be no, or significantly less, dissolution of the interphases in all-solid state batteries. The techniques for analyzing the electrode interphases are often performed *ex situ* [63] and require the disassembly of battery cells. For solid polymer electrolytes, this cannot be done without material loss if the polymer electrolyte adheres to the electrodes, which is a common issue with sticky polymers. The surface of interest would then be destroyed or partially removed during the removal of the polymer electrolyte. This can be amended by tuning the mechanical properties of the polymer electrolyte, but because the mechanical properties of a polymer electrolyte are closely related to its ability to conduct ions, this solution is not always desirable.

iv. Cathode Materials

Most lithium-ion batteries, commercial or research cells, contain a cathode based on a transition metal oxide or phosphate, either layered or olivine type of compound. There are also spinel oxides, fluorophosphates, silicates, and organic compounds used as cathodes, but many challenges follow these difficult chemistries, bringing them further from commercialization than the cathode materials which will be discussed in this section.

The evolution of cathodes for lithium-ion batteries started with cobalt, led to various mixtures of nickel and manganese with cobalt oxides, and is today working at enabling the use of nickel-manganese oxides without cobalt and alternative chemistries featuring benign transition metals like iron, see **Table 1**. The move away from cobalt was due the anticipated scarcity, high cost, and limited electrochemical storage capacity of lithium cobalt oxide (LiCoO_2 , LCO), and the ethical dilemmas surrounding the mining of this metal [64].

LCO was first discovered as a viable cathode material for high energy density batteries in 1980 [65], and in 1991 it was commercialized by Sony. This layered oxide features high electrical and lithium-ion conductivity, low self-discharge, good structural stability, and good reversibility during charging and discharging. But with the rapid development in portable technologies, a desire for batteries with a rechargeable capacity of more than 200 mAh g^{-1} was growing, and thus, work to improve LCO was focused on improving the cycling stability and performance, preferably with environmentally benign transition metals; surface coatings and doping of the LCO crystal structure were viable methods to achieve this.

During the same era, lithium manganese oxide (LiMnO_2 , LMO) was also studied. The low cost and the use of manganese was considered favorable,

however, this material suffered from thermodynamically unstable crystal structure, and due to the high mobility of manganese ions (Mn^{3+}), dissolution of the LMO' and resulting structure change were big challenges. LMO'-type cathodes found structural stabilization with the addition of nickel, and manganese dissolution could be prevented by coating the cathode particles with cobalt. Interestingly, nickel is a sort of middle ground between cobalt and manganese [66]; when it comes to the structural stability, electrical conductivity, abundance, and environmental benignity, nickel is rated between manganese and cobalt. However, unlike the other two transition metals, the use of pure lithium nickel oxide (LiNiO_2 , LNO) is not recommended due to the reactivity of the compound.

Because of the positive effects of using both nickel and manganese as coatings and dopants for both LCO and LMO' [8, 67], the move to use equimolar amounts of cobalt, manganese, and nickel was eventually made, and in 2001 Ohzuku et al. [68] showed the cycling performance of $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$, or NMC-111.

Today, NMC is available in other combinations of nickel-manganese-cobalt ($\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$), see **Table 1** for some examples, as each transition metal has a purpose and a disadvantage if too much of it is used. Manganese and nickel improve the chemical stability of the layered oxide, but worsen the electrical conductivity and structural stability. Nickel increases the storage capacity, but decreases the thermal stability. Aluminium can also be used instead of manganese to decrease the reactivity of nickel, this compound is commonly referred to as NCA ($\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$). Both NMC and NCA are considered to be the most promising cathode materials for lithium-ion batteries today [11, 69, 70].

Despite showing great promise in commercial lithium-ion batteries, neither NMC nor NCA has shown any implementation in solid-state cells. Instead, in the commercialized solid-state cells, lithium iron phosphate (LiFePO_4 , LFP) is used as cathode material. This is partially because of challenges like the chemical and electrochemical stability of solid electrolytes, but also because many solid electrolytes require elevated temperatures to exhibit acceptable ionic conductivity, and the thermal instability of the layered oxides reduces their compatibility with solid electrolytes. Generally, olivine structures are known for their thermal stability, their stability during battery cycling, and when exposed to water and electrolyte solvents [8, 10]; this combined with operating at a lower voltage makes LFP compatible with most solid electrolyte systems, but unfit for high-energy-density applications.

LFP was first considered as a cathode material for rechargeable lithium-ion batteries in 1997 when Padhi et al. [71] showed that it was possible to reversibly extract lithium from the material. LFP needed further tweaking until it became commercially viable though. Due to the poor electrical and ionic conductivity, LFP needed to be synthesized with an optimally small particle size and coated with carbon to achieve values practical for use as cathode material.

This carbon coating leads to a lowered energy density of the final battery cell, and until recently LFP was deemed inadequate for use in electric vehicles, and only viable for stationary energy storage devices. Developments in the nickel market and recent improvements to LFP are pushing more and more manufacturers to release electric vehicles with LFP batteries.

When reflecting over the discovery and invention of the cathode materials mentioned so far, one can notice the involvement of John Goodenough in each one of them, and this is also true for the final class of cathode materials which will be mentioned here. Spinel oxides are the class of cathode materials most fit for high-energy-density applications due to their high operating voltage.

Lithium manganese dioxide (LiMn_2O_4 , LMO) and lithium manganese nickel oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, LNMO or LMNO) have an operating voltage around 4.1 V and 4.7 V vs. Li^+/Li , respectively. These are the two spinel compounds most commonly seen in literature, and LNMO is essentially LMO with nickel substituting some of the manganese in order to improve the electrochemical performance, the structure stability, and suppress the Jahn–Teller effect³, making it the most promising spinel material. Unlike the layered oxides, LNMO has a high thermal stability, it also has a large reversible capacity, stable structure, is environmentally friendly, and has a low cost [8, 72]. The main issue with LNMO is its high operational voltage and the severe capacity fade that happens during cycling due to the lack of suitable electrolytes that can handle such high voltages; the commonly used carbonate solvents and the LiPF_6 salt deteriorates well below the operational voltage needed for spinel oxides [66].

³Also known as Jahn–Teller distortion. Spontaneous change in the crystal structure of LMO and LNMO leading to severe capacity fading.

Table 1. Characteristics of a selection of intercalation-type cathode materials; their crystal structure, the cathode material, the theoretical and the practical specific capacity, and the average potential. Reproduced from Ref. [73], [74], and [11].

Crystal structure	Abbreviation	Cathode material	Theoretical specific capacity	Practical specific capacity	Average potential
			mAh g ⁻¹	mAh g ⁻¹	
Olivine	LFP	LiFePO ₄	170	165	3.4
Layered oxide	LCO	LiCoO ₂	270	150	3.9
	LMO'	LiMnO ₂	285	140	3.3
	LNO	LiNiO ₂	240	150	3.8
	NMC-111	LiNi _{0.33} Mn _{0.33} Co _{0.33} O ₂	280	160	3.7
	NMC-622	LiNi _{0.6} Mn _{0.2} Co _{0.2} O ₂	280	170	3.7
	NMC-811	LiNi _{0.8} Mn _{0.1} Co _{0.1} O ₂	280	190	3.7
	NCA	LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	280	188	3.7
Spinel	LMO	LiMn ₂ O ₄	150	110	4.1
	LNMO	LiNi _{0.5} Mn _{0.15} O ₄	150	140	4.7

1.3 Solid Polymer Electrolytes

Polymers, or plastics as they are called in the common tongue, are an extremely versatile class of materials with a partly bad reputation. The word *polymer* is a combination of two Greek words *poly-*, which in chemistry has the meaning “many, much”, and *-mer*, from the Greek word *méros* meaning “part, portion”. This accurately reflects the chemical structure of a polymer, which is formed from many repeating units or for example monomers, or as the IUPAC Gold Book states

Polymers are substances composed of macromolecules, very large molecules with molecular weights ranging from a few thousand to as high as millions of grams per mole.

The remaining part of this Introduction will highlight the possibilities, and limitations, of polymer materials as alternative electrolyte materials to liquid electrolytes. When discussing sustainability and global issues, polymers are often associated with something negative, but in battery research, the polymer electrolyte is a safer, less-toxic option compared to many liquid electrolytes.

The history of solid polymer electrolytes, often abbreviated as SPEs, starts as early as in the 1970s. In 1978, Michel Armand shared the idea that solid polymer electrolytes could be used in batteries during the Second International Meeting on Solid Electrolytes [75]. In fact, the credit goes to Armand et al. [75–78] for directing and pushing the field toward researching solid polymer electrolytes in battery applications.

The initial research was performed on poly(ethylene oxide) (PEO). P.V Wright et al. [79] added sodium and potassium salts and found a surprisingly high ionic conductivity in this solid material. For many years it seemed like PEO was the only viable polymer host material for solid polymer electrolytes. To this day it is still the only ionically conductive polymer to be commercially used as a solid polymer electrolyte, and can be found in Bolloré Bluecar® and Bluebus®, which utilizes a PEO-based electrolyte. Research is being conducted on finding appropriate alternative polymer host materials.

i. Advantages and Disadvantages of Liquid vs. Solid Electrolytes

There are many different requirements for a “good” battery; all components have properties and standards that they need to meet. For electrolytes, we have properties such as: good ionic conductivity, good electrochemical stability, safety (non-flammability), non-toxicity, and more. A simple comparison of different electrolytes is presented in **Table 2**, based on the following reviews [14, 26, 39, 80–82]. Some of these properties are met in solid polymer electrolytes, but not all. For instance, the ionic conductivity is generally poor, especially when compared to liquid electrolytes. Most solid polymer electrolytes

Table 2. A ranking of different electrolyte systems for lithium batteries (by a 4-point system). The ionic conductivity of the electrolyte at room temperature, and safety in terms of flammability, are considered here.

Electrolyte	Liquid	Gel	Ceramic	Polymer
Electrochemical stability	*	**	****	***
Thermal stability	*	**	****	***
Mechanical stability	*	***	**	****
Flexibility	**	***	*	****
Ionic conductivity	****	***	**	*
Safety	*	**	****	***
Price	**	***	*	****

fail to achieve the minimum requirement in ionic conductivity ($\geq 1 \text{ mS cm}^{-1}$) [83] to be considered for commercial applications, but only at ambient temperature. Generally, solid polymer electrolytes show good ionic conductivity at higher temperatures, where the liquid electrolytes suffer from thermal decomposition or are unsafe for use due to the flammability of the organic solvent. Unfortunately, the mechanical properties of solid polymer electrolytes also change when the temperature is raised.

At high temperature, liquid electrolytes might decompose, in benign cases this might only result in an increased cell resistance or shortened battery-life, while in more extreme cases the decomposition might result in a fire or an explosion caused by thermal runaway [41, 42, 84], with the flammable organic solvent acting as a fuel. So, from the aspect of safety, solid polymer electrolytes have a clear advantage over liquid electrolytes. Since solid polymer electrolytes do not contain any volatile or flammable solvents they are less likely to have dramatic reactions during heating; additionally, many polymer host materials adapted for the use in batteries, were originally studied for use as biomaterials [17, 85, 86], making them non-toxic. All-solid-state batteries containing solid polymer electrolytes could even potentially be more versatile to manufacture and process [87].

Despite having a much lower ionic conductivity than liquid electrolytes, research is being performed on solid polymer electrolytes with the intention of enabling the use of metallic lithium as anode [62, 88–90]. Exchanging the graphitic anode for an anode of metallic lithium is beneficial for achieving a higher gravimetric energy density in rechargeable batteries [14, 62, 89]. A major drawback of using metallic lithium is the formation of dendritic growth during cycling due to uneven lithium plating, but an aspiration is that the use of a solid polymer electrolyte will suppress or negate the formation of lithium dendrites, provided sufficient mechanical stability can be achieved for the polymer electrolyte [91].

We are not yet in the position where solid polymer electrolytes can replace the use of liquid electrolytes. And we might never be. But the versatility (in terms of structures and chemical composition) that the polymer platform offers, gives us the possibility to use solid polymer electrolytes in ways that

liquid electrolytes cannot be used, and in applications where liquid electrolytes are inadequate for use.

ii. Polymer Host Materials: Now and Then

As previously mentioned, PEO is the most extensively researched polymer host material for use as electrolyte. PEO, alongside with other ether-based polymers like poly(propylene oxide) (PPO) [77, 78] and poly(tetrahydrofuran) (PTHF) [92], were among the first polymer materials showing ionic conductivity when doped with various salts. These polymers were chosen due to their structural similarity to PEO, see **Table 3**, but due to the low ionic conductivity of both PPO and PTHF, the focus was returned to PEO with the intention of improving this material.

During the 70s, and for a number of years later, it was not clear how or why PEO was coordinating and transporting cations. Taking inspiration from the structure of natural polymers, like DNA, it was hypothesized that PEO formed similar structures. Ion conductivity in PEO was described as e.g. lithium ions moving inside the center of a PEO tunnel or along the outside of a helical structure. However, at the melting temperature of PEO (65 °C) the behavior of the ionic conductivity abruptly changes – a behavior that could not be explained with the helical model.

By the mid-80s, it was recognized that ion conduction was taking place in the amorphous phase of the polymer electrolyte, and efforts were placed in reducing the crystallinity of PEO and trying out polymer host materials that were fully amorphous. Inspiration was also taken from the molecular structures of successful solvents for liquid electrolytes, see **Figure 8**. An example of this was the carbonate-based liquid electrolytes composed of ethylene carbonate and propylene carbonate; by the end of the 1990s polycarbonates were also explored as possible host materials for solid polymer electrolytes [93, 94]. An important thing to note is that the earliest work with polycarbonates was done on either mixtures of polymers or as copolymers, with PEO as the dominating component, as opposed to polycarbonate homopolymers.

In liquid electrolytes, the carbonate-based solvents were first used due to their high dielectric constant, making them very effective at separating salt ions. When using carbonate-based polymers as electrolytes, such as poly(ethylene carbonate) (PEC) [95, 96] and poly(trimethylene carbonate) (PTMC) [97], they provide high transference numbers, but poor ionic conductivity. This was attributed to the comparatively high glass transition temperature (T_g) of these materials compared to PEO.

Further exploring the coordination possibilities between different oxygen-containing functional groups and lithium ions, polyesters like poly(ϵ -caprolactone) (PCL) were investigated [98]. PCL has a lower glass transition

Table 3. Examples of (homo-)polymer host materials used as polymer electrolytes

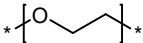
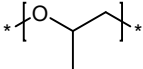
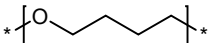
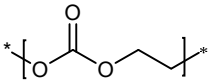
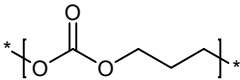
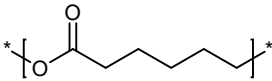
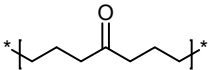
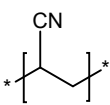
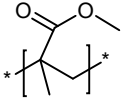
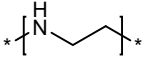
Class	Structure	Abbreviation
Ether		PEO
		PPO
		PTHF
Carbonate		PEC
		PTMC
Ester		PCL
Ketone		POHM
Nitrile		PAN
Other		PMMA
		PEI

Table 3. cont. their glass transition temperatures (T_g) and melting temperatures (T_m).

Material	T_g	T_m
	°C	°C
Poly(ethylene oxide)	−64	65
Poly(propylene oxide)	−60	Amorphous
Poly(tetrahydrofuran)	−58	42
Poly(ethylene carbonate)	5	Amorphous
Poly(trimethylene carbonate)	−15	Amorphous
Poly(ϵ -caprolactone)	−65 to −60	55 to 70
Poly(1-oxoheptamethylene)	−37 (with salt)	160 to 170
Polyacrylonitrile	85	317
Poly(methyl methacrylate)	105	Amorphous
Polyethylenimine	−47 to −23.5	59 to 60

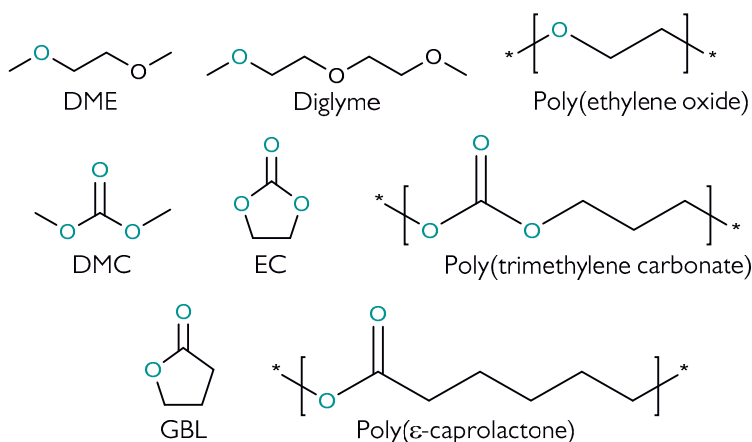


Figure 8. Structural comparison of solvents used for liquid electrolytes and the corresponding (homo-)polymers. The functional groups have been colored for easier identification, for example, the ester-group oxygens in both γ -butyrolactone, GBL, and poly(ϵ -caprolactone) are colored green.

temperature, and higher ionic conductivity than PTMC, highlighting the correlation between these two material properties. However, PCL could only be cycled at moderate rates at elevated temperatures where the material was fully melted.

As another candidate for polymer electrolyte material, the nitrogen-containing analogue of PEO, poly(ethyleneimine) (PEI) [99] was also proven to coordinate to lithium ions. But the ionic conductivity of amine-containing polymers is very low compared to PEO, and not much work has since been published on them, despite their promising ability to form hydrogen bonds. Hydrogen bonding could potentially give the polymer self-healing abilities and enhance the mechanical stability of these materials.

A new and very challenging class of polymers for the function as polymer electrolyte is polyketones [100]. Poly(1-oxoheptamethylene) (POHM) [101] is structurally analogous to PCL, and shows interesting properties which suggest that they could be suitable as high-temperature solid polymer electrolytes, after some fine-tuning to the material.

