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ALL-SOLID LITHIUM-ION BATTERIES FOR HIGH SAFETY AND STABILITY

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ALL-SOLID LITHIUM-ION BATTERIES FOR HIGH SAFETY AND
STABILITY

BY
LUKAS DUWE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
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MASTER OF SCIENCE THESIS
OF
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UNIVERSITY OF RHODE ISLAND

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ABSTRACT

Operational safety and cycle stability are important attributes for all rechargeable batteries. To meet these stringent demands specifically for biomedical applications, an all-solid lithium-ion battery (ASLIB) consisting of a polyethylene oxide (PEO)-based polymer electrolyte with a lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) salt, lithium titanate (LTO) anode and lithium iron phosphate (LFP) cathode is proposed. This work implements fabrication methods, composition optimizations and an assembly procedure, all tailored to the unique cell chemistry and ending in the all-solid LTO-PEO/LiTFSI-LFP cells. Subsequently, these ASLIBs are tested close to body temperature at 40 °C. This assures solid-state, but augments bulk electrolyte and interfacial resistance compared to frequent investigations of polymer electrolyte cells at even more elevated temperatures. In spite of these drawbacks, LTO-PEO/LiTFSI-LFP cells are successfully charged/discharged with a C-rate of C/20. In order to understand observed capacity fading, the cycling behavior of these cells is related to several electrochemical phenomena through impedance measurements and investigations of respective half- and symmetric cells. In the end, a unique electrode composition and assembly procedure is proposed to minimize interfacial resistance.

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LIST OF ABBREVIATIONS

ASLIB	all-solid lithium-ion battery
CPE	composite polymer electrolyte
DBPM	Dynamic Bond Percolation Model
DEC	diethyl carbonate
DMC	dimethyl carbonate
EC	ethylene carbonate
EMC	ethylene methyl carbonate
EIS	electrochemical impedance spectroscopy
EMImTFSI	1-ethyl-3-methylimidazolium
GPE	gel polymer electrolyte
IBE	ideal blocking electrode
LEC	liquid electrolyte cell
LFP	lithium iron phosphate
LIB	lithium-ion battery
LiTFSI	lithium bis(trifluoromethane)sulfonimide
LiX	lithium salt
LPEG	lithium polyethylene glycol
LTO	lithium titanate
MMT	montmorillonite
NMR	nuclear magnetic resonance
OCV	open-circuit voltage

PC	propylene carbonate
PE	polymer electrolyte
PEO	poly(ethylene oxide)
PEG	polyethylene glycol
PIL	polymer ionic liquid
PPE	plasticized polymer electrolyte
PPO	poly(propylene oxide)
PTFE	polytetrafluoroethylene
RPE	rubbery polymer electrolyte
RTIL	room temperature ionic liquid
SEI	solid electrolyte interface
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
SOC	state of charge
TFSI	bis(trifluoromethanesulfonyl)imide
THF	tetrahydrofuran
VTF	VOGEL-TAMMANN-FULCHER

LIST OF SYMBOLS

Latin Characters

A_0	-	number of available charge carriers
a_i	-	activity
C	1/h	C-rate
C_{max}	A	maximal discharge capacity
E_A	J	activation energy
F	C/mol	Faraday constant
I	A	current
k_b	J/k	Boltzmann constant
M	g/mol	molecular weight
n	mol	number of moles
R_0	J/mol K	ideal gas constant
r	mol/mol	molar ratio
T	K	temperature
T_0	K	ideal glass transition temperature
T_g	K	glass transition temperature
T_m	K	melting temperature
t	s	time
t_i	-	transference number of ion species i
U	V	voltage
v_i	-	stoichiometric coefficient
x	g/g	mass fraction
Z	Ω	impedance

Greek Characters

η	V	overpotential
σ	S/cm	conductivity
φ	rad	phase shift
Φ	V	potential
ω	rad/s	angular frequency

CHAPTER 1

Introduction

1.1 Motivation and Challenges

Conventional lithium-ion batteries are favored for small and large-scale applications, from portable electronic devices (cell phones and laptops) to electric vehicles. Furthermore, they represent a promising battery chemistry to fulfill the increasing demands of stationary energy storage, and thus could play an important role in the transition from fossil fuels and nuclear energies to renewable alternatives. All in all, no other battery system threatens its dominance today. This is illustrated in Figure 1.1(a), which compares the share of different battery chemistries on the worldwide market [1].

Figure 1.1: Comparison of different battery technologies

The triumph of LIBs is due to a combination of several advantages: First, they show a favorable specific energy and power density, as shown in the RAGONE-diagram in Figure 1.1(b). The lithium-ion chemistry covers a great range in this diagram with great combinations of specific power and energy density. This enables a huge

number of applications across numerous different energy or power requirements. In addition to that, the lithium-ion system exhibits an excellent cycle and calendar life, great efficiency, low maintenance and a small self-discharge rate [4]. Most striking reason for the superiority of LIBs is the alkali metal lithium. Under standard conditions (0 °C, 1 bar), it is not only the lightest metal but also the lightest solid element on the periodic table, and consequently exhibits a high gravimetric capacity of 3862 Ah/kg. Moreover, it shows a low ionization energy (520.22 kJ/mol) and the highest standard potential in the galvanic series of metals, -3.02 V vs. SHE (Standard Hydrogen Electrode), resulting in the high power density of the battery [5].

In spite of these great characteristics, the classical structure of LIBs still exhibits disadvantages. Conventional LIBs are composed of two electrodes with a liquid electrolyte in between (see Section 2.1.1 for more detail). It is this liquid electrolyte which causes several limitations. Decomposition due to its low electrochemical stability window against the active materials induces the deposition of a solid electrolyte interphase (SEI) on the anode. The initial formation of this SEI, continuous decomposition of the electrolyte and an overall loss of lithium-ions within this layer lead to an ongoing capacity loss of the cell, limiting further cycling stability improvements [6]. Furthermore, the possible leakage and flammability of the liquid electrolyte cause additional safety risks [7]. Environmental incompatibility and human toxicity aggravate the safety concerns even further [1].