Some polymer materials commonly seen in literature on solid polymer electrolytes have purposely been left out so far. These polymers could be classed as non-conductive “polymer host materials”. Examples of these polymers include polyacrylonitrile (PAN), poly(vinyl alcohol) (PVOH), and poly(vinyl acetate) (PVAc) [102, 103]. Sometimes, electrolytes based on these polymer materials can appear to be ionically conductive, but more often than not the preparation of the polymer films was done using dimethyl sulfoxide – a solvent that is notoriously difficult to remove from polymer electrolytes – and the remaining solvent traces are responsible for the ionic conductivity. PAN is included in **Table 3** to show how its thermal properties differ from the thermal properties of ionically conductive polymer host materials.

ii. Copolymers and PCL-PTMC

As mentioned earlier in this section focusing on polymer electrolyte host materials, polymers can come in different structures, compositions, molecular weights, etc. These all require synthetic modification to be produced, which can vary from being a very facile process to extremely advanced synthesis [104–108], with some of the simpler syntheses being the ring-opening of e.g. TMC. For precise design of polymers, techniques like atom transfer radical polymerization, nitroxide-mediated polymerization, anionic/cationic polymerization, click reactions, and reversible addition/fragmentation chain-transfer exist.

The engineering of polymers, by tailoring the polymer backbone and/or side-chains, is a powerful approach to achieve desired polymer electrolyte properties. A lot of the work concerning the structure of polymers has been performed in the biomaterial field. There, shapes and architectures have been explored with the purpose of tuning the properties of polymers and oligomers for applications like drug release, surface adsorption, surfactants, and stimuli-responsive materials. Different geometrical constraints give rise to a plethora of different shapes and structures, such as: brush-, comb-, hyperbranched-, pom pom-, and star-shaped polymers. There are also simple, single-strand structures like copolymers (see **Figure 9**) and ring blocks. Copolymers can be produced when attempting to combine the properties of two different polymers, this technique is regularly utilized for polymer electrolyte host materials [109]. The overall performance of the polymer electrolyte can be improved by, for example, inserting mechanically stabilizing blocks to a soft polymer, or by breaking up the crystallinity of a polymer by copolymerization. A polymer which will be named a lot in this thesis is the product of such reasoning. Poly(ϵ -caprolactone-*co*-trimethylene carbonate), or PCL-PTMC, was first introduced to eliminate the deficiencies of both homopolymers. Some of these deficiencies have been mentioned in the previous section, but to recap and further detail the properties of both polymers: PCL has a high ionic conductivity and a low glass transition temperature (approx. $-65\text{ }^{\circ}\text{C}$), but is semi-

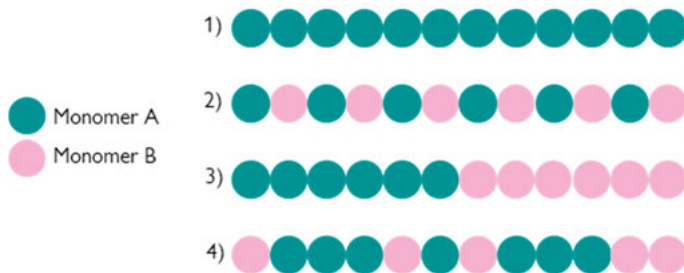


Figure 9. The simplified structures of 1) a homopolymer, 2) an alternating copolymer, 3) a block copolymer, and 4) a random copolymer.

crystalline; PTMC is fully amorphous, with a fairly high glass transition temperature of $-15\text{ }^{\circ}\text{C}$, and has a high transference number but poor ionic conductivity. This copolymer, and the equivalent homopolymers, have been intensively investigated in the biomaterials field as materials for repairing and replacing tissue; its biocompatibility is well known as is its degradability [110].

When synthesised by a bulk ring-opening procedure, one gets a random copolymer which is amber in color and with the mechanical properties of asphalt on a hot summer day. The solid polymer electrolyte based off of PCL-PTMC, and moderate amounts of LiTFSI, has good ionic conductivity, is fully amorphous, and has a low glass transition temperature; see **Figure 10**. This copolymer, especially at a composition of 80 mol-% ϵ -CL and 20 mol-% PTMC, also has excellent cycling capabilities at room temperature and with low-voltage cathodes like LFP [111–113], but the mechanical properties are not sufficiently high to allow for long-term cycling at elevated temperatures unless it is mechanically stabilized somehow. A successful attempt to improve the mechanical properties of PCL-PTMC was done using gamma radiation [114], this enables the copolymer host material to covalently crosslink without any additives. Unfortunately, not only does the irradiation treatment have a negative influence on the battery cycling, the ionic conductivity suffers when the solid polymer electrolyte is mechanically enhanced in this way. The cycling of high-voltage cathodes when using this solid polymer electrolyte is still insufficient, and the electrochemical stability is a target for further improvement.

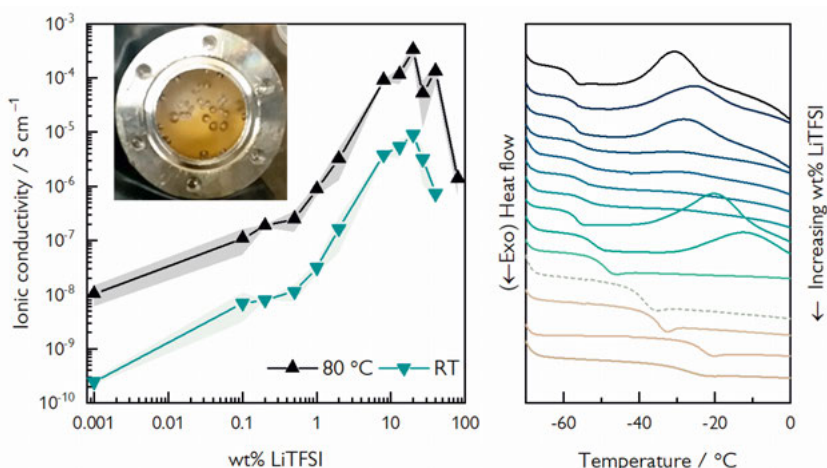


Figure 10. The ionic conductivity and thermal behavior of PCL-PTMC with different concentrations of LiTFSI salt. PCL-PTMC with 20 wt% LiTFSI is drawn with a dashed line in the differential scanning calorimetry plot. An inset in the ionic conductivity graph shows the appearance of PCL-PTMC (80:20) immediately following the bulk ring-opening synthesis, with the polymer still in the stainless-steel reactor.

iii. Additives in Solid Polymer Electrolytes

Changing the mechanical properties of a polymer electrolyte, by using additives, is sometimes done with the aim of making the polymer electrolyte more liquid-like on a molecular level. Such an additive would be called a plasticizer. Plasticizers used in polymer electrolytes are generally organic solvents that reduce the electrochemical stability and increase the flammability, compared to the solvent-free polymer electrolyte.

Additives that are used to improve the mechanical stability of polymers are crosslinking agents and, if necessary, the initiators that are needed to form crosslinks, some examples are shown in **Figure 11**. More details on modifying the mechanical properties will be given when the bulk properties of polymers are discussed. Generally, the use of additives to modify electrolyte properties, other than the mechanical ones, are rarely employed for solid polymer electrolytes, and is a subject with a lot of potential for development.

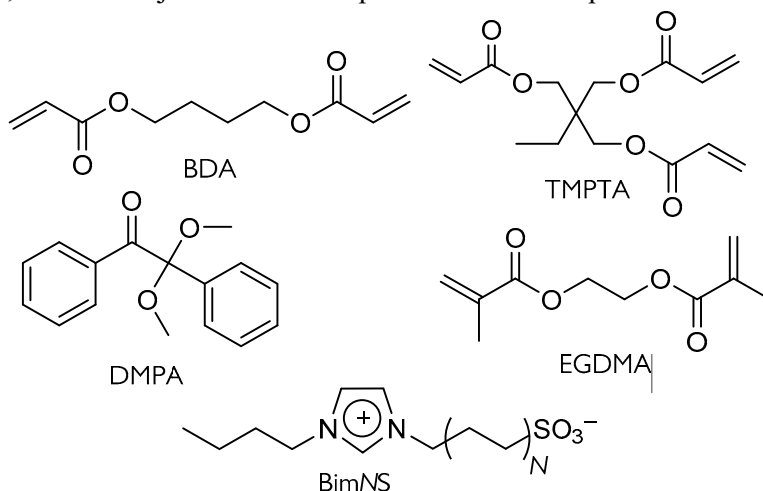


Figure 11. Electrolyte additives used in solid polymer electrolytes (from left to right, and top to bottom): 1,4-butanediol diacrylate (BDA), trimethylolpropane triacrylate (TMPTA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), and ethylene glycol dimethacrylate (EGDMA). A zwitterion is depicted as BimNs, as the spacer length between the sulphur group and the imidazolium group can be varied.

Electrolyte properties that are beneficial to improve in both liquid electrolytes and solid-state electrolytes are the electrochemical stability and the ionic conductivity. Especially in solid polymer electrolytes, additives that increase the ionic conductivity are common. One reason for poor cycling and poor cycling behavior with solid polymer electrolytes, is the unsatisfactory ionic conductivity, poor lithium plating which leads to dendritic growth, and the formation of ion pairs and ion clusters at moderate-to-high salt concentrations. A reduction in the amount of ion pairs and ion clusters improves the ionic conductivity, ion diffusion, and formation of the electrolyte interphases, by improving

the mobility of lithium ions and the solid electrolyte interphase morphology, as well as improves the stripping and plating of lithium. In semi-crystalline solid polymer electrolytes, increasing the ionic conductivity can be done by additives that reduce the crystallinity, such as by adding ceramic fillers that interact with the polymer and disrupts the formation of crystalline regions [26, 115, 116].

Zwitterions are additives which have demonstrated their usefulness in both liquid and solid electrolytes. Zwitterionic additives can facilitate the dissociation of salts, and prevent the formation of neutral ion pairs and clusters due to the high local dipole moment owing to their structure. In most cases they also improve the electrochemical stability of electrolytes as well as the cycling behavior [117–120]. Generally, an improvement to the charging and discharging behavior of cells is seen when zwitterionic additives are used. The mechanism behind this is believed to be the formation of a protective layer of zwitterions on the electrolyte–electrode interphases, or by interactions between the zwitterions and the lithium salt that prevent the salt from decomposing at the electrodes [121].

1.4 Bulk Properties in Solid Polymer Electrolytes

It is generally understood that the segmental motion of polymer chains is closely related to the ionic conductivity in solid polymer electrolytes. Owing to the large size of polymers in comparison to solvent molecules, due to steric hindrances of the polymer chains and the sluggishness of polymeric systems, the dynamics at a molecular level are fundamentally different. This can sometimes become apparent in measurement techniques showing the ionic conductivity, mechanical properties, and thermal properties of solid polymer electrolytes. Explanations for behavior seen in techniques that were developed for liquid systems sometimes need to be modified and reconsidered in order to be applicable for solid systems.

i. Thermal and Mechanical Properties

At room temperature, polymers can be in a so-called rubbery state, which is not a true solid state since there is still movement in the material at the molecular level. When a polymer is in its real solid state, called the glassy state, the polymer chains are frozen in place; there may be some vibrational movement in the material, but the chain segments are immobile. The glass transition temperature, T_g , describes the temperature at which polymer chains start to move, and is a metric that has been talked about but not formally introduced in previous sections. Below this temperature, the polymer is hard, rigid, and brittle. Above this temperature, the amorphous regions of the polymer gain enough energy to overcome steric barriers, and segments of the chains are able to

move. Due to the time scale for these processes, the polymer materials might appear macroscopically solid despite behaving as liquids at the molecular level. The transitions and their effect on the mechanical properties (modulus) are illustrated in **Figure 12a**. If the temperature is increased further, the polymer will eventually start to flow like a viscous liquid. In a semi-crystalline polymer, the amorphous regions start behaving as a rubbery solid at the glass transition temperature, while the crystalline regions stay rigid until the melting temperature, T_m , is reached. In this thesis, polymers will be referenced to as solid if they behave as such on a macroscopic level on a reasonable time scale.

The modulus describes how rigid the polymer material is, and can be divided into the storage modulus (G') and the loss modulus (G'') to describe the viscoelastic properties of a polymer during applied shear. It is this material property which has motivated research on high-modulus polymers for use with lithium metal anodes, as it is believed that a shear modulus of ≥ 6 GPa can suppress the growth of dendritic lithium [122]. Measurement techniques like rheology measure the shear modulus. The time scale, i.e., the shear rate/frequency, of the measurement dictates whether the polymer material is perceived as a solid or a liquid.

The appearance of the rheological measurement curves gives information about the viscoelastic properties of the material. At frequencies where the loss modulus is larger than the storage modulus, $G'' > G'$, the material behaves as a liquid. When the storage modulus is larger than the loss modulus ($G' > G''$), the material is solid-like. For behavior which is neither of these, e.g. when the storage modulus and the loss modulus has a frequency dependency, the material has a gel-like response. This is exemplified in **Figure 12b** where a solution of surfactants can appear as a solid at frequencies above 3 rad s^{-1} or when the container is vigorously shaken by hand. This type of viscoelastic behavior can explain why polymers with high modulus can still be subjected to penetration

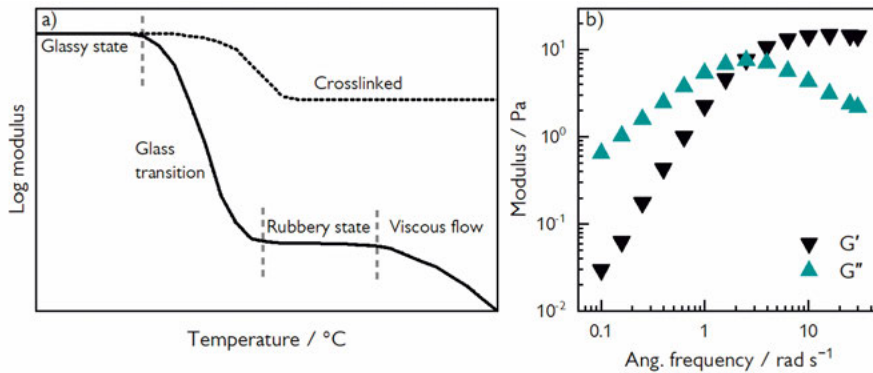


Figure 12. a) Influence of polymer mechanical properties as a function of temperature. The dotted line shows the enhanced mechanical properties of a crosslinked polymer. b) Frequency dependence on the modulus for a cetyltrimethylammonium bromide and sodium salicylate solution, measured at 25 °C.

by dendritic lithium growth. Because there is more rapid movement on the molecular scale with higher temperature, the time scale in which polymeric materials will move is also affected by temperature.

The bulk properties of a polymer originate from the molecular components of the polymer chain. When it comes to the mechanical stability of a polymer, it is altered by modifying properties like the chain length and molecular weight. Crystallinity, the presence and length of side-chains along the main chain, adding functionalities to the polymer backbone or side-chains, physical and chemical cross-links, additives, and the addition of solvents also affect the mechanical properties of the polymer. The final example is mainly used to plasticize the polymer, i.e. make it softer and increase the mobility of the polymer chains. If a polymer electrolyte contains a solvent, and despite any advantages or disadvantages of plasticizing the polymer with a solvent, it is inherently no longer a solid polymer electrolyte.

Modulus, toughness, and tensile strength generally increase with increasing molecular weight of the polymer to a certain extent. The longer the polymer chains become, the slower the mobility is, until a certain threshold is eventually reached above a critical molecular weight. This is due to physical entanglement of the linear polymer chains. When the polymer chains become long enough, they can entangle in such a way that their movement is restricted. It is easier to entangle soft and long polymer chains, the steric restrictions in rigid polymers decrease entanglement. Adding side-chains and branching structures generally leads to a decrease in both the crystallinity and the mechanical stability, this is because the formation of ordered arrangements of the chains is hindered. An exception to this is if the added side-chains can introduce chemical or physical bonds, such as cross-links, to the polymer.

Crosslinking is a method of enhancing the mechanical properties in polymers; several crosslinking types are presented in **Figure 13**. It has been extensively explored for polymers, particularly hydrogels, for biomedical applications, in order to tune the mechanical properties and the degradation rates [123, 124]. It can be done by adding a crosslinking agent to the linear polymer and allowing it to react and form a network with, or surrounding, the linear polymer. They come in different shapes and with different functionalities, with varied spacer arm lengths, chemical specificity, and reactivity, and has always at least two reactive ends which can react and form crosslinks. They frequently feature double bonds which are capable of crosslinking, such as allyl groups or (meth-)acrylate groups.

Crosslinking agents are typically polymerized through free radical polymerization, with the free radicals being supplied by an initiator. The initiator forms radicals when subjected to heat, pH change, or UV-radiation, which then react with the functional groups of the crosslinking agent. They can be utilized in semi-crystalline systems to disrupt the crystallinity if the cross-links are prepared when the polymer host is in an amorphous state, e.g. above the melting temperature, during polymerization, or when the polymer

is dissolved. If a crosslinking agent is used as an additive to form a crosslinked network around a linear polymer, the resulting material will be a semi-interpenetrating network (SIPN). In solid polymer electrolytes this can be advantageous, because the chain mobility of the linear ion-conducting polymer will not be as severely affected by the crosslinking as it would be if the ion-conducting polymer itself was involved in the covalent crosslinking.

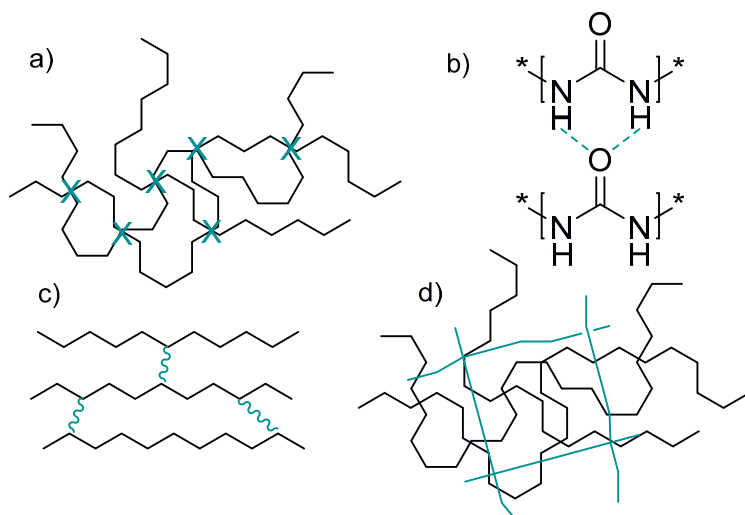


Figure 13. Crosslinking by a) physical entanglement, b) hydrogen bonding, c) covalent cross-linking, and d) semi-interpenetrating network.

Another common method of crosslinking is incorporation of functional groups to the polymer, such as amines ($-\text{NH}_2$), carboxyls ($-\text{COOH}$), carbonyls ($-\text{CHO}$), or thiols ($-\text{SH}$) to the polymer backbone or attached as side-groups [123]. In some cases, the crosslinking agents are reactive toward specific functional groups. Some common methods for forming covalent crosslinks in a polymer is by the addition of functional groups along the chain or as side-groups, by the addition of crosslinking agents, or by high-energy ionizing radiation, like electron-beam, gamma, or X-ray radiation. For linear polymers, crosslinking can be performed through physical crosslinking, e.g. entanglements as previously mentioned, by phase separation, metal–ligand interactions, or by hydrogen bonding. The technique of crosslinking which can be used in various applications depends on the chemical structure of the polymer and the desired outcome. While metal–ligand interactions are expected in solid polymer electrolytes (between the cation and the coordinating group of the polymer host), hydrogen bonding and chemical crosslinking require that the crosslinkable groups are present in the polymer chain.

Methods based on irradiation and additives are available to crosslink a polymeric material without any synthetic modifications [125, 126], and can therefore be easier to implement. Because high-energy radiation can cause damage

to the polymer material, crosslinking by addition of crosslinking agents is potentially a less destructive and just as easily applied method for crosslinking solid polymer electrolytes without modifying the chemical composition of the polymer material.

ii. Thermal and Ion Conduction Properties

In an all-solid-state battery, the function of the electrolyte is to physically separate the electrodes and to facilitate ion transport; therefore, besides good mechanical properties, the ionic conductivity of the solid polymer electrolyte is also very important. However, these two properties respond in an inverse fashion to one another, sometimes described as an antagonistic relationship. The mechanical properties and the ionic conductivity in a polymer electrolyte are thoroughly entwined, so that any manipulation to improve one property will generally lead to the worsening of the other. One such example is, increasing the ionic conductivity by reducing the molecular weight of the polymer chain, which in turn would lead to weaker mechanical properties. Another example is cross-linking of the polymer host to increase the mechanical stability, which results in a reduced ionic conductivity due to the restricted chain mobility.

The mobility of the polymer chains is crucial for the ionic conductivity. Conductivity (σ), both ionic and electronic, is the product of the mobility (μ), the concentration of free charge carriers (c), and the carrier charge (q),

$$\sigma = \mu c q \quad (4)$$

Ionic conductivity is denoted by the symbols κ or σ . Commonly, σ is used to denote ionic conductivity in solid polymer electrolytes.

A reason as to why polymer electrolytes generally have lower ionic conductivity than liquid electrolytes, is that the mechanism of ionic transport is fundamentally different, and much slower. In liquids, the conduction of lithium ions is through vehicular motion, where the solvent forms a shell around the lithium ions which it then transports through migration and diffusion. Meanwhile, in a solvent-free polymer electrolyte, the ion conduction occurs in the amorphous regions of the polymer through the segmental motion of the polymer chains (**Figure 14**). The vehicular mechanism is not applicable to solid polymer electrolytes due to the slow kinetics of the polymer chains, as there is no long-range diffusion of polymer chains. Instead, in solid polymer electrolytes, the ion is coordinated to the oxygens in the polymer chains, commonly to an ester, ether, or carbonate ester oxygen.

The mechanism of ion conduction is predominantly driven by sequences of ligand exchanges between the lithium ion and the polymer chains. Lithium ions are coordinated to a number of oxygens on the polymer chains, and as the

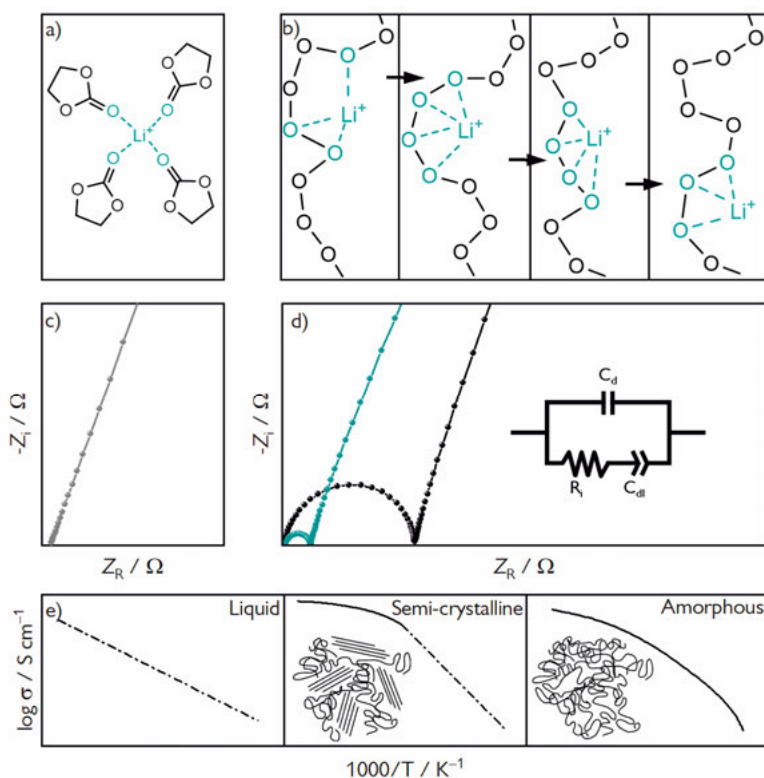


Figure 14. Visualization of a) the solvation shell during vehicular transport in a liquid electrolyte, and of the lithium-ion interaction b) in a solid polymer electrolyte, the oxygens colored green are participating in the ligand exchange with the lithium ion. Nyquist plots of c) a liquid electrolyte and d) a solid polymer electrolyte, at low and high temperature in black and green symbols, respectively. The inset shows a Debye circuit that describes the polymer electrolyte system. e) Illustrations of the typical conductivity behavior of different electrolytes.

segmental motion occurs in the polymer, the lithium ion exchanges the coordinating environment, one oxygen at a time. Whereas the vehicular transport model assumes that the initial solvent shell that forms around the ion migrates with the ion, in solid polymer electrolytes, the coordination site for the ion is constantly changing at the rate of the segmental motions in the polymer matrix [127–131]. The mobility of the polymer chains is therefore crucial for the ionic conductivity of a solid polymer electrolyte, and a polymer electrolyte with a lower glass transition temperature is optimal.

For semi-crystalline polymer host materials, their main area of use is only above the melting temperature of the materials, since only their amorphous regions conduct below this temperature. Excessive cross-linking of the polymer host, either by temporary interactions between the salt and the polymer chain, or permanently by covalent bonds between the polymer chains, will result in a lowered mobility, a higher glass transition temperature, and lower

ionic conductivity, while moderate cross-linking does not appear to have a significant effect [132].

Because the ion conduction is governed by the segmental motion, an increase in temperature also increases the mobility of the polymer chain and in turn increases the ionic conductivity, see **Figure 14d**. This can be seen by an ionic conductivity which is temperature-dependent and follows the Vogel–Fulcher–Tamman (VFT or VTF) equation, which can be seen as a modified Arrhenius equation describing the temperature dependence of viscous materials [130]

$$\sigma = \sigma_o \exp\left(-\frac{B}{T - T_0}\right) \quad (5)$$

In many studies, this can easily be seen when the ionic conductivity of an electrolyte is plotted against the temperature, such as in **Figure 14e**; a liquid electrolyte has a different shape compared to a polymer electrolyte (which features a bent line), due to a much higher mobility in liquids compared to solids, and because the measurements are performed well above their melting temperature. The molecular weight of the polymer host, the type of oxygen coordinating to the lithium ions, and the polarity of the polymer host are all properties that affect the segmental motion and the ionic conductivity of the polymer electrolyte. A lower molecular weight allows the polymer to behave more like a liquid. The influence of the molecular weight on ionic conductivity is only valid until a certain molecular weight is reached, this threshold is also related to the threshold where molecular weight no longer has an influence on the modulus, as was mentioned in the previous section. The ionic conductivity of a solid polymer electrolyte is found by performing an electrochemical impedance spectroscopy (EIS) measurement on a polymer electrolyte sandwiched between two blocking electrodes [133]. The blocking electrodes should not have any Faradaic reactions with the electrolyte, but only allow charges to build up at the electrode–electrolyte interfaces, thus behaving as capacitors. Commonly, stainless steel electrodes are utilized as blocking electrodes. Following data collection, an equivalent circuit is fit to the data, with a resistor to describe the ionic resistance of the bulk polymer electrolyte. Fitting the data to a Debye equivalent circuit (inset in **Figure 14d**) will give the value of the bulk resistance, R_b , and the conductivity can then be calculated using

$$\sigma = \frac{L}{R_b A} \quad (6)$$

where L is the thickness of the polymer electrolyte film, and A is the area of contact between the electrolyte and the electrode. Measuring the ionic conductivity over a range of temperatures yields a plot where the temperature dependence of the solid polymer electrolyte is shown, and with this, the mechanism of ion transport can be discerned by fitting the data to either a VFT or Arrhenius equation, both of which are illustrated in **Figure 14e**. The Nyquist

plot which is shown in **Figure 14d** shows both a tail and a semi-circle; if the measurement had been on a liquid electrolyte, this semi-circle would only appear if there were redox reactions occurring between the electrolyte and the electrodes, or if the ionic conductivity was sufficiently low in relation to the measured frequency. Commonly only the tail part is seen for liquid electrolytes, as the semi-circle describes the relation between the resistance and the (geometric) capacitance at the measured frequency. And, in liquid electrolytes the resistance is usually so low that the semi-circle is not visible. The semi-circle which appears when measuring on polymer electrolytes, however, is visible due to the slow ion conduction in the material relative to the measurement frequencies.

The ionic conductivity on an electrolyte is an important property, because it also has an effect on the cycling stability of the battery cell, as poor ionic conductivity will lead to uneven lithium deposition during cycling [62, 130, 134].

1.5 Stability of an Electrolyte

When it comes to solid polymer electrolytes, both the mechanical stability or the electrochemical stability could be the topic of discussion, as both are measurable properties of the stability of the polymer electrolyte. Mechanical stability is the material's ability to withstand things like the formation of dendritic growth during cycling; electrochemical stability, however, is how well the electrolyte resists unwanted reactions when in contact with the other battery components, i.e. the electrodes, and during galvanostatic cycling. The electrolyte is in contact with both electrodes while they are both charged and discharged, during a range of potentials.

The electrolyte's ability to withstand reactions is often quantified between "the maximum voltage where no oxidation of the electrolyte occurs" and "the lowest voltage where no reduction of the electrolyte occurs", and these potential limits comprise the "electrochemical stability window". This electrochemical stability sets the limit to the operational voltage of the battery during cycling, and determines which electrodes are suitable to be used with the electrolyte. However, this is only true if the electrochemical stability is measured correctly, and even then, one has to accept that the measured electrochemical stability window might only be valid with experimental parameters and material combinations, for very (VERY) specific circumstances.

Ideally an electrochemical method should give values that allows one to either design a battery cell that is electrochemically stable, or suggest an operating voltage range wherein the electrolyte does not decompose. The conventional approaches to measuring the electrochemical stability are often modeled after liquid systems, where we have convection, diffusion, and migration, and on top of this, the theory behind them might be simplified. Such

standard methods are linear sweep voltammetry (LSV) and cyclic voltammetry (CV). While these methods are still widely used, in the past years they have faced a lot of criticism [135–137], especially in the solid polymer electrolyte community, for not giving values of the electrochemical stability window that reflect the actual stability of solid state cells during galvanostatic cycling. A common issue with both experimental and theoretical methods that evaluate the electrochemical stability for solid polymer electrolytes is that the stability is often overestimated [137].

An example of this is the difficulties faced when attempting to cycle PEO against high-voltage cathodes like NMC. Although PEO is often cited as having an electrochemical stability of up to 4.6 V, it does not perform well during galvanostatic cycling with NMC-111. Some blame is placed on the mechanical stability of the polymer, claiming that stable cycling can be achieved by either mechanically stabilizing the polymer by crosslinking [134] or by increasing the thickness of the polymer electrolyte [138] or adding a spacer around the polymer electrolyte [139].

Poor galvanostatic cycling, due to an unstable electrolyte can be seen by things like: increase in resistance during cycling, due to the build-up of degradation products, deterioration of the electrolyte and electrodes, or consumption of the electrolyte to form new solid electrolyte interphases; “voltage noise” behavior, in which the voltage profile stops being smooth and instead starts to fluctuate wildly; (what appears to be) “infinite” charging or discharging; and either rapid or soft short-circuits. These are all behaviors that can be witnessed in solid-state battery cells; examples from real solid-state cells are shown in **Figure 15**.

To study the areas that require improvement, new tools and methods for accurately defining the electrochemical stability of solid polymer electrolytes are needed. Recognizing the mechanisms behind degradation is only one step in preventing decomposition of the electrolyte; the first step is to realize when decomposition occurs. Otherwise, the quest for realizing all-solid state battery cells with high-voltage cathodes will be a search in the dark – with random moves, until a modification or chemistry that works is discovered.

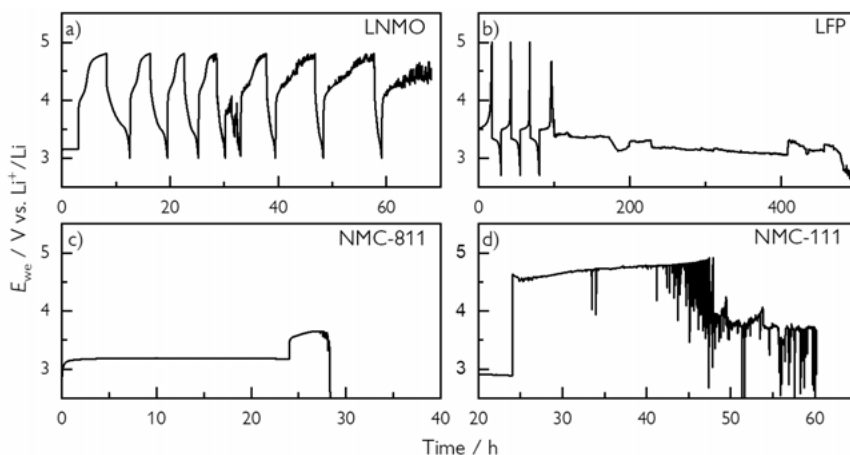


Figure 15. Solid-state cells with different failure behaviors; a) voltage noise; b) “infinite” charging, the fourth charging step continued for over 400 hours; c) rapid and sudden short circuit; d) many “soft short-circuits”. The cells have the configuration $\text{Li}^0\text{PCL-PTMC}:\text{LiTFSI}|\text{cathode}$, with the type of cathode specified in the figure legend.

i. “Standard” Electrochemical Methods

The most commonly used techniques for determining the electrochemical stability window are linear sweep voltammetry and cyclic voltammetry. The difference between them is that an additional reverse scan, or several cycles of scans, are performed in CV. The experimental cell is constructed of a working electrode, a reference electrode, and a counter electrode. A two-electrode set-up can also be used, in which the counter electrode also plays the role of the reference electrode. Not only is the two-electrode set-up more convenient and simpler to produce, it can also exactly mimic the set-up in a real battery cell. In a three-electrode set-up, the counter and reference electrode are separate, and the reference needs to have a constant potential which can be used to measure the potential of the working electrode. While this is the preferred set-up for certain analyses, choosing an appropriate reference electrode can be difficult, especially with a solid-state electrolyte.

Often the working electrode is an inert, non-porous material such as glassy carbon, gold, platinum, or stainless steel when examining the oxidative stability, and copper or nickel when examining the stability during reduction. If the electrochemical stability of only the electrolyte is of interest, choosing inert electrodes is important to avoid other faradaic processes than the ones of degradation of the electrolyte, as well as to avoid catalytic effects of the electrode surface.

When combining the different components of a battery cell, they undoubtedly interact with each other, which could result in catalytic, passivating, and other chemical reactions to occur at both rest and when either a potential or current is applied. While the components of the battery could be separated and

studied one by one, from an application point of view, the analysis of the entire system is more significant and relevant. Some authors have suggested to improve the accuracy of LSV and CV by using an active material as working electrode [140]; the composite electrodes that are used during real galvanostatic cycling can have catalytic effects that promote the decomposition reactions in the electrolyte. Thus, when using an inert working electrode, it is easy to overestimate the electrochemical stability of an electrolyte.

During voltammetric measurements the current density is measured as the voltage is swept. Any changes in current response, such as a rapid increase in current, would suggest an electrochemical reaction is occurring, such as decomposition of the electrolyte. The charging or discharging of an active material would generate a current, the same type of response which is indicative of degradation of the electrolyte. Calculating the current, which is due to the charge or discharge of the active material, and subtracting it from the charge generated during the measurement, would be necessary in this case. An alternative solution, would be to look at the coulombic efficiency of charge and discharge.

Other processes that would generate a current are the formations of passivating films, the solid electrolyte interphase and cathode electrode interphase as mentioned in earlier sections of the thesis. If a passivating film is being formed during the first cycle in cyclic voltammetry, the following cycles should have less current generated at the potential where the passivating film was formed – unless the generated current was in fact only from degradation of the electrolyte. A resistive layer of decomposition products could also decrease the amplitude of the current density.

The popularity of these voltammetric techniques is due to how fast results can be acquired and the simplicity of the set-up. The most problematic step is the analysis of the results. This is partially made worse by the large number of experimental parameters that affect the outcome of the measurement. The magnitude of the measured current response will depend on the electrodes used, the temperature, the ionic conductivity of the electrolyte, the thickness of the solid polymer electrolyte film, the concentration of the electrolyte, and the scan rate. Due to the iR -drop, an increase in resistance will appear to shift e.g. oxidative degradation reactions to higher potentials. This is true in liquid electrolytes, and becomes more problematic in polymer electrolytes which generally have more sluggish kinetics. This shift in potential scales with the scan rate. Most researchers tend to perform voltammetric measurements on solid polymer electrolytes at moderately slow scan rates (0.1–1 mV/s), although many are also using higher scan rates (>5 mV/s).