To overcome the drawbacks of liquid electrolytes, ASLIBs with polymer electrolytes were proposed. The underlying motivation can be summarized as follows:

- (i) **Safety:** The solid nature of the polymer electrolytes greatly improves the safety of the LIB: First, it prevents possible leakage of the system, which is of great importance in all applications. Furthermore, the ASLIB is more resistant to external shock, vibration or deformation. Hard metal containers are used for the packaging and leakage prevention of conventional LIBs, which can not only result in the development of internal pressures and corrosion, but also adds to material costs. In contrast, LIBs with polymer electrolytes can be packaged more cost effective with vacuum sealed plastic bags, decreasing pressure build-up and hence preventing the risk of explosion. In addition to that, the use of polymer electrolytes suppresses the propagation of hazardous dendritic growth of metallic lithium on the anode's surface. Polarization of the negative electrode resulting in a potential decrease of the anode below 0 V vs. Li/Li⁺ results in lithium deposition on the electrode's surface, which tends to grow in a dendrite form. These lithium dendrites can break through the separator, contact the cathode and cause a short circuit in the cell. The solid and non-porous polymer electrolyte provides much higher resistance, preventing dendrite propagation successfully [8, 9].
- (ii) **Stability:** ASLIBs are not only mechanically more robust, but also show a wider electrochemical stability window compared to liquid electrolytes. This leads to less reactivity towards the electrodes and consequently minimized decomposition of the polymer electrolyte. As a result, ASLIBs are less limited in their cycling stability as is the case for conventional LIBs [8].
- (iii) **Manufacturing:** The all-solid construction results in a less expensive production cost of the battery since all layers can be fabricated with well developed coating techniques. Additionally, replacement of the thick metal containers

with vacuum sealed plastic bags saves on volume. Furthermore, the use of solid electrolytes enables thin film batteries, leading to flexible and highly adaptable battery structures, facilitating novel device geometries [8, 10].

Many different applications could benefit from these safe and stable ASLIBs. For example, this technology seems to be tailor-made for biomedical applications: New innovations in medical technologies include internet- or communication-enabled devices, such as fully internal cochlear implants. These novel technologies require miniature and safe batteries with particular high cycling stability to avoid additional surgery for only replacing the power source [11]. Furthermore, ASLIBs could be a potential solution for space energy storage systems. The Japanese start-up company ISPACE just started to test an all-solid battery on the moon [12]. So far, the extreme lunar temperatures, which can vary from $-173\text{ }^{\circ}\text{C}$ to up to $127\text{ }^{\circ}\text{C}$, prohibited a use of conventional LIBs. Although the cold temperatures will lead to a much slower charge/discharge rate, ASLIBs could at least survive the extreme temperatures in space since the polymer electrolyte does not degrade at these high temperatures. Besides this great thermal stability, a good environmental compatibility and the spill-proof and nonvolatile nature of this technology also makes it attractive for unmanned underwater vehicles [13].

Despite the great advantages, two major drawbacks still have to be surmounted: First, the polymer electrolyte's resistance is orders of magnitude higher when compared to liquid electrolytes due to its lower bulk ionic conductivity. This hinders high power applications. Secondly, a high interfacial resistance is present due to insufficient contact of the solid electrolyte with the electrode's active material particles. In contrast to liquid electrolytes, the solid alternative cannot soak into the electrodes and penetrate their pores, increasing the interfacial

resistance. Also, since the interface is between two solids, volumetric changes of the electrodes lead to an increased amount of damage in this area [14].

1.2 Structure of this Work

This master’s thesis is structured into a theoretical background in the beginning, followed by three parts of experimental investigations and a conclusion in the end.

The theoretical background in Chapter 2 reviews the present state on ASLIBs with a specific focus on the LTO-PEO/LiTFSI-LFP cell chemistry. Basics including the operating principle and cell structure are explained. This is followed by reviewing the single cell components: first, background on the polymer electrolyte as the key component differentiating all-solid from conventional LIBs is given; secondly, an overview of the electrode materials is presented, ending with the motivation of using LTO and LFP in this work. Attention is then devoted to the electrode/electrolyte interface due to its significance on the performance of ASLIBs. In the end of this chapter, electrochemical impedance spectroscopy (EIS) is introduced as the most frequently used measuring method in this work.

The first part of experimental investigations is presented in Chapter 3. These include ex-situ experiments performed on the polymer electrolyte component with the goal of manufacturing the best-performing PEO/LiTFSI films for ASLIBs: EIS for measuring the electrolyte’s conductivity is explained in the beginning, followed by the implementation of a fabrication method, optimization of the salt concentration and testing of BaTiO₃ filler particles as a possible electrolyte additive.

Chapter 4 presents the cycling behavior of the LTO-PEO/LiTFSI-LFP

cells at a temperature of 40 °C. In order to understand capacity fading, impedance investigations are performed and respective half- and symmetric cells are tested. Based on this, electrochemical phenomena can be formulated to explain the obtained cycling results for the LTO-PEO/LiTFSI-LFP cells.

Chapter 5 proposes two approaches to reduce interfacial resistance. First, the electrode composition is investigated; secondly, a unique assembly procedure is tested in order to improve electrode/electrolyte contact.

Finally, this work ends by summarizing the most important results and with a personal recommendation on how to further proceed in this project is given.

CHAPTER 2

Theoretical Background

2.1 Basics about All-Solid Lithium-Ion Batteries

This chapter gives a background on all-solid lithium-ion batteries (ASLIB). The basic structure and operating principle of ASLIBs are explained. Next, some electrochemical fundamentals are described as a basis for understanding the investigations in this thesis. Frequently used battery terminologies in this work are introduced afterwards.

2.1.1 Operating Principle of Lithium-Ion Batteries

The operating principle of a conventional and all-solid LIB is illustrated in Figure 2.1.

Figure 2.1: Schematic structure and operating principle of a conventional and all-solid LIB

In both cases, the cell includes two electrodes, which consist of an electrochemically reactive (active) material mixed with various additives and coated on a metal foil, which is referred to as the current collector. In a conventional LIB (compare Figure 2.1(a)), the physical contact between these electrodes is prohibited by a thin and ion permeable membrane, the separator. The whole setup is soaked with an electrolyte, which is generally a solution of an organic liquid and lithium salt. For the all-solid alternative, the separator and liquid electrolyte is replaced by only one component, the solid electrolyte (compare (Figure 2.1(b))) [15].