Methods for determining onset of the electrolyte degradation are often arbitrarily chosen and lack theoretical significance. Often, an exponential increase in the current is used to determine the electrochemical stability of the electrolyte. Other times, a specific (but arbitrarily chosen) current density is chosen as the start of degradation. In an attempt to have a more reliable method for finding the onset of degradation, some authors suggested choosing the

electrochemical stability limit as the intersection between two tangents – the tangent before exponential current increase, and the tangent of the exponential current region [135, 136]. These methods are not always implemented in the same way between groups, (especially since there is no well-defined tangent to the exponential region) some degree of subjectivity is to be expected, still adding some inconsistencies when using these methods of drawing tangents to determine the degradation onset potential. Additionally, they do not consider if the degradation is reversible or irreversible. An advantage when using CV over LSV, is that irreversible degradation can be spotted more easily by monitoring the coulombic efficiency; an excess in charge capacity compared to discharge capacity can be attributed to irreversible reactions.

ii. "Novel" Electrochemical Methods

Steps have been taken within the research community to develop new electrochemical methods that are more reliable, with the intention to avoid subjectivity during data analysis, to reduce the dependence on experimental parameters, and to suggest standard procedures and parameters.

Chronoamperometric measurement techniques are seeing increased implementation for solid polymer electrolytes. Under terms like staircase voltammetry and potentiostatic hold (or potentiostatic intermittent titration technique) [137], these chronoamperometric techniques are used with solid polymer electrolytes because the step allows the sluggish polymer electrolyte to fully react. When the potential step is long enough, even the polymer electrolyte will have sufficient time to react and reach an equilibrium. The onset potential for the reaction will not be shifted due to overpotential associated with the scan rate in voltammetric techniques. In these techniques, the electrolyte is assumed to be stable if the current relaxes to zero, or to some value of residual current that is seen at a voltage where the electrolyte is thought to be stable. If the current increases, or shows some other erratic behavior, the electrolyte is decomposing.

The voltammetric methods are supported by years of theoretical and experimental work. Using this, Li et al. [141] used a modified procedure for CV in order to calculate the irreversibility of the electrolyte system. Multiple cycles of CV are performed on a single sample, with increasing upper cut-off potential. Based on the anodic and cathodic current, they show that a value for the system's irreversibility can be found.

In the publication by Mathew et al. [142], sweep voltammetry is used with a potential sweep that follows a specific voltage profile. The voltage profile used in the measurement is recorded from a reference sample; this voltage profile is then applied to the cell of interest. The gradient of the integrated current (dQ/dE) that is produced from the sample is then analyzed. The validity of the method is tested with liquid electrolytes; however, the technique is

also applicable to solid electrolytes by choosing cycling rates that are appropriate for these.

iii. Non-electrochemical Methods

Even with the methods mentioned above, it is not always possible to evaluate the electrochemical stability of polymers using only one method. In fact, combining several methods is not only appropriate, but also beneficial for a thorough analysis.

As technology advances, it becomes more and more common to find publications where two or more techniques are combined to analyze the electrochemical performance of battery cells. Post-mortem analysis is frequently seen, especially for cells with liquid electrolytes. In these, the cells are subjected to an electrochemical technique, disassembled, and the interfaces or bulk materials are analyzed with a separate technique. It could be, for example, a CV or LSV measurement followed by X-ray photoelectron spectroscopy (XPS) measurement of the decomposition products produced during the voltammetric sweep(s) [143, 144]. There are many combinations of complementary techniques to be used to study the electrochemical behavior of battery cells.

The ideal combination of methods to precisely evaluate the electrochemical stability of solid polymer electrolytes would be (1) in a cell configuration that mimics the real battery cell. If the intention is to use the polymer electrolyte with metallic lithium and NMC, these are the electrodes which should be utilized during the electrochemical evaluation as well. The implementation of (2) a three-electrode set-up is also beneficial in order to see which electrode is reacting with the electrolyte during the decomposition. The decomposition of the electrolyte is most likely accompanied by an increase in resistance, therefore, (3) a method to analyze the change in resistance of the electrolyte should be employed. If possible, the electrochemical methods should be supplemented with (4) an in situ spectroscopic method in order to evaluate if degradation products are being formed.

2. Scope of This Thesis

The previous outline in **Chapter 1** described the different components of a lithium battery, with a focus on the electrolyte and the electrodes which are in direct contact with it. The lithium battery with a liquid electrolyte was briefly illustrated, and was then followed by the historical developments of solid polymer electrolytes. Key challenges for solid polymer electrolytes used with high-voltage cathodes were presented, and both previous and current attempts at dealing with these challenges were mentioned, with more and more arrows pointing to issues regarding the stability of the polymer electrolytes. When it comes to the stability, both mechanical and electrochemical stability are of interest.

Much like the **Introduction** goes through the various battery components, one at a time, the Thesis is organized by looking over the electrochemical performance of solid polymer electrolytes, one technique or one electrolyte-modification strategy at a time. This approach and the relevant papers for each topic are illustrated in **Figure 16**. The studies detailed herein had the primary goal of developing a solid polymer electrolyte that could be cycled at extreme conditions. Extreme conditions, in the context of solid polymer electrolytes, includes the use of metallic lithium as anode, high temperatures that cannot be achieved with common liquid electrolytes (i.e., $>55\text{ }^{\circ}\text{C}$), and the use of high-voltage cathode materials like NMC and LNMO.

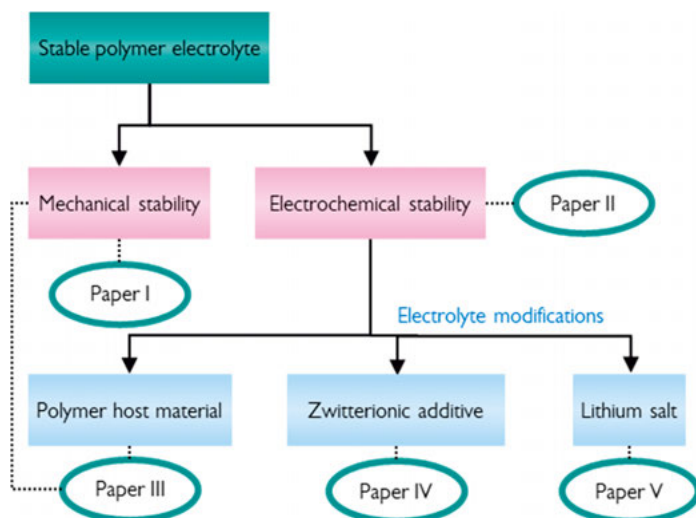


Figure 16. Schematic representation of the papers included in the Thesis, and the different approaches to improve the electrolyte stability.

The random block copolymer PCL-PTMC is one of many alternative polymer host materials with many excellent properties, although the mechanical stability of the material at elevated temperature and the electrochemical stability can be further improved. Thus, in **Paper I**, the mechanical properties of PCL-PTMC are tackled through the use of crosslinking additives and UV-radiation. Crosslinking by the use of additives could be the necessary approach in order to achieve mechanical stability without adverse effect on the ionic conductivity or the electrochemical stability of the electrolyte.

Being able to measure the electrochemical stability of a solid polymer electrolyte, in a relevant and reproducible way, is of high importance when attempting to formulate a solid polymer electrolyte that can handle demanding conditions during battery cycling. The standard voltammetric methods are not sufficient for describing the electrochemical performance of a solid polymer electrolyte. In **Paper II**, different electrochemical methods for determining the electrochemical stability of solid polymer electrolytes are explored. By targeting and showcasing the different shortcomings of the standard LSV and CV, three alternative methods are presented. The first is a voltammetric technique: staircase voltammetry (SV), which addresses the issue of mass transfer in sluggish electrolyte systems. The second technique utilizes an appropriate voltage profile during LSV. And the third technique is based on galvanostatic cycling of a real battery cell, wherein the upper cut-off is increased during cell cycling, called cut-off increase cell cycling (CICC).

Paper III evaluates different polymer host material classes, including a polyketone. The thermal properties, ionic conductivity, mechanical properties, and electrochemical stability according to standard methods are measured and compared between polyketones, polyesters, and polycarbonates, in order to find alternative polymer host materials that might be suitable for extreme cycling conditions. The unexpectedly high ionic conductivity in the polyketones, despite its high crystallinity and mechanical stability, makes it interesting to study as a solid polymer electrolyte.

In **Paper IV** and **Paper V**, the composition of the PCL-PTMC electrolyte, which was featured in **Paper I**, is modified, either by supplementing the electrolyte with additives or by exchanging the salt anion. Zwitterionic additives have shown to improve the electrochemical properties of electrolytes, and in order to enable cycling with NMC, two different zwitterions were added to PCL-PTMC. The most interesting finding in this work was that XPS measurements on post-mortem cells showed the decomposition of TFSI during cycling with NMC. Thus, in **Paper V**, the anion was exchanged, and the effect on electrochemical stability was evaluated with PCL-PTMC combined with alternative lithium salts.

3. Results and Discussion

A solid polymer electrolyte differs from a liquid electrolyte in many ways. The inherent properties of polymers, and the variety of modifications that can be made to their structures, can make them advantageous to use as electrolytes. Ideally, these inherent properties should be enhanced and further developed, and any limitations with them should be overcome, in order for solid polymer electrolytes to become viable for use in batteries at extreme conditions. Inspiration should be taken from the high chemical, electrochemical, mechanical, and thermal stability of solid polymer electrolytes when considering possible applications, instead of focusing on their shortcomings.

But the reality is that, without modifications, polymer electrolytes can either have a high ionic conductivity or good mechanical properties, but not both at the same time. That is, unless the ionic conductivity can be decoupled from the segmental motion, or the mechanical stability can be improved in a way that does not have a negative impact on the ionic conductivity. Another barrier that solid polymer electrolytes are facing deals with the characterization of their electrochemical stability and apparent lack of stability toward high-voltage cathodes.

Literature on solid polymer electrolytes is dominated by poly(ethylene oxide) and its analogues [26, 145] – this polymer is featured in **Paper II** and **Paper III** – but there are many other suitable polymer host materials which are available as alternatives to PEO, for example, the random block copolymer of ϵ -caprolactone and trimethylene carbonate (PCL-PTMC) [27]. PCL-PTMC is featured in **Paper I**, **Paper IV**, and **Paper V**. Its main shortcoming is the poor mechanical stability at elevated temperatures, the topic of Section 3.1 and **Paper I**.

Section 3.2 concerns the techniques used to measure the electrochemical stability of solid polymer electrolytes (**Paper II**). The techniques suggested in **Paper II** are used in Section 3.4 (**Paper IV**) and Section 3.5 (**Paper V**) to evaluate the viability of modifying the solid polymer electrolyte with either zwitterionic additives or by exchanging the anion of the lithium salt.

3.1 Crosslinking with Additives

Mechanical stabilization through crosslinking is a fairly common practice for solid polymer electrolytes, for PCL-PTMC it has previously been done by high-energy gamma irradiation [114]. This proved to be a successful method of enhancing the mechanical stability, but at the cost of reduced ionic conductivity and worsened cycling capabilities of the polymer electrolyte. Another

drawback was the need to use specialized equipment to irradiate the samples. A mechanically stabilizing block has also been added to PCL-PTMC [146], however, synthesizing an ordered block copolymer typically requires additional synthetic steps. In **Paper I**, the irradiation was instead done in-house, with a simple UV-lamp set-up, and with additives that are added to the polymer solution during the solvent casting procedure. Because of the antagonistic relationship between ionic conductivity and stiffness in solid polymer electrolytes, the rheological properties and the ionic conductivity of these materials should be measured to optimize the electrolyte.

Crosslinking by the use of additives is a common procedure for polymers used as biomaterials, as it can produce polymers that are both tough and flexible, and has previously been used on PTMC and a PTMC-PCL-PTMC block copolymer [125]. In biomaterials, it is important to consider the toxicity of any additives, such as crosslinking agents and initiators; this is not as much of a problem for battery applications. For this purpose, additives that are reliable and with short reaction times were chosen. Two crosslinking agents were chosen in **Paper I**, the trifunctional trimethylolpropane triacrylate (TMPTA) and difunctional 1,4-butanediol diacrylate (BDA), which are expected to give different crosslinking densities and affect the ionic conductivity to different degrees. To initiate the crosslinking reaction, 2,2-dimethoxy-2-phenylacetophenone (DMPA) was chosen as initiator. DMPA forms radicals when exposed to UV irradiation, which are capable of reacting with the acrylate groups of the crosslinking agents, and can efficiently react even within thick samples [147], this component was kept at 5 wt% in all crosslinked samples.

The exact classification of the crosslinked solid polymer electrolytes was not performed in **Paper I**, as only mechanical enhancement was deemed important for the application, however, the DSC measurements (see Supporting Information for **Paper I**) showed no significant change in T_g between the pristine and crosslinked polymers. This suggests that the crosslinking had little to no effect on the segmental mobility of PCL-PTMC, and that crosslinking was due to the formation of a semi-interpenetrating network. This procedure should not have an adverse effect on the mobility of the conducting polymer, aside from potential radiation damage, such as chain scission. Chain scission is the degradation of polymer chains as they are broken into smaller components by prolonged high-energy radiation. There is also the possibility that the PCL-PTMC chains are participating in the crosslinking to some degree; the hydrogens on ϵ -caprolactone could potentially react with the radicals that are formed during UV-irradiation, and this reaction would form crosslinks through chain transfer.

The modulus of the polymer electrolyte shows a significant enhancement upon crosslinking, see **Figure 17a**. The enhancement was enough to mechanically stabilize the polymer electrolyte up to 120 °C. For all compositions, the crosslinked polymer electrolytes have a higher storage modulus and decreased frequency dependence, in both the storage and loss modulus, compared to the

pristine electrolyte. This indicates that the polymer electrolytes have a higher mechanical stability and are less likely to flow. The highest storage and loss modulus was found in the sample containing 10 wt% BDA, a decrease in storage modulus was seen when more of the crosslinking agent was added.

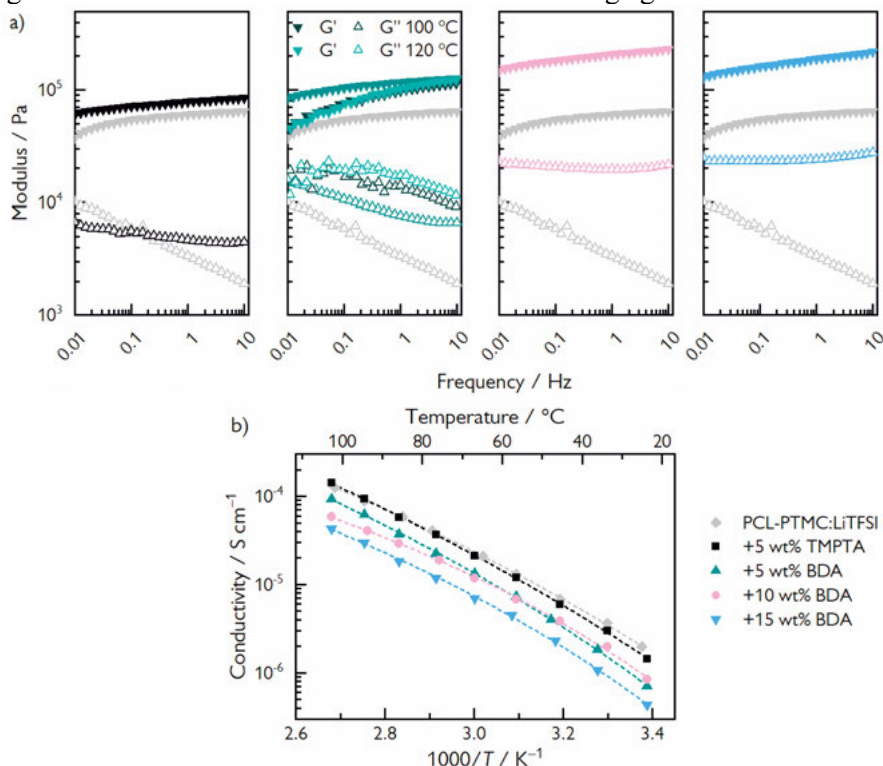


Figure 17. a) Frequency sweeps, and b) ionic conductivity of the pristine polymer and the crosslinked polymers. All samples contain 20 wt% LiTFSI, the crosslinked samples also contain a crosslinking agent and 5 wt% DMPA and were exposed to UV-radiation for 5 minutes. a) Rheological measurements were performed at 25 $^{\circ}\text{C}$, with additional high-temperature measurements for the sample with 10 wt% BDA. Filled triangles represent the storage modulus and hollow triangles represent the loss modulus.

The modulus was expected to increase when PCL-PTMC is incorporated in a crosslinked network, since this would restrict the movement and flow of the copolymer, but some negative impact on the ionic conductivity can also be expected with the restricted movement of PCL-PTMC. In **Figure 17b**, the ionic conductivity can be seen to decrease with higher content of crosslinking agent. The crosslinked electrolyte with 5 wt% TMPTA is performing almost as well as the pristine electrolyte; with increasing wt% BDA the ionic conductivity becomes lower and lower. This could be attributed to a decrease in chain mobility when the polymer is crosslinked. Since the T_g is largely unchanged

in the crosslinked samples, a likely explanation for the decline in ionic conductivity is that the crosslinked network disrupts the ion conduction pathways, or because the concentration of ionically conductive polymer is decreased. Still, if the ionic conductivity of the polymer electrolyte is too low to support a desired cycling rate, the temperature can simply be increased to achieve a higher ionic conductivity, a solution only possible for a polymer electrolyte that is mechanically stable.

The cycling performance of the crosslinked polymer electrolytes was tested with both rate tests and temperature tests, see **Figure 18**. The mechanical stabilization of the solid polymer electrolytes would allow them to be tested at higher temperatures than the pristine polymer electrolyte; the high temperature would also mean that the application of higher current densities should be possible during galvanostatic cycling due to the increased ionic conductivity. The cycling performance of the crosslinked polymer electrolytes was excellent at 80 °C, allowing stable cycling with an acceptable discharge capacity even at 1C, see **Figure 18a**. Typically, battery cells with solid electrolytes need to be cycled at slow rates due to low ionic conductivity. While 1C was possible, increasing the C-rate to 1.5C causes the discharge capacity to fall below 125 mAh g⁻¹ and the coulombic efficiency to become unstable.

The possibility to use PCL-PTMC electrolytes at high temperatures, where liquid electrolytes are unstable and potentially unsafe for use [42], is improved with crosslinking. Without crosslinking, this electrolyte is very prone to short-

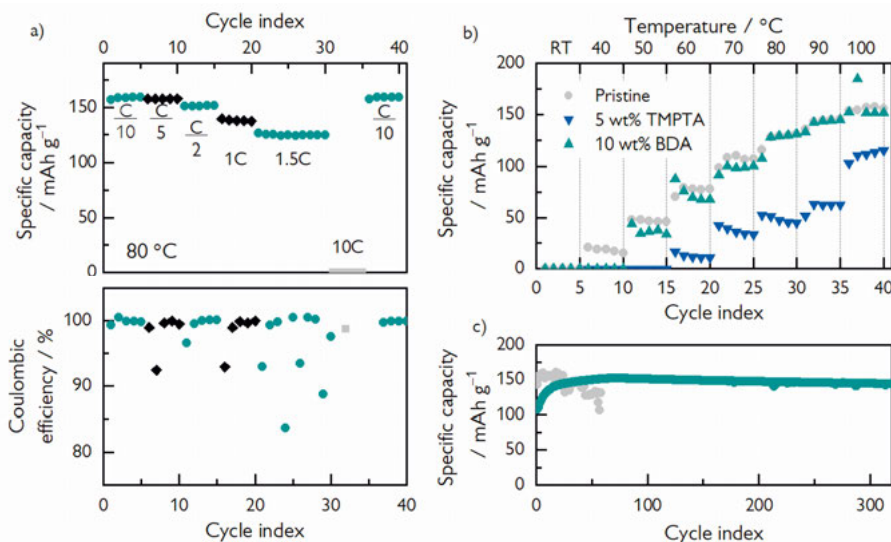


Figure 18. Cycling performance of Li⁰|SPE|LFP cells between 3.0–3.8 V vs. Li⁺/Li. The a) discharge capacity and b) coulombic efficiency during C-rate tests. c) Discharge capacity as the temperature is increased every five cycles, with a cycling rate of 1C (0.29 mA cm⁻²). d) Long-term cycling at 80 °C with a cycling rate of C/2 (0.16 mA cm⁻²). a), b) and c) feature a crosslinked polymer electrolyte with 10 wt% BDA.

-circuiting within hours at elevated temperature. Here, in **Figure 18b**, the cell with BDA crosslinking agent reaches the same discharge capacity as the pristine sample at ≥ 80 °C despite the difference in ionic conductivity. Although the trifunctional crosslinking agent gave the highest ionic conductivity, and the lowest storage modulus of all crosslinked solid polymer electrolytes, it had the lowest specific capacity at all temperatures. It is possible that TMPTA is more reactive than BDA, and forms resistive films on the electrodes in the battery cell set-up. In **Figure 18c**, cycling at 80 °C with LFP cathode is shown; the cell with pristine polymer electrolyte short-circuits after several unstable cycles, while the cell with crosslinked polymer electrolyte shows successful and stable long-term cycling.

As evidenced by publications with similar crosslinking strategies [109, 114, 126, 148], this approach to improve the mechanical properties of polymer electrolytes with additives is both successful and easily applied to many polymer host material systems. The degree of crosslinking can be tuned to achieve sufficient mechanical stability while attaining a high ionic conductivity; however, the impact on the electrochemical stability should not be ignored. The crosslinked systems often show reduced electrochemical stability (see **Figure 19**), perhaps an effect of the irradiation of the sample or due to the reactive crosslinking additives.

Just like the mechanical stability can be enhanced by additives, so can the electrochemical stability be increased by additives. The oxidative stability of the polymer electrolyte is most affected by crosslinking, this could be seen in the cycling profiles of these electrolytes during charging (**Figure 19a**), and remedying this is more important when cycling is performed at higher temperature, as electrochemical side-reactions are more likely to occur more rapidly at higher temperatures, which would have a negative impact on the long-term stability of the battery.

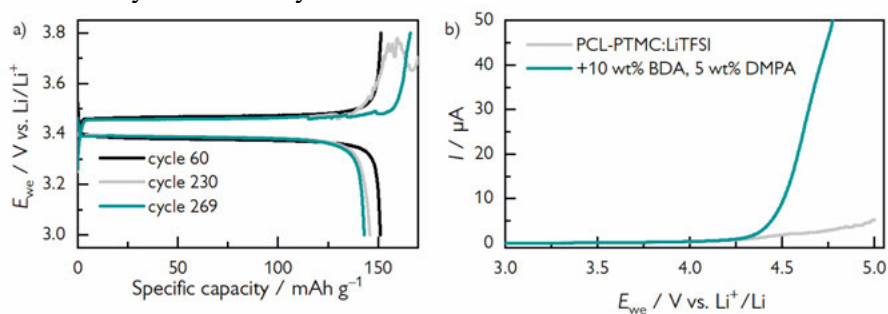


Figure 19. a) Cycling profile of $\text{Li}^0\text{PCL-PTMC:LiTFSI}+10 \text{ wt\% BDA}+5 \text{ wt\% DMPA/LFP}$, cycled at 80 °C with a cycling rate of C/2. b) Linear sweep voltammetry of crosslinked and pristine PCL-PTMC:LiTFSI . The crosslinked electrolyte was exposed to UV-radiation for 5 minutes. The measurements were performed at 80 °C, at a scan rate of 0.1 mV s^{-1} , with the polymer electrolyte sandwiched between metallic lithium and carbon-coated aluminum.

3.2 Electrochemical Methods

We are constantly moving toward using more high-voltage materials in batteries, but so far there has not been an adequate method for measuring the electrochemical stability of solid polymer electrolytes. This is clear by the variety in reported onset potential for degradation in the PEO:LiTFSI system, which is reported as anywhere between 3.2–5.7 V vs. Li^+/Li [81, 137, 143, 149–151].

When there is this much variety in the measured values, how would one predict if a polymer that is being developed is suitable as a polymer electrolyte for use with high-voltage cathodes? Many of the “standard” methods used when evaluating the electrochemical stability are unreliable and overestimate the polymer electrolyte, resulting in disappointment and confusion when the cell is finally cycled with an active material and shows signs of degradation. This was apparent in **Paper I**, where only LSV was employed to determine the electrochemical stability of the crosslinked solid polymer electrolyte, although both electrolytes should have been able to cycle up to 4.2 V vs. Li^+/Li , no successful cycling with NMC-111 could be produced at the time.

Determining the electrochemical stability of a solid polymer electrolyte is important for the practical application of the electrolyte. Due to the large number of experimental parameters that affect the measurement, it is not only difficult to compare and draw conclusions from data between research groups, but also within research groups. Because there are no strict standards for how to perform electrochemical measurements, the evaluation of the results can in many cases also be biased.

The “standard” methods that are usually employed for measuring the electrochemical stability are CV and LSV, and their main issues are that the onset potential for degradation is not clearly defined; the scan rates and the voltage profiles that are used do not reflect the ones used in a real battery; nor is the working electrode the same composite cathode – of active material, binder, and conductive carbon – that is used for galvanostatic cycling. Despite 1 mV s^{-1} being considered a slow scan rate in LSV, it is considerably faster than the equivalent of cycling a battery. The C-rate $C/20$ is commonly used for all-solid state cells; if the cell is cycled between 2.7 and 4.7 V vs. Li^+/Li , that would translate as approximately 0.02 mV s^{-1} . However, this translation should not be applied literally, as the cycling profile during galvanostatic cycling is seldom a straight line from the lower to the upper cut-off potential. Choosing an appropriate scan rate is important because of the effect of the iR -drop, which shifts the (over)potential needed to drive an electrochemical reaction. The iR -drop can be compensated for, with most instruments, if the resistance of the electrolyte is known and as long as it is not changing during the measurement. Because the voltage is continuously swept with these voltammetric methods, we see contributions from both thermodynamics and kinetics in the polymer electrolyte.

In **Paper II**, the aim was to see if it would be possible to develop a method which more accurately assesses the electrochemical stability, and cycling capabilities, of solid polymer electrolytes. To do this, the comparison with commonly used methods was important, and at the same time, the ability to illustrate the inherent biases with the standard LSV and CV methods, as well as the, by necessity, arbitrary methods of determining the onset of degradation.

Two different polymer hosts were chosen for the measurements, PEO and PTMC; in this summary, only the results of PEO are shown. These polymer host materials have different properties, such as different oxygen coordinating groups (ether vs. carbonate), PEO has a higher ionic conductivity than PTMC at the same salt concentration, etc.; this was expected to highlight any advantages or disadvantages with the presented methods.

First LSV measurements were performed, and the data was evaluated through several methods. One of the inherent issues with voltammetric techniques is visible in **Figure 20a**; a change in the scan rate affects the response in current, and therefore the perceived electrochemical stability of the electrolyte. The slower ion conduction and higher bulk resistance in solid electrolytes, compared to in liquid electrolytes for which the technique was developed, has to be considered. In liquid electrolytes, any issues due to mass transport are solved by stirring the electrolyte, for obvious reasons this is not possible with a solid electrolyte. With increased scan rate, the amplitude in current is increased, but at the same time a polymer electrolyte with its slow kinetics and slow mass transfer might have a build-up of resistive degradation products at the interface, which increases the polarization in the cell, moving the degradation potential to a higher value.

Mousavi et al. [136] and Olson et al. [135] suggested methods for determining the oxidation onset which are subject to less bias; these rely on drawing tangents to the current before and after the exponential increase in current. However, these methods are not completely free of bias, because there is still the need for subjective judgement when deciding where the exponential region is and where it is not. In **Figure 20a**, the onset potential when the scan rate is 0.1 mV s^{-1} is different from the one obtained when the scan rate is set to 10 mV s^{-1} , and as illustrated by the dotted lines the placement of the tangents determines the value for the onset potential.

The mass transport issue, due to high resistance and slow kinetics, can be overcome by gradually and slowly increasing the applied potential⁴, by performing a so-called staircase voltammetry (SV) measurement, see **Figure 20c**. If the step time is long enough that the system has time to react and equilibrate, issues due to low ionic conductivity are bypassed. Here, the onset of degradation is still not a completely unbiased assessment; is an increase in initial current the result of the electrolyte degrading, or is a higher current at

⁴ This is how the instrument itself functions even during “voltage sweeps”, although with much smaller and faster increments to the potential than what is implied here.

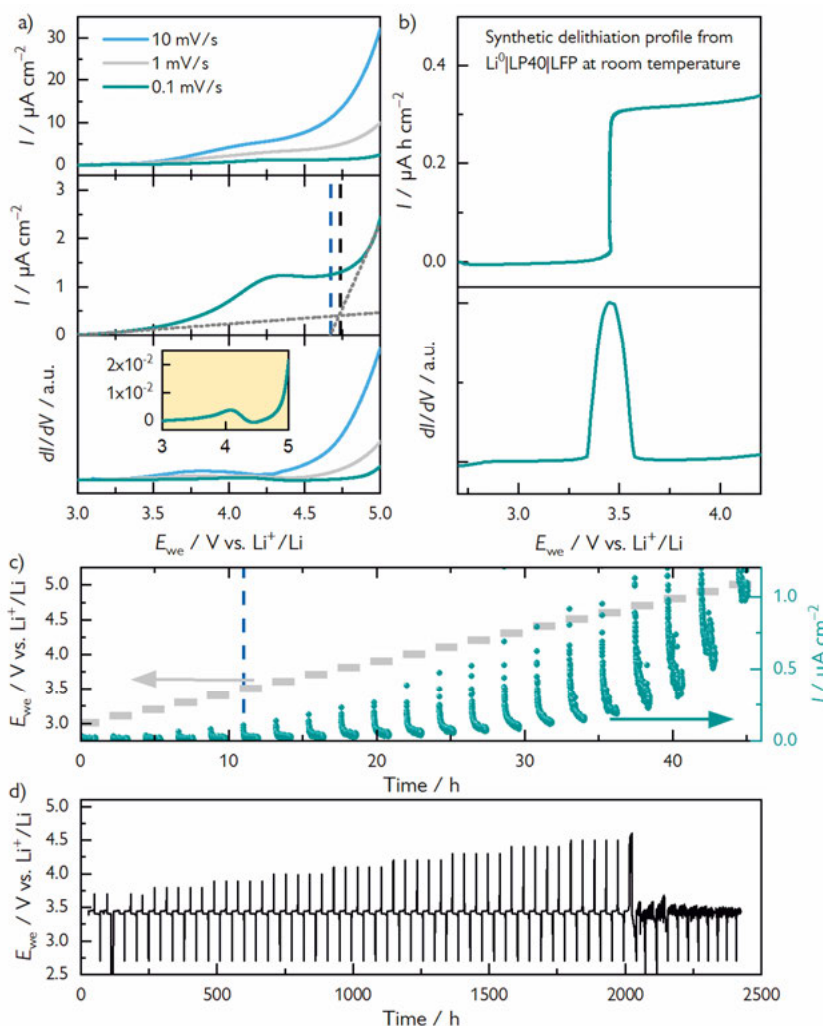


Figure 20. Different electrochemical methods to quantify the electrochemical stability of PEO:LiTFSI at 60 °C. a) LSV with varied scan rates, analysis of the data is done by linear fits to different current regions and by the derivative of the current response; b) the current generated, and the derivative of this response, during synthetic charge–discharge profile voltammetry; c) the staircase voltammetry measurement between 3–5 V vs. Li^+/Li ; and c) voltage profile versus time for a $\text{Li}^0|\text{PEO:LiTFSI}|\text{LFP}$ cell with cut-off increase cell cycling.

equilibrium, or the lack of equilibrium, due to decomposition of the electrolyte?

Even with this technique, since the cell is allowed to reach equilibrium, the cycling profile of a real battery is not imitated. In a real battery, the cycling profile varies depending on which cathode material is used, meaning that the electrolyte will only be subject to high voltages for a shorter period of time.

This is taken into consideration in the synthetic charge–discharge profile voltammetry (SCPV) technique [142], see **Figure 20b**. Usage of the LSV, CV, SV, and SCPV techniques should be for qualitative evaluation of the electrolytes; being able to compare the results with some reference is necessary for drawing conclusions with them. That is because the electrodes used are still not representative of the ones used in a real battery, and determination of the electrochemical stability using these methods is still not entirely free from bias.

A time-consuming, but more accurate, method of determining the practical electrochemical stability of an all-solid state battery is one based on galvanostatic cycling with the relevant electrodes; by incrementally increasing the upper cut-off voltage after a set number of cycles, the voltage at which the electrolyte degrades can be found. This technique is presented in **Figure 20d** and allows the electrolyte to be evaluated in a real cell, with relevant electrode materials and a real cycling profile.

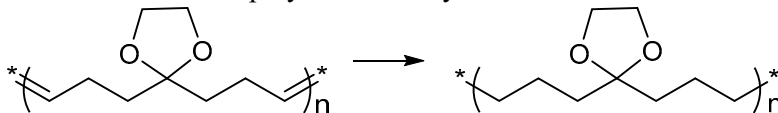
Analysis of this data is based on the coulombic efficiency and the voltage profiles; irreversible degradation of the electrolyte is expected to result in a coulombic efficiency that deviates from 100% and by the stability of the coulombic efficiency over several cycles, while the voltage profiles give information about side reactions that occur during cycling. Degradation of the electrolyte would result in an excess charge capacity being generated compared to the discharge capacity, which is expressed as a coulombic efficiency that is less than 100% and decreases during cycling. At the same time, an increase in resistance due to breakdown of the electrolyte would cause the cell to reach its upper cut-off before full charge is achieved, which is seen as a growing polarization in the cycling profile.

All four methods highlight that there is a difference between the electrochemical stability of the electrolyte versus the full battery cell. The methods that utilize inert working electrodes – LSV, CV, SCPV, and SV – are capable of determining the stability of the solid polymer electrolyte in contact with the (supposedly) inert electrodes, with SV more accurately showing the thermodynamic stability of the polymer electrolyte. However, the stability of the electrolyte alone is insufficient in predicting the stability of the full battery cell. This becomes obvious when attempting to determine a single potential that describes the oxidative stability limit of PEO:LiTFSI in **Figure 20**; the methods presented above give the range 3.5–4.8 V vs. Li^+/Li as the oxidative stability of PEO:LiTFSI. The results from the voltammetric methods differ from the CICC measurement, and none of the voltammetric techniques were able to predict the potential at which the battery cell would fail during galvanostatic cycling. The compatibility of the electrolyte with different cathode materials is only tested with CICC. In the end, of the qualitative methods, LSV is the fastest and easiest to implement as an initial evaluation of an electrolyte, but the CICC method is the most reliable method for evaluating the cycling capabilities of a solid polymer electrolyte.

3.3 Polymer Host Materials

Some alternative polymers that have been explored as polymer electrolyte host material have already been discussed in the **Introduction**; in **Paper III** the focus is on polyketones as polymer electrolytes, as this class of polymers not yet been fully explored for this type of application. The structural and thermal differences between POHM and the more commonly seen PEO and PTMC (see **Table 3**), makes POHM an interesting candidate for high temperature battery cycling.

Due to its complicated synthesis and being relatively unknown, POHM was only recently considered for use as a polymer host material [100, 101]. For the purpose of reducing the crystallinity and making it more manageable, a partially hydrogenated variant of POHM was synthesized, see **Scheme 1**, with 75% hydrogenation of the polymer backbone (POHM-75). It is both interesting to explore how (and if) these polyketones can be utilized for high-temperature cycling, but also how the partial hydrogenation affects the different properties that are relevant for polymer electrolytes.



Scheme 1. Hydrogenation step during the polyketone synthesis [100].