It is worthwhile noting that it is convention in the field of batteries to always refer to the negative electrode as the anode and to the positive electrode as the cathode. Usually, the anode is defined to be the electrode at which oxidation occurs while reduction takes place at the cathode. However, in the field of batteries, this matches the naming convention only for the discharging of the cell. The misleading naming has its origin in primary (non-rechargeable) batteries [15, 16].

Driven by a potential difference of the electrodes, spatial separated oxidation and reduction of the active material particles takes place at the anode and cathode, respectively. For example, in the case of discharging, the anode active material is getting oxidized, emitting lithium-ions and electrons. Since the electrolyte is conducting only for cations but insulating for electrons, the charge carriers get separated. Lithium-ions get solvated by the liquid electrolyte or complexed by its solid alternative, and migrate to the cathode under the influence of the applied field as well as diffusive transport. A more detailed explanation of the charge transport mechanism in polymer electrolytes can be found in Section 2.2.4. In order to satisfy charge neutrality, the electrons follow the lithium-ions via an

external conducting path, resulting in an electrical current flowing through the energy consumer. At the cathode side, reduction of lithium-ions occurs via reaction with the electrons and the cathode active material. The separator membrane or solid electrolyte prevents an internal short circuit of the cell, since physical contact between the electrodes would induce a spontaneous reaction of the active materials without spatial separation of lithium-ions and electrons. During charging, these processes reverse [4].

2.1.2 Electrochemical Background

The driving force for the electrochemical reactions inside a battery is the cell voltage, defined as the potential difference between the cathode and anode:

$$U = \Phi_c - \Phi_a \quad (2.1)$$

The voltage difference causes the migration of lithium-ions from one electrode to the other and changes the lithium concentration in the anode and cathode. This results in an increase or decrease in the concentration-dependent electrode potentials. If the battery is at rest, meaning that no current is flowing, the equilibrium electrode potentials $\Phi_{c/a}^{eq}$ can be modeled with the NERNST-equation [17]:

$$\Phi_{c/a}^{eq} = \Phi_{c/a}^{eq,\circ} + \frac{R_m T}{zF} \ln \frac{\prod a_{ox}^{|v_{ox}|}}{\prod a_{red}^{|v_{red}|}} \quad (2.2)$$

- with R_m : ideal gas constant (=8.314 J/mol K)
- T : temperature
- z : number of electrons transferred per formula conversion
- F : Faraday constant (= 96485.34 C/mol)
- v_i : stoichiometric coefficient
- $\Phi_{c/a}^{eq,\circ}$: standard redox potential
- a_i : activity

where the concentration dependency is described with the activity a_i , and the standard redox potential $\Phi_{c/a}^{eq,o}$ describes the potential difference to a reference electrode, typically the standard hydrogen electrode or metallic lithium, at standard conditions. The difference of these resting potentials $\Phi_{c/a}^{eq}$ is called the open-circuit voltage (OCV) while the influence of lithium concentration on the OCV is shown in respective OCV/state of charge (SOC)-curves. However, the cell voltage also depends on the flowing current, which induces overpotentials $\eta_{c/a}$. In order to calculate the electrode potentials under current, and subsequently the cell voltage, these have to be accounted for [18]:

$$\Phi_{c/a} = \Phi_{c/a}^{eq} + \eta_{c/a} \quad (2.3)$$

The overpotentials can be negative or positive, depending on the direction of the current in the respective electrodes. In the field of batteries, three main overpotentials have to be considered; (1) ohmic (2) charge transfer or activation and (3) diffusion overpotentials [18, 5]: The ohmic overpotential describes the voltage drop produced by the ohmic resistances of individual battery components which current has to pass. At the interface between active material particles and the electrolyte, electrons and lithium-ions meet. As a consequence, an electrical double layer (EDL) forms here. The EDL has to be passed for the redox reaction to occur, requiring an activation energy. The accompanying potential difference for a passing current is called charge transfer or activation overpotential. A diffusion overpotential results if the transport of the reactants to the reaction sites is a limiting process. This is the case especially for high currents, when a large concentration gradient forms in the diffusive layer of the EDL.

2.1.3 Terminology

In this work, several battery specific terminology is used. Without claiming completeness, most frequent ones are explained in the following:

C-rate: In order to compare the charge/discharge current for batteries of different sizes, a charge/discharge rate is specified relative to the cell's maximum capacity. The C -rate is the charge/discharge current normalized with the cell's maximum capacity:

$$C = \frac{I}{C_{max}} \quad (2.4)$$

Thus, the unit of the C -rate is 1/h. For example, a 1 C -rate will charge or discharge the battery in 1 hour [19].

Glass transition: For polymers, the glass transition describes the change from a non-ordered, hard, “glassy” state with little mobility to a more “rubbery” state with more flexibility of the polymer chains. The glass transition temperature T_g describes the temperature at which this phase transition occurs [20].

Impedance: The electrical or complex impedance Z describes the relation between the complex representations of a sinusoidal current $\hat{I}(\omega, t)$ and voltage $\hat{U}(\omega, t)$ [21]:

$$Z(\omega) = \frac{\hat{U}(\omega, t)}{\hat{I}(\omega, t)} = \frac{U_0 \cdot e^{i(\omega t + \varphi)}}{I_0 \cdot e^{i\omega t}} = |Z| \cdot e^{i\varphi} \quad \text{mit: } |Z| = \frac{U_0}{I_0} \quad (2.5)$$

Given its similarity to the ohmic law, the impedance is often referred to as AC resistance. It holds information about the magnitude of the impedance $|Z|$, which is related to the drop of the voltage amplitude U_0 when the current amplitude I_0 is applied or vice versa. Additionally, the impedance describes the phase shift φ between the voltage and current. Due to the complex nature of the impedance, a real and imaginary part can be defined:

$$\text{Re}(Z) = |Z| \cdot \cos(\phi) \quad (2.6)$$

$$\text{Im}(Z) = |Z| \cdot \sin(\phi) \quad (2.7)$$

The respective plot of $\text{Im}(Z)$ vs. $\text{Re}(Z)$ is called the NYQUIST-plot [22].

State of charge (SOC): The SOC is a measure of how much the battery is charged. It is calculated from the relationship between currently available discharge capacity to the battery's total capacity in the completely charged state in the beginning of the cycle [23].