Both POHM and POHM-75 have a high degree of crystallinity, see **Figure 21a**. Typically, crystallinity in polymer electrolytes is undesirable as it results in lower ionic conductivity for the electrolyte because the crystalline regions of the polymer do not contribute to the conduction of ions. This is not necessarily the case with POHM-based electrolytes, as these have shown interesting ion conduction behavior despite the high crystallinity. Utilization of the mechanical stability that crystallinity offers and the high melting temperature of POHM is of interest for high-temperature applications.

The ionic conductivity of the polyketones increases with higher salt concentration, unlike PEO:LiTFSI and PTMC:LiTFSI which both see a decrease in ionic conductivity at the highest salt concentration, see **Figure 21c**. However, it is only at very high temperatures that the polyketones get a practically useful ionic conductivity, further motivating their use as electrolytes at high temperatures. To evaluate if high-temperature cycling would be possible with the polyketones, rheology measurements were performed to study their mechanical stability at elevated temperature. For long-term cycling to be feasible, the polymer electrolyte must not flow even at high temperatures. The moduli of the solid polymer electrolytes, with high salt concentration, was analyzed at a high temperature (60 °C) that is commonly used for polymer electrolytes and a more extreme temperature even for solid polymer electrolytes (120 °C).

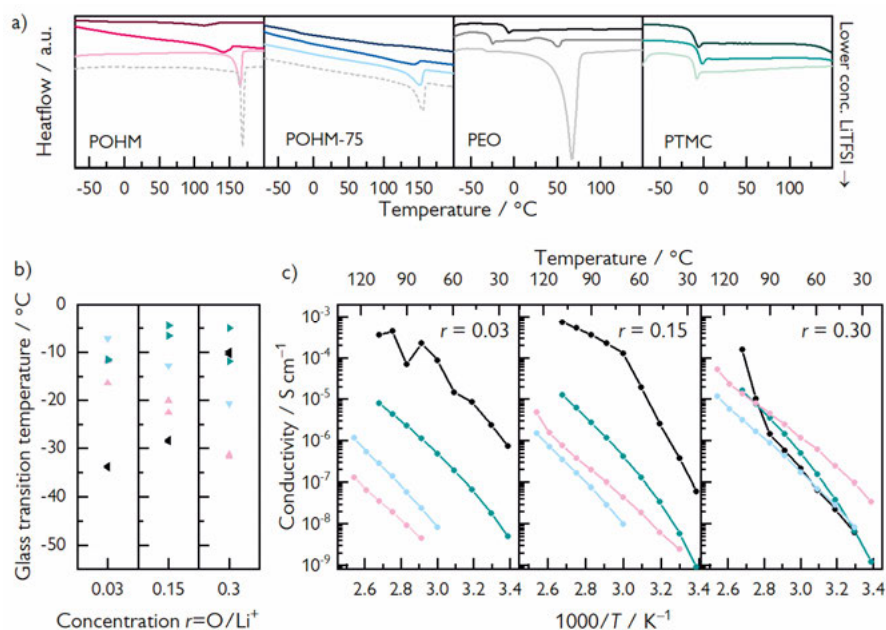


Figure 21. Thermal properties and ionic conductivity of POHM (pink), and POHM-75 (blue), PEO (black), and PTMC (green). a) DSC thermograms, grey dotted lines show polyketones without salt, and b) the glass transition temperature taken from the second heating scan. T_g was only found for POHM-75 without salt, at approx. -17°C . c) Ionic conductivity as a function of temperature with varied salt concentration.

The mechanical stability of the polyketones is superior to PTMC:LiTFSI at both temperatures and comparative to PEO:LiTFSI at 120°C , see **Figure 22**, with an exceptionally stable performance for POHM-75 even at 120°C . The motivation to use the polyketones at extremely high temperatures is further solidified by their high storage and low loss modulus at these high temperatures. The combination of high ionic conductivity and mechanical stability for a polymer electrolyte that is also highly crystalline is a seemingly impossible combination.

As previously discussed in the **Introduction** and in **Paper II**, cyclic voltammetry is affected by many experimental parameters and inherent flaws, such as cell set-up, that makes it unsuitable for determining the cycling performance of solid polymer electrolytes in battery cells. The method may still be suitable for an initial evaluation of the electrolytes and determination of which type of cathode material might be suitable for battery cycling. While a CV measurement cannot give an assessment of the electrochemical stability of a polymer electrolyte in contact with the active material of a cathode, it is possible to evaluate if the polymer electrolyte passivates.

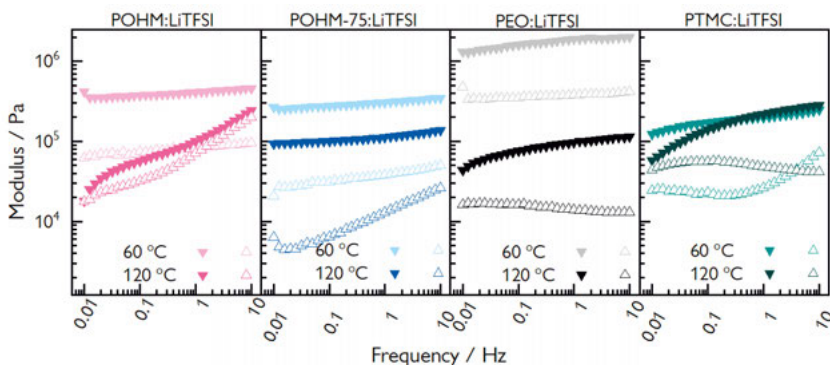


Figure 22. Oscillatory frequency sweeps at 60 °C and 120 °C for the solid polymer electrolytes with $r=0.30$; storage modulus G' as filled symbols and loss modulus G'' as hollow symbols.

Based on the total current density in **Figure 23a**, the polyketones have the poorest electrochemical stability, with almost four times as much current being generated in POHM:LiTFSI compared to PEO:LiTFSI. Of the two polyketones, POHM-75 is more electrochemically stable in this type of cell set-up, and while the reactions during the measurement are shifted to a higher potential during the second cycle, there is no apparent reduction in the amount of current that is generated. However, the differences in current generation before 4.2 V vs. Li^+/Li are not as palpable, suggesting that the polyketone electrolytes should at least be stable for cycling with LFP. Initial cycling with the polyketone electrolytes shows that the high resistance in the cells is limiting its performance, despite a very low C-rate. Further cell or electrolyte optimization might be necessary in order to enable high-temperature cycling with polyketone electrolytes.

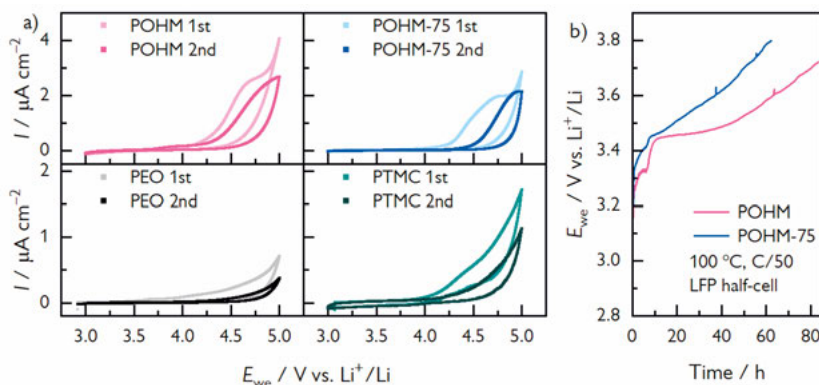


Figure 23. a) Cyclic voltammograms of the solid polymer electrolytes at 60 °C and 1 mV s^{-1} rate, showing the first and second cycle, note that there is a different scale to the y-axis. b) Galvanostatic cycling of polyketone electrolytes, in $\text{Li}^0|\text{SPE}|\text{LFP}$ cells, at 100 °C and C/50 rate.

3.4 Zwitterionic Additives

The struggle to precisely determine the electrochemical stability of a solid polymer electrolyte not only makes it difficult to determine the electrochemical window, but also hinders the understanding of, e.g., why PCL-PTMC:LiTFSI does not cycle well against high-voltage cathodes like NMC. According to a standard LSV, the oxidative stability of this electrolyte (see **Figure 19**) is well above the voltage range used when cycling this cathode material. Despite many reports of the large electrochemical window for polymer electrolytes, sometimes upwards of 5 V vs. Li^+/Li , most papers only feature cycling with low-voltage electrodes like LFP which can be cycled between 3 and 3.8 V vs. Li^+/Li (see **Paper I**). This is not only an issue for PCL-PTMC, but also PEO [137, 152, 153].

PCL-PTMC has so far not been successfully cycled with NMC for extended periods of time, and in **Paper IV** this was attempted to be remedied with an additive that improves the electrochemical performance. Zwitterions as additives have previously been shown to improve the charge/discharge capabilities of battery cells, as well as to increase the electrochemical stability even in small quantities [117, 118]. In this study, two zwitterions with varying molecular structure, see **Figure 24**, were added to PCL-PTMC:LiTFSI to evaluate their effect in this polymer electrolyte system. In this study, several electrochemical techniques were employed to evaluate the electrochemical performance of the modified solid polymer electrolyte and to give further insight into the origin of the incompatibility with NMC, as suggested in **Paper II**.

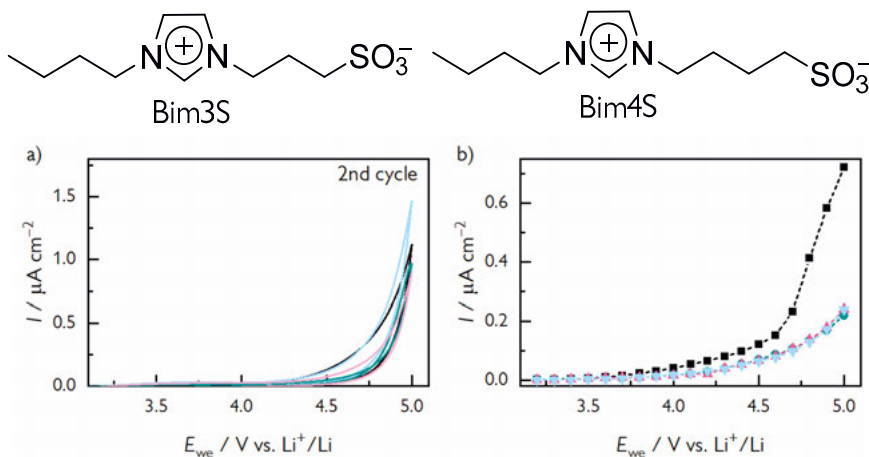


Figure 24. The molecular structures of zwitterions Bim3S and Bim4S. The current-voltage response during a) the second cycle of cyclic voltammetry and b) staircase voltammetry of PCL-PTMC:LiTFSI (black), +1.5 wt% Bim3S (green), +1.5 wt% Bim4S (pink), and 5 wt% Bim4S (blue). During staircase voltammetry, the potential was applied for 1 h at each step, the cell was then allowed to rest for 1 h before the next step.

The results from LSV were puzzling (see **Figure 24a**), showing a current response which is unchanged between cycles in the polymer electrolyte containing Bim3S, while also showing that the polymer electrolyte with Bim4S reaches a maximum current before 5 V vs. Li^+/Li , thus making it difficult to evaluate which zwitterion would have the best effect on the cycling performance. It was also not clear what effect the zwitterions would have on the galvanostatic cycling. Because of this, the staircase voltammetry method, as presented in **Paper II**, was used to suppress any differences due to variations in ionic conductivity, and to allow the systems to get closer to thermodynamic equilibrium. Unlike for LSV, the SV measurements showed a clear trend between the reference electrolyte and the electrolytes containing zwitterions, see **Figure 24b**. When the system was allowed to reach equilibrium, it was clear that the zwitterions decreased the current response of the electrolyte when compared to the reference electrolyte, and the exponential increase in current after 4.5 V vs. Li^+/Li was eliminated or shifted to a higher potential.

The CICC method was employed to see if this electrochemical enhancement would be enough to allow cycling with NMC, see **Figure 25a,b**. The redox reactions and charging of NMC-111 start at a relatively high potential, in **Figure 25a** the reference cell showed signs of failure before reaching a high enough voltage to generate any significant capacity during charging. While the SV measurements showed a similar response for all polymer electrolytes with zwitterions, there is a widely different response in the CICC data. The Bim4S zwitterion seems to improve the electrochemical stability more than the Bim3S zwitterion; however, at 5 wt% Bim4S the cell reaches its upper cut-off before any significant amount of charge is delivered to the cell.

The voltage for all of these cells reached the upper cut-off before any meaningful capacity could be delivered, which is an indication that the resistance in the cells was high. This could be due to the formation of a passivating, but poorly conductive, film on the electrode(s). A passivating film is in many cases desirable as it can prevent the decomposition of the electrolyte, but it should not be so highly resistive that it prevents cycling of the battery. Standard galvanostatic cycling was then performed on a cell containing with 5 wt% Bim4S, the cell managed to cycle without any aberrant behavior for nine cycles, see **Figure 25c**, which is a small but significant improvement.

XPS measurements were performed on cells that had been cycled, with and without zwitterionic additives, see **Figure 26**. From the S2p and N1s spectra there was a clear decomposition of the salt, which was suppressed when zwitterions were added to the electrolytes. Computational studies, combined with experimental measurements, by other groups have shown that the zwitterions can prevent the salt anion from reaching the cathode, thus preventing its decomposition at the electrode surface. If the zwitterions are blocking the salt ions from reaching the cathode it would explain why the SV measurements show that all zwitterions have the same effect on the electrochemical stability

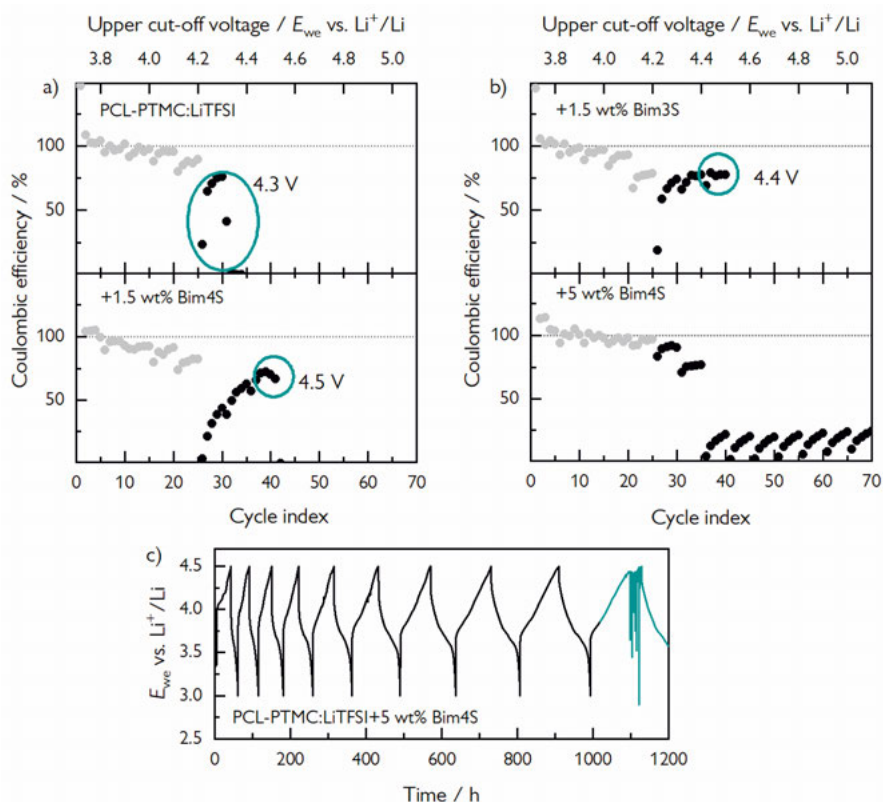


Figure 25. a,b) The coulombic efficiency during CICC method and c) cycling profile during standard galvanostatic cycling ($9.1 \mu A cm^{-2}$), both at $40^\circ C$. The cell set-up is $Li^0|PCL-PTMC:LiTFSI|NMC-111$, with or without zwitterionic additive. The voltage at which failure occurs is marked in green.

of the polymer electrolyte – with a long enough pause, the effect of the zwitterions is the same, and the resistivity due to the passivating film that the zwitterions form is negated. However, in the CICC measurements, the cells do not have the time to reach an equilibrium and the resistance posed by the zwitterions covering the interfaces is greater. This would explain why the overpotential is much larger in the cell with 5 wt% Bim4S – it has a higher coverage of zwitterions on the electrode surface. Out of the two zwitterions, Bim4S has superior capability of enhancing the electrochemical stability of the polymer electrolyte PCL-PTMC:LiTFSI. With a higher content of zwitterions, the protection of the cathode interface is greater, both enhancing the protection of the TFSI anion and increasing the resistance in the cell. Overall, the cells with zwitterionic additives showed increased stability against NMC-111.