Transference number: The transference number t_i describes the fraction of an electrical current carried by an ion species i :

$$t_i = \frac{I_i}{I_{tot}} \quad (2.8)$$

Consequently, the sum of the transference numbers for all of the ions in the electrolyte equals unity [24].

2.2 Polymer Electrolytes

In this work, a polymer electrolyte based on poly(ethylene oxide) (PEO) and lithium bis(trifluoromethane)sulfonimide (LiTFSI) is investigated for its use in ASLIBs. This is motivated by good ionic conductivity, transference number, thermal stability and non-toxicity compared to other combinations [25]. For the purposes of completeness it should be noted that alternatives including inorganic solid electrolytes exist [26]. This section focuses on giving a background on the general class of polymer electrolytes and specifically on the PEO/LiTFSI chemistry. After a short historical introduction, general required properties for polymer electrolytes are defined. Next, the most frequently used materials for the two component polymer/salt system are presented, and the specific PEO/LiTFSI chemistry is characterized. Subsequently, the major conduction models and influencing factors are explained. The most investigated modifications to optimize the properties of the polymer electrolyte are described afterwards. Finally, an overview of the most popular fabrication methods to obtain the thin film polymer electrolytes is given.

2.2.1 Historical Background

Interactions of inorganic salts with PEO were first investigated by LUNDBERG et al. [27] in 1966. They stated that an incorporation of 10-30 % of salt in the polymer host leads to a decrease in crystallinity while retaining compatibility with the PEO. Moreover, they stated a polyelectrolyte-like behavior of these mixtures at low salt concentration: the introduction of the salt changed the polymer from insoluble to soluble in methanol. Further investigation of the ionic nature of these systems was done by FENTON, WRIGHT and coworkers [28] in 1973, resulting in the discovery of the first ion conducting polymer material: They reported moderate ionic conductivity for PEO complexes with dissolved sodium and potassium thiocyanates

and even performed measurements of σ at different temperatures. However, the relevance of this publication was not considered until 1978, when ARMAND et al. [29, 30, 31] finally pointed out the potential of these materials as polymer electrolytes. It was this work which heightened research interests of polymer electrolytes, including experimental studies of the charge transport, modeling of conduction mechanisms, investigation of chemical structure and evaluation of physical/chemical properties [8].

2.2.2 Required Properties

The polymer electrolyte needs to satisfy several requirements to develop a functional ASLIB. From a practical point of view, the most important ones are the following:

- (i) **Ionic conductivity:** It is crucial for the basic operating principle of every battery that the electrolyte is both, a good ionic conductor and an electrical insulator. Commercial liquid electrolytes typically consist of a solution of the salt lithium hexafluorophosphate (LiPF_6) in mixtures of organic solvents, such as ethylene carbonate, dimethyl carbonate or propylene carbonate. These show ionic conductivities in the range of 10^{-3} to 10^{-2} S/cm [32]. The polymer electrolyte should exhibit a conductivity of at least 10^{-4} S/cm at ambient temperatures for practical battery applications [8].
- (ii) **Transference number:** The transference number for lithium ions in the solid electrolyte should optimally be close to unity. Electrodes in lithium-ion batteries are only active towards lithium ions. Thus, the electrolyte should ideally be a single-ion conducting system for Li^+ , otherwise the energy used to transport further species is lost. Polymer electrolytes developed so far typically show a cationic transference number below $t_{\text{Li}^+} = 0.5$, indicating that less than half of the current is transported via lithium ions. Thus,

maximizing the transference number would reduce the energy loss due to the unnecessary transport of other charged species and hence increase the power density of the cell [8, 25].

(iii) Mechanical properties: On the one hand, polymer electrolytes need to exhibit a certain degree of mechanical robustness: They must stop hazardous dendritic growth of metallic lithium from the anode surface, which would lead to an internal short circuit of the cell when getting in contact with the cathode. In addition to that, the thin electrolyte sheet has to remain structurally stable during its processing and the cell assembly. Especially for large scale manufacturing a high mechanical stability is desirable. On the other hand, polymer electrolytes need to be soft to promote good contact with the electrodes' active material particles. High stiffness of the polymer electrolyte sheet would lead to gaps at the electrode/electrolyte interface and therefore greatly increase the interfacial resistance [8].

(iv) Compatibleness with the electrodes: The solid electrolyte has to be inert against both electrode materials used in the ASLIB. No chemical reactions at the electrode/electrolyte interface should take place. The electrochemical stability window needs to be high enough to avoid electrolyte decomposition [33].

2.2.3 Materials for a Two Component Polymer/Salt Complex

The traditional polymer electrolyte consists only of two components: an ion coordinating and high molecular weight polymer host with a dissolved lithium salt. In this section, typical representatives for both components are introduced and the specific PEO/LiTFSI chemistry used in this work is characterized.

Several different host materials have been investigated in the past. The most frequently ones are shown in Table 2.1, together with their respective chemical formulas and phase transition temperatures.

Table 2.1: Polymer host materials for polymer electrolytes [8]

Polymer	Repeat unit	T _g /°C	T _m /°C
poly(ethylene oxide) (PEO)	$-\text{[CH}_2-\text{CH}_2-\text{O}]_n-$	-67	65
poly(propylene oxide) (PPO)	$-\text{[CH}(-\text{CH}_3)\text{CH}_2\text{O}]_n-$	-60	<i>a</i>
poly(dimethylsiloxane) (PDMS)	$-\text{[SiO}(-\text{CH}_3)_2]_n-$	-127	-40
poly(acrylonitrile) (PAN)	$-\text{[CH}_2\text{CH}(-\text{CN})]_n-$	125	317
poly(methyl methacrylate) (PMMA)	$-\text{[CH}_2\text{C}(-\text{CH}_3)(-\text{COOCH}_3)]_n-$	105	<i>a</i>
poly(vinyl chloride) (PVC)	$-\text{[CH}_2\text{CHCl}]_n-$	82	<i>a</i>
poly(vinylidene fluoride) (PVDF)	$-\text{[CH}_2\text{CF}_2]_n-$	-40	171
poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP)	$-\text{[CH}_2\text{CF}_2]_n-\text{[CF}_2\text{CF}(\text{CF}_3)]_m-$	-65	135

a=amorphous polymer

At the present state, the majority of the polymer electrolytes are based on PEO or PPO. Salt-polymer complexes with these materials exhibit a superior stability and ionic conductivity compared to the other chemistries listed in Table 2.1. It is believed that this is due to their high concentration of ether groups, which are necessary for conduction as explained in Section 2.2.4 [34].

Typical lithium salts used in liquid electrolytes such as LiPF_6^- , LiAsF_6^- or LiBF_4^- are not suitable for polymer electrolytes, as their anions are sources for Lewis acids. Consequently, the use of these species in a polymer environment would

lead to an increased risk of chain scission [34]. Frequently used lithium salts for polymer electrolytes are lithium bis(trifluoromethane)sulfonimide ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiTFSI) and lithium tris(trifluoromethanesulfonyl)methide ($\text{LiC}(\text{SO}_2\text{CF}_3)_3$), as they offer great thermal stability and exhibit the highest known ionic conductivity for organic anion-based lithium salts [35].

In this work, the polymer electrolyte is based on a PEO/LiTFSI chemistry. A higher thermal stability and an increased ionic conductivity has been observed compared to other combinations [25]. Structural formulas of PEO and LiTFSI are shown in Figure 2.2:

Figure 2.2: Structural formulas of PEO and LiTFSI [36]

PEO ($\text{C}_{2n}\text{H}_{4n+2}\text{O}_{n+1}$) belongs to the class of polyethers. For molecular weights below $2 \cdot 10^4$ g/mol it is also known as polyethylene glycol (PEG). Its monomer, ethylene oxide (EO) with the chemical formula $\text{C}_2\text{H}_4\text{O}$, provides a molecular mass of 44.03 g/mol. Synthesis of high molecular weight PEO is typically done by ring-opening oxanionic polymerization of EO. To obtain a narrow polydispersity, a living anionic polymerization is performed. This can be achieved by using alkali metal hydrides, alkyls, aryls, alkoxides, hydroxides or amides as initiators in a polar and aprotic solvent. Popular initiator systems are alkoxides with sodium or potassium as counter ions in tetrahydrofuran (THF). Partial deprotonation of the initiator of around 10 to 20 % is sufficient for starting the polymerization of the EO monomers. The propagation reaction is accompanied by degenerative

chain transfer: the active alkoxide endgroups can either react further with EO monomers or transfer their negative charge to the initiator species to build hydroxyl-terminated chains. This results in an equilibrium between active alkoxides and dormant PEG. No irreversible termination reaction takes place, which is why a living polymerization can be accomplished [37]. Glass transition of the amorphous parts of pure PEO with a molecular weight of 10^5 g/mol occur at $T_g = -67$ °C, the melting temperature of the crystal regions is $T_m = 65$ °C and the flash point is stated to be $T_f = 229$ °C. PEO is susceptible to oxidative degradation when in contact with air. Therefore, contact with oxygen or processing at higher temperatures should be avoided if this degradation is undesirable [36, 38]. At room temperature, PEO has a high degree of crystallinity of about 70-84 %. The remaining amorphous elastomeric phase is trapped by these crystals [39].

The hydrophilic salt, LiTFSI, with a molecular weight of 287.09 g/mol has a melting temperature of about 236 °C [40]. It consists out of a Li cation and a bistriflimide anion. KALHOFF et al. showed that the use of LiTFSI instead of the commercially common, but toxic and environmentally unfriendly lithium hexafluorophosphate (LiPF_6) leads to substantially safer electrolytes [41]. Since the bistriflimide anion is large relative to other investigated lithium salts, anion migration in the polymer electrolyte is minimized, resulting in a higher lithium ion transference number. Anion migration is undesirable in LIBs as it not only reduces the transference number, but might also induce a self-discharge of the cell and lead to electrode surface degradation. LiTFSI also has a plasticizing effect on the PEO. This is not only attributed to the anions size, but also its high dislocation of the electrons. These characteristics decrease the interactions between the polymer chains and therefore hinde crystallization, leading to a more flexible

and amorphous polymer/salt complex [25]. A superior conductivity, salt diffusion coefficient and transference number for LiTFSI compared to other salts was also shown by BURIEZ et al. [42].

2.2.4 Conduction Mechanism

Understanding the charge transport mechanism in polymer electrolytes is of tremendous importance to optimize their conductivity. However, because of their complex structure, the conduction mechanism still remains not fully understood. In general, conduction can be described on a macroscopic and microscopic level.

(i) Macroscopic approach: Conductivity in most polymer-salt complexes can quite satisfactorily be modeled using the VOGEL-TAMMANN-FULCHER (VTF) equation:

$$\sigma = A_0 T^{-1/2} \exp\left(\frac{-E_A}{k_B(T - T_0)}\right) \quad (2.9)$$

In this equation, A_0 is a pre-exponential factor related to the number of available charge carriers and therefore depends on the salt concentration. E_A is a pseudo-activation energy related to segmental motion of the polymer chains. T_0 is the ideal glass transition temperature and k_b the Boltzman's constant. The equation has an empirical origin, but can be derived from quasi thermodynamic models such as the free volume theory and the configurational entropy [33, 43].

(ii) Microscopic approach: In the original publications by WRIGHT [28] and ARMAND [29, 30], a microscopic approach for explaining conductivity in polymer electrolytes was introduced. They proposed that it was the “hopping” of lithium cations inside of the polymer helix which induces charge transport. However, this model was not supported by structural studies of the polymer salt complex: HIBMA et al. [44] found that the

alkali ions are mostly located outside of the polymer helix. Based on conductivity studies on mixed anion complexes of PEO with BH_4^- and BF_4^- , DUPON et al. [45] suggested that cation transport in PEO is not limited by motion through the helical channel, concluding that conduction between the polymer chains would be the dominant process. Subsequent investigations showed that the alkali ion in the polymer/salt complex is tightly coordinated to the ether groups in the polymer chains. In fact, based on molecular dynamics simulations, it was suggested that lithium ions are complexed to polymer chains via approximately five ether oxygens [46]. These interactions between the polymer chains and the lithium ions would result in lower mobility of the cations. Taking this into account, polymer dynamics play an important role in the conduction mechanism.