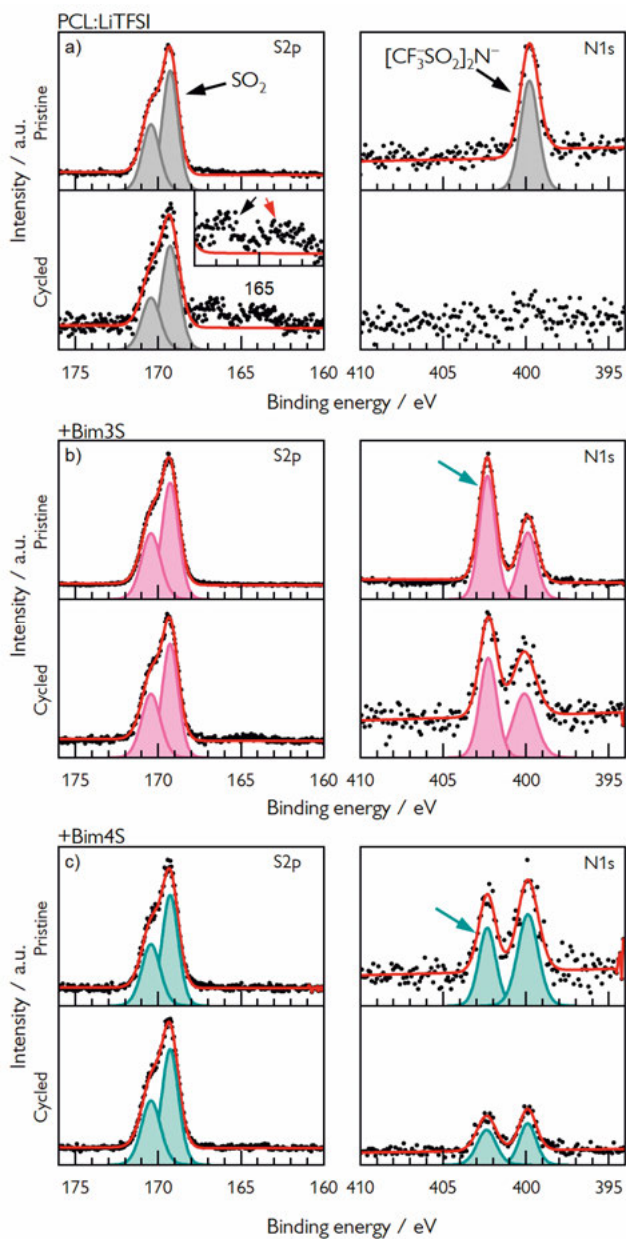


Figure 26. Post mortem analysis of Li0|SPE|NMC-111 cells, the polymer electrolyte a) PCL:LiTFSI and PCL:LiTFSI + 1.5 wt% b) Bim3S or c) Bim4S. XPS spectra S2p and N1s of the polymer electrolyte interface adjacent to NMC-111, a) the SO₂ salt peak in S2p, marked with an arrow, was used for energy calibration; the inset for the cycled PCL:LiTFSI cell shows a black arrow highlighting the Li_xS_yO_z signal and a red arrow highlighting Li₂S. The signal of the TFSI anion is marked with an arrow in the N1s spectrum of pristine PCL:LiTFSI. Green arrows (b,c) indicate peaks which are assumed to originate from the zwitterionic additive. The data has been normalized.

3.5 Anions of Lithium Salts

One major finding in **Paper IV** was that the LiTFSI salt decomposes during cycling with NMC-111, see **Figure 26**. As mentioned in the **Introduction**, there are a plethora of different lithium salts that can be used in electrolytes, either as the main conductive salt or as additives, and they feature different advantages and properties. Some of these salts are even used as additives in liquid electrolytes for their ability to enhance the battery cycling performance. Despite this, exchanging the salt in polymer electrolytes is seldom done, and the standard salt to use has historically been LiTFSI. In **Paper V**, the effect of substituting LiTFSI in PCL-PTMC is studied, and the evaluation of the electrochemical performance of the electrolyte with different salts is the focus. Six different salts, including LiTFSI, were included in the study, see **Figure 27**.

The ionic conductivity was more clearly affected than the T_g of these electrolytes. The ionic conductivity is in the order of LiFSI>LiBOB>LiDFOB>LiTFSI, the ionic conductivity as a function of temperature is shown in **Figure 27**; so, although LiTFSI is the most commonly used salt in polymer electrolytes, it gives the lowest ionic conductivity out of these four salts. However, it should be noted that only one concentration was tested for all salts, which is not necessarily the concentration that gives the highest ionic conductivity for each salt. Interestingly, LiPF₆ and LiBF₄ give the lowest ionic conductivity by a large margin; at 30 °C the ionic conductivity with LiFSI is $4 \times 10^{-5} \text{ S cm}^{-1}$ while LiBF₄ gives $5 \times 10^{-7} \text{ S cm}^{-1}$. The low ionic conductivity when using LiPF₆ and LiBF₄ could be because these salts do not dissolve well in PCL-PTMC. If the salts do not dissociate to their respective ions, they are not contributing to the ionic conductivity of the electrolyte. These small and highly fluorinated salts therefore do not seem to be appropriate for PCL-PTMC.

Initial electrochemical testing of the polymer electrolytes was done with standard CV to qualitatively evaluate the electrolytes, see **Figure 27b,c**. Although cyclic voltammetry does not give absolute information about the electrochemical stability of the polymer electrolyte performance in a battery cell, it is possible to analyze reversible and irreversible electrochemical reactions, such as formation of passivating films, which was especially interesting with the PCL-PTMC:LiBOB and PCL-PTMC:LiDFOB electrolytes. CV showed that all electrolytes all have similar behavior, with the exception of LiFSI which did not passivate during cycling. The failure to passivate could be detrimental for the long-term stability of the battery cell.

The cycling performance of cells featuring these electrolytes was then examined. LFP cathodes were utilized for standard galvanostatic cycling, and NMC-111 electrodes were used with the cut-off increase cell cycling with NMC, see **Figure 28**. When cycled against LFP, LiTFSI gives the best cycling performance and lowest polarization. Use of the other salts led to a larger

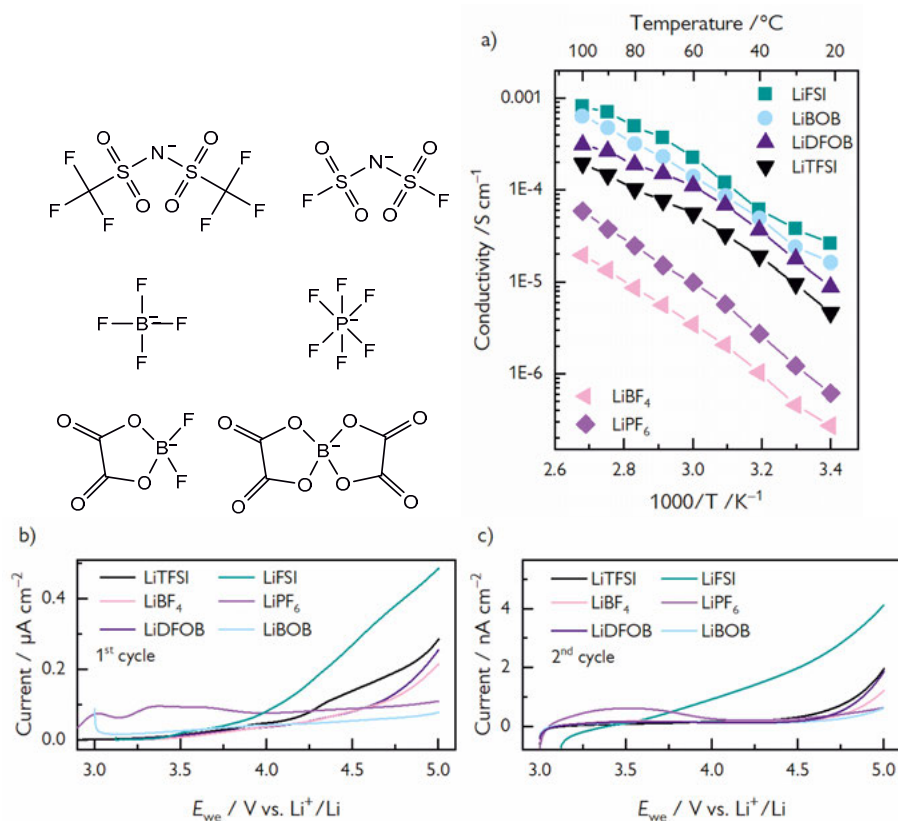


Figure 27. Molecular structures of different anions, a) the ionic conductivity, and b,c) CV measurements of the electrolyte when these salts are used with PCL-PTMC. The amperometric response, with a scan rate of 1 mV s^{-1} at 60°C , during the b) first and c) second sweep is shown.

overpotential in the order $\text{LiFSI} < \text{LiBOB} < \text{LiDFOB}$; in electrolytes with the borate salts the overpotential was so large that 50 mAh g^{-1} was barely achieved during cycling because the upper cut-off was met so rapidly. The cycling performance of electrolytes with LiBF_4 and LiPF_6 was abysmal; the cells had a huge overpotential of over 0.5 V , and they were both showing signs of degradation by soft short circuits and “infinite charging”. For this reason, polymer electrolytes with the salts LiBF_4 , LiPF_6 , and LiDFOB were excluded from the CICC measurements that are presented here in **Figure 28b,d**.

To really test the electrochemical limits of these salts, the electrochemical stability was evaluated with CICC using NMC-111 electrodes. Although it gave the highest ionic conductivity, LiFSI does not seem to be a suitable salt to use with PCL-PTMC when cycling against NMC. Out of the three electrolytes shown here, it has the worst performance. Just as the PCL-PTMC:LiFSI electrolyte was unable to passivate during the CV measurements (see **Figure 27b,c**) it was unstable during CICC, failing once the upper cut-off was set to

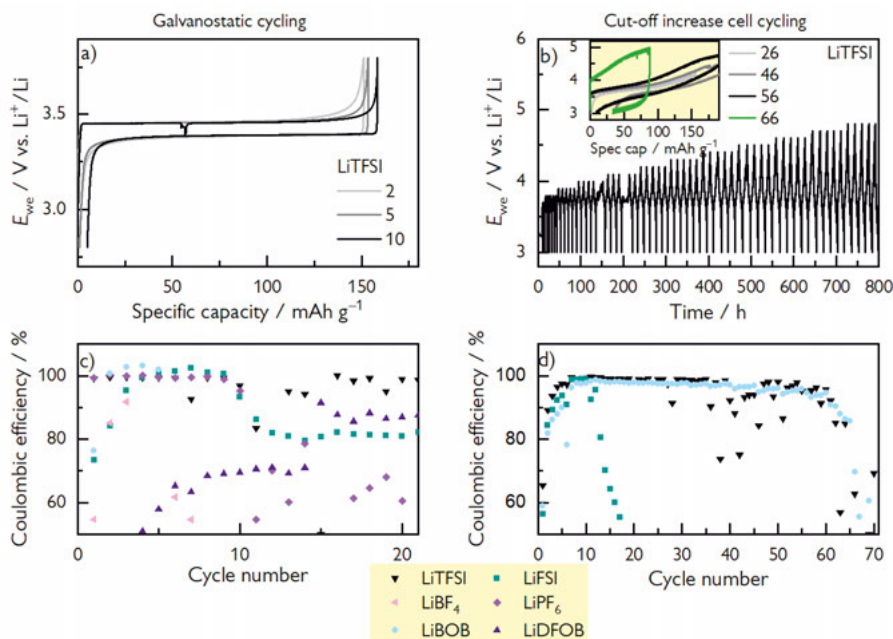


Figure 28. Galvanostatic cycling of PCL-PTMC with different salts at $5 \mu\text{A cm}^{-2}$ and 60°C . a) The cycling profiles of PCL-PTMC:LiTFSI and c) coulombic efficiency of the cell set-up $\text{Li}^0|\text{SPE}|\text{LFP}$. b) CICC cycling of PCL-PTMC:LiTFSI with an inset showing its cycling profile and d) coulombic efficiency of the best performing salts. Coulombic efficiency is shown between 50–110% for legibility.

3.9 V vs. Li^+/Li . Despite its comparatively low ionic conductivity, the cycling performance of PCL-PTMC:LiTFSI was fairly good. In **Figure 28b** the cycling profile during CICC of this electrolyte is shown for specific cycle numbers. Cycle number 26, 46, 56, and 66 correspond to an upper cut-off voltage of 4.2, 4.6, 4.8, and 5.0 V vs. Li^+/Li , respectively. The polarization in this cell is fairly low, but slowly increasing up to cycle 26. It is possible to compare the increase in polarization in the cycling profiles at each cut-off increase with the coulombic efficiency. In fact, the coulombic efficiency reveals that there is some instability during the cycling starting at cycle 35. Between cycle 55 and 66, the resistance increases significantly. At the same time the coulombic efficiency rapidly drops below 90%.

In the CICC measurements, PCL-PTMC:LiBOB has the highest electrochemical stability, owing to its ability to form passivating layers on the electrodes [52]. But, just like PCL-PTMC:LiTFSI, it slowly starts to deteriorate once the upper cut-off reaches 4.4 V vs. Li^+/Li . It is possible that this value corresponds to the electrochemical stability of PCL-PTMC. If this is the case, it should be possible to get stable cycling with both PCL-PTMC:LiTFSI and PCL-PTMC:LiBOB as long as the upper cut-off is kept below 4.4 V vs. Li^+/Li . But then the question becomes: why is PCL-PTMC:LiTFSI unable to cycle with NMC-111 most of the time?

This could potentially be answered by the measurements of electrolytes containing LiBF_4 and LiPF_6 . These salts had both the lowest ionic conductivity and the poorest battery. Often, the requirement for electrolytes to have 1 mS cm^{-1} at room temperature is set for the battery cell to achieve practically useful charging and discharging rates. It is possible to cycle high-voltage cathodes like NMC with liquid electrolytes, and the main difference, in terms of properties as electrolytes, is that the ionic conductivity in liquid electrolytes is much higher than that of polymer electrolytes.

It is indeed the belief of some groups, especially the Kasnatscheew group [138, 139], that the electrochemical stability of polymer electrolytes is not the issue, but the mechanical stability and the thickness of the polymer electrolyte. However, if the mechanical stability was the only thing lacking, the PCL-PTMC electrolyte should have been able to cycle with NMC when cross-linked, as in **Paper I**. A spacer of PE (50 μm thick) was introduced to the battery cells cycled in **Paper IV** and **Paper V**, which reduced the occurrence of short circuits, but had no effect on the other types of failure behaviors seen in **Figure 14**. Instead, it seems like the cut-off and temperature had a more profound effect in this case.

If the ionic conductivity is what limits the cycling against high-voltage cathodes, it could simply be remedied by increasing the temperature for the solid-state system. If, however, the electrochemical stability of the polymer (electrolyte) is what limits the cycling performance, cycling with NMC should be possible as long as the upper cut-off is below 4.4 V vs. Li^+/Li for PCL-PTMC electrolytes. This experiment and its results are shown in **Figure 29**. Here, the harshest condition is at 60 $^\circ\text{C}$ with the upper cut-off set to 4.5 V vs. Li^+/Li . None of the polymer electrolytes perform well; rapid failure is seen with PCL-PTMC:LiBOB, PCL-PTMC:LiPF₆ shows soft short circuiting, and a general decline with PCL-PTMC:LiTFSI. It is clear that the cells face rapid failure at 60 $^\circ\text{C}$ and 4.5 V vs. Li^+/Li , but it should also be noted that the coulombic efficiency for PCL-PTMC:LiTFSI is above 100% for some cycles also at 60 $^\circ\text{C}$ when the upper cut-off is 4.2 V. This indicates that there are some temperature dependent side-reactions occurring during discharge of the cells which cannot be avoided at the lower cut-off. Since the XPS measurements in **Paper IV** showed that the TFSI anion decomposes during cycling with NMC, it is possible that the excess charge during discharge is due to the decomposition of the TFSI anion.

In terms of specific capacity, it makes little difference whether the upper cut-off is set to 4.5 V or 4.2 V vs. Li^+/Li , the upper cut-off mostly affects the polarization of the cell and how rapidly it degrades, indicative of excessive formation of passivation layers when the cells are cycled up to 4.5 V vs. Li^+/Li . The effect of the temperature is related to the ionic conductivity of the polymer electrolyte, and here it has a larger impact on the cycling than the upper cut-off does. This was especially evident for the cell with PCL-PTMC:LiBOB electrolyte. When cycled at 60 $^\circ\text{C}$, more capacity can be extracted due to lower

polarization compared to at 40 °C, regardless of what the upper cut-off is. The biggest challenge for this electrolyte seems to be the high resistance when utilizing LiBOB as the main conductive salt. For the PCL-PTMC:LiTFSI electrolyte, it is necessary to have both a high temperature and an upper cut-off below the degradation potential to achieve stable cycling with NMC-111. Additionally, the use of LiBOB as an additive could prove beneficial for the long term cycling of these cells, especially due to the passivating film that is formed by introducing small amounts of LiBOB to electrolytes, see **Figure 30**.

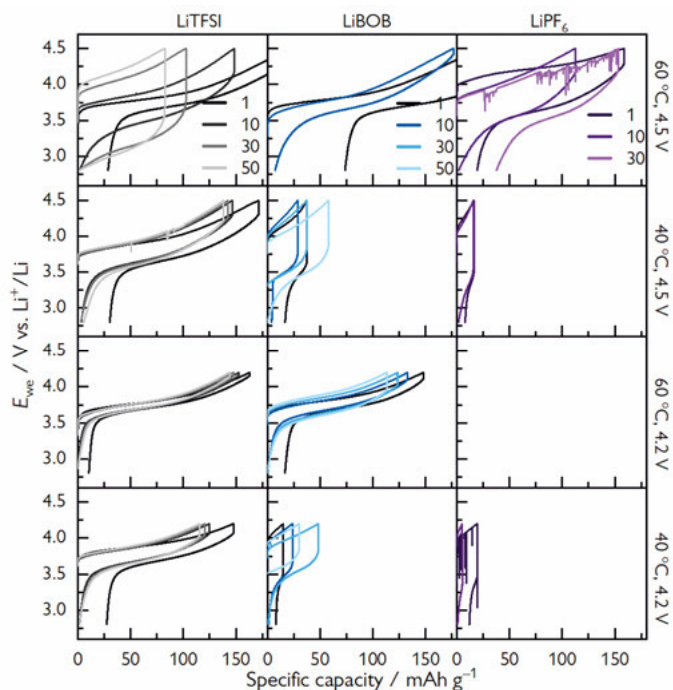


Figure 29. Galvanostatic cycling profiles of $\text{Li}^0|\text{PCL-PTMC:salt}|\text{NMC-111}$, salt is either LiTFSI, LiBOB, or LiPF_6 , with a current density of $5 \mu\text{A cm}^{-2}$. The cycling is grouped by operational temperature (60 °C or 40 °C), and by the upper cut-off (4.5 V or 4.2 V vs. Li^+/Li).

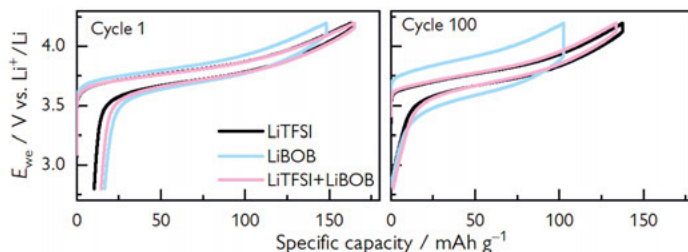


Figure 30. Galvanostatic cycling profiles of the 1st and 100th cycle, of $\text{Li}^0|\text{PCL-PTMC:salt}|\text{NMC-111}$ cells, salt is either LiTFSI, LiBOB, or a LiTFSI with LiBOB ($r=0.005$ or 0.7 wt%), cycled with the current density of $5 \mu\text{A cm}^{-2}$ at 60 °C.