At present it is believed that lithium transport in the polymer host predominantly arises from a combination of two effects, which are illustrated in Figure 2.3:

Figure 2.3: Conduction mechanisms in the polymer electrolyte [46]

The first major conduction mechanism is believed to be the hopping of lithium ions between two complexation sites, shown in Figure 2.3(a). This would be assisted by segmental polymer motion, creating a liquid like

environment around the ion [46]. The Dynamic Bond Percolation Model (DBPM) is introduced to describe the mechanism mathematically and to increase understanding of the microscopic processes. The DBPM assumes the polymer/salt complex to be a statistically disordered medium that undergoes dynamic rearrangement processes, which is believed to be the case for the amorphous parts of the electrolyte. Diffusion of the alkali ions is modeled as a random walk process in the dynamic lattice: Ion hops taking place between lattice sites (complexation sites) are dependent on the either open or closed state of the bonds between them. The motion of the polymer host results in the assignment of these bond states. The DBPM leads to one master equation describing the ion hops between sites. It is characterized by three parameters: an average hopping rate, a percentage of open bonds and a renewal time. The latter describes the frequency of the rearrangement of the open and closed states of the bonds, and therefore represents the polymer motion [47, 48, 49]. The second dominant conduction mechanism taking place in the polymer electrolyte is often referred to as "vehicular diffusion" [50, 51, 52, 24]. As illustrated in Figure 2.3(b), it describes the diffusion of entire polymer chains with the coordinated lithium cations.

For both conduction mechanisms, the polymer is required to be in an amorphous state as mobile polymer chains are necessary for the transport of the lithium ions. This explains the observations, that conductivity in the amorphous phase is several orders of magnitude higher than in the crystalline ones [53].

2.2.5 Influencing Factors

Electrical and mechanical properties of the polymer electrolyte are dependent on several different factors. The influence of salt concentration, temperature and the host's molecular weight on the conductivity of the polymer/salt complex are described below:

- (i) **Salt concentration:** The conductivity of the polymer electrolyte is strongly dependent on the quantity of lithium ions intercalated into the polymer host. The salt concentration in the electrolyte is expressed in terms of the molecular ratio of lithium ions to oxygen atoms in the polymer (r), or vice versa O/Li . For PEO, the monomer ethylene oxide (C_2H_4O) provides only one oxygen atom. Therefore O/Li and r are defined as

$$O/Li = \frac{1}{r} = \frac{n_{EO}}{n_{Li+}} \quad (2.10)$$

where n_{Li+} is the number of lithium ion moles and n_{EO} the number of ethylene oxide moles.

Figure 2.4(a) shows the ionic conductivity as a function of salt concentration for a PEO/LiTFSI electrolyte at two different temperatures.

When a dopant salt is introduced to the polymer matrix, the ionic conductivity rises at low salt concentrations due to the increasing number of available charge carriers. However, it has been stated by many research groups that a further increase of r leads to a conductivity maximum, followed by a decrease of σ [33] as illustrated in the diagram. This drop of ionic conductivity after reaching a critical O/Li ratio is attributed to the following two effects: First, high salt concentrations can lead to a decrease of polymer

Figure 2.4: Influence of salt concentration on the conductivity and glass transition temperature of polymer electrolytes

chain motion. This effect can be explained by the observed rise of the glass transition temperature with increasing salt concentration, as is shown in Figure 2.4 (a) for the PEO/LiTFSI and PEO/NaI system. A higher glass transition temperature results in a decrease of the amorphous regions in the electrolyte and therefore a reduction of polymer chain motion, which promotes ion transport. Second, the high salt concentration can lead to incomplete dissociation of the salt, causing the number of "free" lithium ions to decrease. This is mainly caused by the formation of ion pairs, triplets or even larger cluster of ions, which decrease mobility in the polymer host and result in a reduced ionic conductivity [25, 56]. Ion association at high salt concentrations was verified in NMR studies by BRUCE et al. [57]. The optimal salt concentration is dependent on the specific chemistry of the polymer/salt complex, which can be influenced by the presence of other components and experimental conditions (e.g. temperature).

- (ii) **Temperature:** The behavior of polymer electrolytes is strongly dependent on temperature. As such, the phase and thus the stiffness of the system varies with it. This influence is shown in respective temperature/composition

phase diagrams for specific polymer/salt systems (see [58, 59] for example). In addition to these mechanical properties, temperature also influences both the conductivity and transference number of the polymer electrolytes, as shown in Figure 2.5. In general, an increase in temperature leads to a rise of

Figure 2.5: Influence of temperature on the conductivity and lithium ion transference number of polymer electrolytes

the conductivity, as indicated in the conductivity/temperature curve in Figure 2.5 (a) for PEO/LiTFSI electrolytes. This is due to a decreasing activation energy for conduction with higher temperature, which can be attributed to an increasing mobility of both, polymer chains and coordinated ions. As a result, increasing segmental motion of the polymer chains and decreasing ion-ion and ion-polymer interactions lead to an increase in conductivity. Mathematically, the temperature dependency of traditional polymer electrolytes is typically described using the VFT-model from Equation 2.9 [24]. The lithium ion transference number also rises with an increase in temperature, as shown in Figure 2.5 (b) based on studies of BRUCE et al. This effect can be ascribed to different stabilities of the anion and cation coordination in the polymer host: Anions coordinating to OH-end groups would be more stable than the lithium cations coordinating to the oxygen atoms in the polymer chains. Therefore,

an increased temperature would primarily enhance the mobility of the lithium ions due to the weak oxygen-cation bond, whereas the OH-anion bond is only marginally affected. This results in an increasing contribution of lithium ions in the overall charge transfer [62].

(iii) **Molecular weight of the polymer:** TERAN et al. studied the influence of polymer chain length on the conductivity of the polymer/salt complex. Conductivity as a function of molecular weight was measured at three different temperatures. Each curve shows the same qualitative behavior: The curve rapidly decreases at low molecular weights, and then reaches a constant value as the molecular weight increases. Their experimental results are shown in Figure 2.6.

Figure 2.6: Influence of the molecular weight on the conductivity of polymer electrolytes [50]

This behavior can be explained by the influence of the polymer's chain length on the conduction mechanism: Intersegmental cation hopping and vehicular diffusion were presented as the predominant mechanisms. The former takes

place independent of the polymer’s molecular weight, while the latter is mainly present for only short chain lengths. This is due to a higher diffusion coefficient of the lower molecular weight polymer [50]. In spite of the enhanced ionic conductivity of polymer electrolytes with low molecular weight hosts, they are typically not used for ASLIB applications. This is due to the well-known direct correlation between polymer stiffness and chain length [63].

2.2.6 Modifications to the Two Component Polymer/Salt Complex

As described in the previous section, the traditional two component polymer electrolyte exhibits limited conductivity at room temperature. For example, the PEO/LiTFSI system shows values in the magnitude of 10^{-6} S/cm at 20 °C. When the temperature is increased, conductivity rises sharply, however mechanical stiffness decreases. In order to overcome these drawbacks, several modifications for optimization of the electrical and mechanical properties have been proposed. To give a broad overview of these modifications, these are roughly divided into three main groups: Plasticized polymer electrolytes (P-PE), rubbery polymer electrolytes (R-PE) and composite polymer electrolytes (C-PE).

Plasticized Polymer Electrolytes (PPE)

Considerable enhancement of the ionic conductivity is observed after introducing a polar or ionic liquid into the polymer/salt complex. As a consequence, adding a plasticizer to traditional polymer electrolytes is one of the most common approaches to enable room temperature functionality. The enhanced conductivity is attributed to the increase of amorphous regions in the polymer electrolyte. Improved segmental motion of the polymer chains promotes cation hopping between different complexation states. Also, the liquid facilitates salt dissociation, increasing the number of available charge carriers. However, the introduction of

liquids in the electrolyte composition is accompanied by a deterioration of the mechanical robustness of the electrolyte film. In addition to that, the electrolytes corrosive reactivity towards the metal electrodes typically increases. Consequently, a compromise between the solid and highly plasticized liquid state of the complex has to be found [25].

When large amounts of plasticizers are added, they are typically referred to as gel polymer electrolytes (G-PE). A gel is defined as a dilute cross-linked polymer network swollen with a solvent. It does not flow and is obtained by physically or chemically crosslinking the polymer chains. In order to enhance this process and therefore obtain a greater mechanical stability of the gel, additives which can easily be crosslinked or thermally cured are often introduced [8].

Many different plasticizers have been investigated. They can be classified as organic solvents, low molecular weight polyethers and ionic liquids [64]:

- (i) **Organic solvents:** Commonly used organic solvents as plasticizers in polymer electrolytes are of a polar nature. Typical examples are ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC). The organic solvents help solvating the ions and facilitate their transport in the polymer electrolyte. Based on this, they are required to have a low viscosity and high dielectric permittivity. To achieve and optimize these properties, mixtures of the solvents are often used. The introduction of these into the polymer electrolyte can increase the conductivity to up to 10^{-3} S/cm. However, these organic solvents are highly flammable and volatile. As a consequence, they cannot be used for applications with high safety requirements [65].

(ii) **Low molecular weight polyethers:** For the polyether group, low molecular weight PEG is a natural representative because it offers the same repeat unit as PEO. ITO et al. [66] characterized PEO/LiCF₃SO₃ complexes using different amounts of PEG with molecular weights from $M_W = 400$ to 2000 g/mol as plasticizers. They measured ionic conductivity of these systems as a function of PEG molecular weight, PEG concentration and temperature. Experimental results showed an increasing conductivity with decreasing molecular weight and higher concentration of PEG. However, the OH-end groups of PEG can react with metallic lithium, prohibiting the use of such plasticizers in lithium-ion batteries. In order to overcome this drawback, the hydroxy-endgroups of the PEG were changed [8]. YANG et al. [67] and KELLY et al. [68] replaced them with less reactive monomethoxy (MMPEG), dimethoxyl (DMPEG) or lithium (LPEG) units and observed an ionic conductivity of 10^{-5} S/cm at 25 °C. In the case of LPEG, an improved compatibility with the metallic lithium electrode was stated as well [67]. PEG-borate ester was synthesized by KATO et al. [69, 65] and studied as a plasticizer for a PEGMA/LiTFSI based polymer electrolyte. Besides great thermal and electrochemical stability, they stated an electrolyte conductivity exhibiting 10^{-4} S/cm at 30 °C. Unfortunately, when such a polymer electrolyte was incorporated in LIBs, a capacity fade was observed when using lithium metal anodes and LFP cathodes. This was ascribed to a decrease of lithium salt concentration in the bulk electrolyte and anion decomposition on the cathode surface, increasing cathode/electrolyte interfacial resistance. [70]. The influence of 12-Crown-4 ether (12Cr4) on a PEO based electrolyte with LiCF₃SO₃, LiBF₄ or LiClO₄ as the lithium salt was examined by NAGASUBRAMANIA et al. Maximum conductivity values for these systems was obtained at a ratio

of 12Cr4/Li of 0.003 for the PEO/LiBF₄ system, again with values around 10⁻⁴ S/cm at 40 °C. Besides the improved ionic conductivity, a decrease in the charge transfer resistance was stated for the addition of 12Cr4 to the investigated polymer electrolytes [71]. FORSYTH studied the effect of tetraethylene glycol dimethyl ether (tetraglyme) as a plasticizer on polymer electrolytes with LiClO₄ salt. They showed an exponential rise of the electrolyte's conductivity with increasing tetraglyme concentration. However, this was accompanied by a deterioration of mechanical properties due to a decrease in density [72]. KIM et al. added poly(ethylene glycol) dimethyl ether (PEGDME) to PEO-based electrolytes and obtained an ionic conductivity of 1.2 · 10⁻⁴ S/cm at 40 °C. Furthermore, they compared PEGDME with EC and PC as plasticizers to determine their effect on transport and electrochemical properties. In this study, PEGDME led to a superior conductivity and diffusion coefficient [73, 74].

(iii) Ionic liquids: Recently, ionic liquids have attracted attention for their use as plasticizers in polymer electrolytes. This is due to their low flammability, high chemical and thermal stability and negligible volatility. Ionic liquids are molten salts at room temperature (often called room temperature ionic liquids, RTILs) and consist of a bulky organic cation and large delocalized inorganic anion [64]. Their incorporation into polymer electrolytes was proposed by SHIN et al. [75], who studied various pyrrolidinium based cations and TFSI anions for their use as plasticizers in polymer electrolytes. Their structure is shown in Figure 2.7 (a). The most promising results showed the incorporation of PYR₁₃TFSI into a PEO/LiTFSI electrolyte, leading to conductivity values of around 10⁻⁴ S/cm at 20 °C. However, it is worth noting that transference numbers decrease with increasing concentrations of PYR₁₃TFSI. Subsequently, several other RTILs have been investigated.