4. Conclusions and Future Work

In battle, there are not more than two methods of attack – the direct and the indirect; yet these two in combination give rise to an endless series of maneuvers.

— Sun Tzu, *The Art of War*

This thesis explores different methods for improving the stability of solid polymer electrolytes, by means of improving the mechanical properties or the electrochemical properties. The perceived advantage of using solid polymer electrolytes over liquid electrolytes, is that they are mechanically stable and more electrochemically stable even at elevated temperatures, where liquid electrolytes are unsafe to use. But the work herein challenges these claims.

Solid polymer electrolytes are often imagined as the replacement material for liquid electrolytes, but in order to make this exchange possible the stability of polymer electrolytes must be improved. The research in this thesis has aimed to improve the stability of polymer electrolytes – the mechanical stability and the electrochemical stability – with the intention to enable galvanostatic cycling of high-voltage electrodes, at high temperatures, with solid polymer electrolytes.

UV-initiated crosslinking was used to improve the mechanical properties of PCL-PTMC:LiTFSI in **Paper I**. At the cost of a slight reduction in ionic conductivity and electrochemical stability, this mechanical stabilization made long-term cycling possible for battery cells with LFP cathodes. The cycling with a high-voltage cathode could not yet be realized with this polymer electrolyte. Since the mechanical properties had been improved, the blame could only lie in an electrochemical instability of the polymer electrolyte.

For a better understanding of the electrochemical stability in solid polymer electrolytes and for better methods of evaluating it, in **Paper II**, several methods were scrutinized and developed for the accurate measurement of the electrochemical stability of polymer electrolytes. The developed methods either offer a qualitative description of the electrochemical stability of a polymer electrolyte, or accurately show the cycling capabilities of battery cells containing solid polymer electrolytes.

As electrochemical methods are developed by researchers, it becomes more and more obvious that the polymer host material PEO is not the optimal one to use. Polyketones are evaluated as polymer host materials in **Paper III** and compared to PEO and PTMC. The evaluation focuses on the possible high-temperature application of polyketones as polymer electrolytes, and shows the performance of this polymer host material that is highly crystalline.

With the methods that were developed in **Paper II**, the electrochemical evaluation and enhancement of PCL-PTMC:LiTFSI was undertaken in **Paper IV**. Through the use of zwitterionic additives, the cycling capabilities of this block copolymer were improved and analyzed. The grand reveal in this paper was that the decomposition of the polymer electrolyte in contact with a high-voltage cathode, was mostly due to the breakdown of the TFSI anion, a decomposition that could be prevented by the zwitterions.

Since the anion appeared to be the weak link in the PCL-PTMC:LiTFSI electrolyte, in **Paper V** salts with different anions were investigated. The electrochemical performance of six lithium salts revealed a connection between the cycling stability and the ionic conductivity of the polymer electrolytes.

In recent years, the general opinions of the low-voltage cathode LFP are changing to become more positive. As a cathode material, it contains only environmentally unproblematic and benign elements. With this cathode material, it is also very easy to achieve good cycling with solid polymer electrolytes, unlike the problematic NMC and other high-voltage cathodes. However, if this shift in opinions is only temporary, there needs to be some improvements made to the electrochemical stability of polymer electrolytes in order to make them more compatible with high-voltage cathodes. And there are many methods to make this improvement possible.

The use of additives is common in liquid electrolytes, often resulting in a cocktail of salts and additives, each with a different purpose. Additives are not yet as utilized in solid polymer electrolytes, though. The bis(oxalato)borate-based salts that were explored in **Paper V** are commonly used as additives, not as the main conducting salt. It is possible that this is the better utilization of these salts, even in polymer electrolytes. Generally, the use of several additives to improve the properties of polymer electrolytes should be popularized. The process of adding additives is a facile and economical method, even to solid electrolytes, which could improve the cycling performance without the need for synthetic modification of the polymer host material.

However, the synthetical modification of polymer host materials should also be more encouraged. One of the main advantages that polymers have over organic solvents is the possibility to vary the architecture and structure of polymers during synthesis. For example, if the inherent electrochemical stability of the PCL-PTMC-based electrolytes is at 4.4 V vs. Li^+/Li , it might be necessary to chemically modify the polymer backbone. Teflon, or poly(tetrafluoroethylene), is well known for its chemical inertness, and although fluorinated compounds and fluorination is generally a bad move from an environmental perspective, it could be a good method of reaching a higher electrochemical stability with PCL-PTMC.

Finally, there is a need to investigate and gain an understanding of the (in)stability mechanisms and degradation of solid polymer electrolytes, in order to understand how we should improve the electrochemical stability of pol-

polymer electrolytes. The combined use of appropriate electrochemical techniques and spectroscopic techniques should be employed, to study any catalytic effects to the degradation of polymer electrolytes by the transition metals commonly found in high-voltage cathodes. The studies presented herein have only been scratching the surface of understanding the art of cycling solid polymer electrolytes, and there is so much more to explore!

Populärvetenskaplig sammanfattning

Polymerer och plaster är en bred klass av naturliga och syntetiska, material med många användningsområden – från förpackningsmaterial till avancerade medicinska implantat – som vi stöter på varje dag. Det är polymerernas mångfald av justerbara materialegenskaper som gör dem användbara för så många och så olika applikationer. Under 1970-talet upptäcktes det även att vissa polymerer har förmågan att lösa upp oorganiska salter och att de kunde leda joner; denna upptäckt öppnade dörrarna för användning av polymerer som batterimaterial, och forskning pågår än idag för att se hur polymerelektrolyter kan forma vår teknologiska framtid.

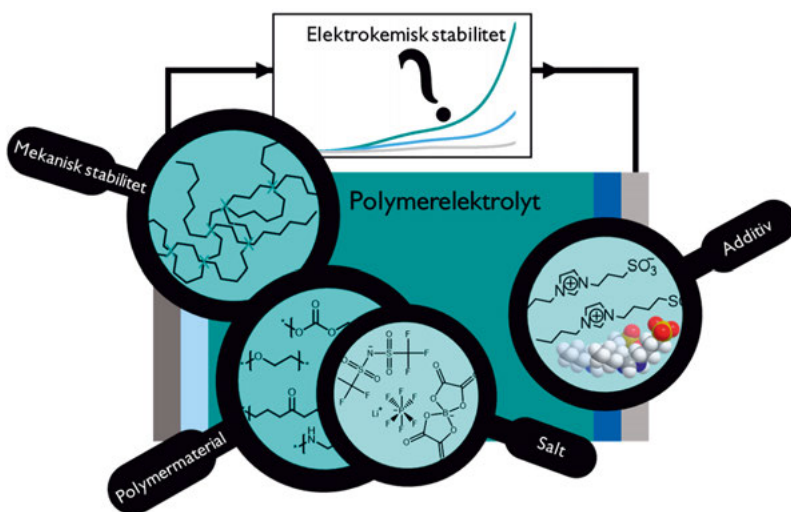
För batterier är polymerelektrolyter ett säkrare och potentiellt mer miljövänligt val jämfört med de elektrolyter som används i moderna kommersiella batterier – dessa är ofta baserade på brandfarliga och flyktiga vätskor. Polymerelektrolyter har unika egenskaper som flexibilitet, låg brandfarlighet, och hög elektrokemisk och mekanisk stabilitet. Det finns även många olika sorters polymerelektrolyter med olika egenskaper och prestanda. De kan även användas med elektrodmaterial som ger batterierna högre energitäthet, exempelvis metalliskt litium. Batterier som innehåller polymerbaserade elektrolyter har därför stor potential inom transportindustrin och för stationär energilagring. Dessa applikationer kräver normalt att batterisystemet kyls ner för att bland annat förhindra nedbrytningen av de traditionella flytande elektrolyterna. Men för att polymerelektrolyter ska kunna användas till sin fulla potential i dessa applikationer behöver de användas vid hög temperatur och med reaktiva elektroder, och då behöver man hitta lämpliga material som uppfyller krav på hög jonledningsförmåga, och termisk, elektrokemisk, och mekanisk stabilitet.

Stabiliteten av polymerelektrolyter är i fokus i denna avhandling. När man pratar om stabiliteten hos polymerelektrolyter, kan man mena både den elektrokemiska stabiliteten och den mekaniska stabiliteten. För polymerer kan den mekaniska stabiliteten ökas med många olika metoder, men vissa metoder är mer lämpliga än andra. Det är nämligen så att jonledningsförmågan i polymerelektrolyter är kopplad till polymerkedjornas rörelse, som i sin tur påverkar den mekaniska stabiliteten. Därför bör mekanisk stabilitet av polymerelektrolyter endast ökas på en makroskopisk nivå, utan att påverka rörligheten av polymerkedjorna på mikronivå. Detta är möjligt om man inkorporerar ett mekaniskt stabilt tvärbundet polymernätverk som polymerelektrolyten är intrasslat i, men som inte nödvändigtvis deltar i jonledningsprocessen. Då upplevs polymerelektrolyten i sin helhet som mer mekaniskt stabil. Just en sådan strategi undersöks i avhandlingens **Papper I**. En polymerelektrolyt som stabiliserats med denna metod skulle kunna användas vid högre temperaturer utan att den smälter eller ändrar form.

Utöver mekanisk stabilitet krävs även elektrokemisk stabilitet av polymer-elektrolyter, främst när de är i kontakt med reaktiva material såsom metalliskt litium och högvoltsskatoder. Utvärderingen av den elektrokemiska stabiliteten hos polymerelektrolyter är dock bristfällig, och de standardmetoder som används ger ofta resultat som inte är relevanta för polymerelektrolyten i en battericell. Anledningen till detta är bland annat den långsamma rörelsen av polymerkedjor och den till detta koppade låga jonledningsförmågan i dessa material. För att motverka detta kan svephastigheten och svepprofilen anpassas för den långsamma kinetiken i polymerelektrolyter. Ytterligare en brist med de standardmetoder som används är att elektrolytens elektrokemiska stabilitet inte mäts i kontakt med de elektroder som används i en battericell. Modifiering av standardcyklingsprogram för batterier kan göra det möjligt att mäta just den elektrokemiska stabiliteten under battericyklning. Till exempel så kan battericellen cyklas mot successivt högre spänning tills nedbrytningsprocesser börjar inträffa. Dessa alternativa analytiska metoder för polymerelektrolyter utvecklas i **Papper II**.

Med elektrokemiska mätmetoder som lämpar sig för polymerelektrolyter kan man undersöka vilka polymermaterial som är lämpliga som polymerelektrolyter, men även försöka ta reda på vilka komponenter i polymerelektrolyter som påverkar den elektrokemiska stabiliteten, se **Figur 30**, och om det finns tillsatser som kan förbättra den elektrokemiska stabiliteten. De polymerelektrolyter som är vanligast i forskningsfältet är inte nödvändigtvis de mest stabila, och då kan undersökning av alternativa polymermaterial och salter ge förslag på andra polymerelektrolytssystem som är mer lämpliga för cyklning vid hög temperatur och hög spänning. Ett exempel på en alternativ polymer med ovanliga egenskaper undersöks i **Papper III**, och **Papper IV** visar hur batteriets elektrokemiska stabilitet kan förbättras genom ett additiv.

Undersökning av batterisystem leder ofta till nya frågor, snarare än nya svar, just eftersom det ingår många komponenter i ett batteri och alla dessa komponenter interagerar med varandra. I studien med additiv visade det sig att litiumsaltet i polymerelektrolyten bryts ner i kontakt med en högvoltsskatod, och i **Papper V** fortsatte då arbetet genom att undersöka effekten av att byta ut litiumsaltet mot andra salter. Med hjälp av de analytiska metoder som utvecklades i **Papper II** kunde sedan slutsatser dras kring batteriets förmåga att cykla och polymerelektrolytens jonledningsförmåga. Det visade sig att så länge jonledningsförmågan i polymerelektrolyten är tillräckligt hög då den är i kontakt med en högvoltsskatod, kan batteriet cyklas inom det spänningsintervall där polymerelektrolyten är elektrokemiskt stabil.



Figur 31. Grafisk sammanfattning av de komponenter av polymerelektrolyter som undersökts i avhandlingen.

Acknowledgements

Sublime is something you choke on after a shot of tequila.

The quote is from *House of Leaves* by Mark Z. Danielewski, just like the quote at the start of this thesis; it is a very interesting book, not for everyone, but it challenges your idea of how a book should be written. I thought of this book when trying to motivate myself while writing, “It doesn’t need to be perfect, it just needs to be done.” With the help of many people, this has become a sublime thesis, and once this is all over I will celebrate with a shot of tequila!

My decision to start a PhD was almost entirely because of the people working in the Department of Chemistry, and partly because I couldn’t have enough of working with gooey solutions and polymers. The first real lab experience I had with polymers was with Polymer Chemistry group; during my short stay there Ayan Samanta and Justina Pupkaitė taught me a lot of things. But because of my aversion to blood and gore – especially the eye-surgery video – I came to the conclusion that polymer electrolytes would be more suitable for a weakling like me.

The studies presented in this thesis have been carried out under the direction of my two supervisors: Jonas Mindemark and Daniel Brandell. For all their wealth of insightful comments and suggestions, I’d like to express my grateful appreciation. As my main supervisor, Mindemark let me have a lot of freedom, while also giving me random tasks and ideas for potential side-projects, while also reigning me in when it was time to focus. If the pandemic hadn’t showed up, I would have accepted all propositions for research exchanges and on-site measurements in Japan, and of course you would’ve had to join for the mandatory Japanese hospitality events.

The iconic duo of Brandell and Mindemark is not something everyone get to encounter, but I got the first-hand experience of attending these meetings, where a quick glance at the world map could mean that you only had 5 out of 45 minutes to present your current progress and questions before they would travel off in time and space. Not that I minded, because I could get a lot of good feedback in those 5 minutes. Brandell, did you know that your distinct laugh rubs off a bit on the students you supervise? HA-HA! Aside from traveling, the iconic duo enjoys naming new methods, papers, and theses. The first draft for my title was too boring and rigid, so they suggested I find inspiration in the music I listen to. Unfortunately, I spent a lot of hours listening to Type 0 Negative while writing my manuscripts – you can take a look at their album titles and see why I went with another route! I would like to thank you both for getting me through this and all the strange stages of the PhD-education. The transition from being a new PhD, who looks forward to eating candies in

my supervisors' office, to becoming a more senior PhD, who wants to show off my latest findings, felt like it happened over a period of weeks – and it only had a little to do with Mindemark switching out the Hi-Chew for hard candies.

Speaking of Hi-Chew, in 2019 I was supposed to have my first trip to Japan, but for various reasons it was postponed and finally happened during the autumn of 2022. Twice! There I got to experience a beautiful and enormous campus, struggle with all the various phrases in keigo, got a glimpse of the working environment through the weekly group discussions (or grilling sessions, as I called them), eat amazing food, and got training in organic chemistry. At the group in Hokkaido University, I'd like to thank Shiva for helping me in the lab and Mana-bae (now Dr Manabe!) for entertaining this lost westerner. You look tired, お疲れ様!

Initially, the visit to Japan was supposed to be for me and Therese, I imagine that we could have gone to lots of cafes to eat delicious cakes and bought cute, pink things to decorate Bodil with. Instead, I got to go there with the fastest member of the PUB-group: Rasmus! It was still fun and cakes, unfortunately for you, you got dragged into my final stressful projects at the end of my PhD – PONPONPON! I'd also like to thank the members of the PUB-group that show up in the lab and for coming up with solutions for sticky situations: Cuc, Edvin, Daniel F, Tamara, Guiomar.

Back in 2018, when I first started in the group, it had a completely different composition, the atmosphere in the lab and the after-works were something else. Although most of the people that introduced me to the department are not here to read this part, I could like to acknowledge them, they really took “work hard, party hard” and ran with it. Thank you for being such wonderful mentors and role models: Andoria, Christofer, Jonas H, Le Anh, Therese, Yu-Chuan! I had a great time in the colonies with you.

To the ones who were my office-mates when we were exiled to the colonies, I had so much fun, thank you!: Yonas, you're an icon, I hope you get your seven wives, and know I wasn't trying to torture you, in fact “*All my life I've been good, Do what my mom and dad and God say I should*”; Tatiana, you and your shark are the coolest, and the day will come when we are able to keep plants alive!; León, you knew me since we were babies at Ångström, thanks for being a weirdo with me at the front row of the lecture hall; Robin, you are that one DnD player that always does weird and unexpected stuff, but in a good way, you also helped me find the courage to say “sju” again.

Speaking of DnD, I would like to thank the people who have been in my various campaigns, for staying through the weird, atrocious, unethical, and long-winded ideas I have been throwing at you. Adriano, Chris, Danish-Simon, Dennis, Esteban, Gustav, Jorge, Mr Candy, Rebecca, Ronnie, Tim N, and Will. Especially Túl for surviving for so long, going through so much

physical and mental torture, for insulting everyone and their mother to death, and for being the (unintentional) main character of the campaign.

I would also like to thank Ian, who helped me out whenever there were IT-related struggles, we first met when we were like twelve and playing with our computers all the time, but look at us now: almost thirty and playing with our computers all the time!

To the temporary visitors to our labs and the bright master's students, you not only bring knowledge, but also bring some sunshine to the dark Swedish lab: Luca, Sophia B, Edison, Anna K, Anne H, Allan, Fengnan. I would also like to thank the Brotherhood (*la confrérie*) for making lab cleaning and maintenance more entertaining, and make sure that Bodil, Dolores, Gertrud, and Gerard are treated with the dignity and respect that they deserve!

Finally, I would like to thank my family, for supporting me and my education in every step of the way. And, Simon Colbin I would like to thank you for a lot of things, for openly being very serious about your research and science in general, and for secretly being a very considerate and appreciative person. He also helped me model the cover for this thesis, which would have been even cooler if they hadn't put up new restrictive guidelines for its design.

To all the master's students and new PhDs who read this, good luck on your journey; make it count.

Tack! Thank you! Salamat po! あざす!



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