For instance, RAGHAVAN et al. [76] synthesized three different ionic liquids based on a 1-alkyl-3-methylimidazolium cation and TFSI anion. The best results arose from the 1-ethyl-3-methylimidazolium (EMImTFSI), whose structure is shown in Figure 2.7 (b). Measured conductivity values were in the range of $2.4 \cdot 10^{-4}$ to $4.5 \cdot 10^{-3}$ S/cm at 25 °C. Most recently, polymer ionic liquids (PILs) attracted interest because of their low flammability and high stability, enhancing high safety LIBs. For example, LI et al. [77] investigated PILs based on guanidinium cations and TFSI anions (see Figure 2.7 (c)). Compared to traditional dry polymer electrolytes they not only observed enhanced conductivity, but also a wide electrochemical stability window and good lithium stripping/plating performance.

Figure 2.7: Influence of temperature on the conductivity and lithium ion transference number of polymer electrolytes [64]

Rubbery Polymer Electrolytes (RPE)

In contrast to the traditional 'salt-in-polymer' complex, this group of polymer electrolytes is often referred to as a 'polymer-in-salt' system: a small amount of high molecular weight polymer is added to a large amount of salt. Typically, the glass transition temperature of these mixtures is low to maintain a rubbery state of the electrolyte at room temperature. Although providing improved ionic conductivity and good electrochemical stability when compared to traditional polymer electrolytes, the disadvantage of this group is poor

mechanical properties. As a result, applications are limited because the salt tends to crystallize at lower temperatures, leading to brittle electrolyte films [25, 64].

The R-PE group was first studied by ANGELL et al. [78], who mixed different lithium salts with small quantities of PEO and PPO. They stated a conductivity of up to 10^{-2} S/cm at ambient temperature. However, the mechanical properties of this electrolyte prohibited its use in LIBs with metallic lithium anodes. FAN et al. [79] studied a rubbery electrolyte based on a $\text{LiClO}_4\text{--LiNO}_3\text{--LiOAc}$ salt mixture and PEO polymer and found conductivity values of 10^{-3} S/cm at room temperature. Furthermore they observed a large rubbery temperature range of 20 to 130 °C and a high Li^+ transference number. Many studies have focused on rubbery electrolytes with PAN and its copolymers as the polymer. This is because interactions between the nitrile groups and lithium ions have been attributed to stabilize ionic clusters in the polymer-in-salt system. In contrast to traditional polymer electrolytes, it is well accepted that ion aggregation is desirable for the ion transport in polymer-in-salt systems [64]. To name only one of many studies on R-PE with PAN polymers, ZALEWSKA et al. [80] studied a LiAlCl_4 system. At room temperature they measured a conductivity of 10^{-4} S/cm.

Composite Polymer Electrolytes (CPE)

Composite polymer electrolytes have developed into one of the most active research areas in the polymer electrolyte field. In this group, small quantities of filler particles are dispersed in the polymer electrolyte. Contrary to expectations of classical theories, where adding small amounts of an insulator to an electrical conductor is believed to decrease conductivity, an increasing effect has been observed in the case of micro- or nanosized particles. In addition to that, an enhanced mechanical stability and reduced electrode/electrolyte interfacial resistance has been stated

for C-PEs [25]. Different approaches to explain these effects were proposed: It has been suggested, that various Lewis acid-base interactions at the surface of the particles would induce pathways for lithium ion transport and result in the enhanced transport properties. Furthermore, the small particles might act as crosslinking centers for PEO segments and salt anions, hindering reorganization of the polymer chains [64]. Regardless, their introduction in the polymer/salt system would lead to a physical barrier for lithium dendrite growth. Fillers in polymer electrolytes are mostly of a ceramic nature. These inorganic particles can be classified into two categories, depending on their role in the conduction process: Passive or inert fillers do not directly participate at the lithium transport process. They play an indirect role, e.g. by increasing the amorphous region or free volume in the electrolyte and therefore induce more segmental motion of the polymer chains. Active fillers on the other hand participate in the charge transport process directly by providing an additional lithium source.

(i) Passive ceramic fillers: Passive ceramic fillers include Al_2O_3 , TiO_2 , SiO_2 , Zr_2O_3 , montmorillonite (MMT), BaTiO_3 , ferroelectric materials and many more [64]. The effect of these on polymer electrolytes has first been studied by WESTON et al. [81] in 1982. In their pioneering work, they added α -alumina to a PEO/ LiClO_4 polymer electrolyte and found an enhanced mechanical stability of the material, improving the ability of this polymer electrolyte for use in LIBs. However, they stated only negligible changes in the ionic conductivity and lithium transference number. In contrast to that, many following works showed the positive effect of the fillers on the charge transport properties of these systems. For example, CROCE et al. [82, 83] studied the influence of 13 nm sized TiO_2 and 5.8 nm sized Al_2O_3 particles on PEO/ LiClO_4 systems by comparing the electrical and mechanical properties of

these composite systems with the respective ceramic particle-free electrolytes. They not only observed excellent mechanical stability in a temperature range of 30 to 80 °C and great electrochemical stability, but also an increase of ionic conductivity. In fact, for the same temperature range, systems without ceramic particles showed a conductivity of around 10^{-7} to 10^{-4} S/cm, whereas the introduction of fillers led to values of 10^{-5} to 10^{-3} S/cm. Similar studies by the same research group have investigated polymer electrolyte systems with SiO_2 [84] and ZrO_2 [85] fillers, also stating improved mechanical strength and charge transport properties. PEO-based polymer electrolytes with several salts (LiClO_4 , LiBF_4 , LiBF_6 , LiCF_3SO_3 and LiTFSI) and ferro-electrical materials (BaTiO_3 , PbTiO_3 and LiNbO_3) have been characterized by SUN et al. [86]. Again, a great enhancement of conductivity was observed: For instance, the addition of 1 wt% of 0.5 μm sized BaTiO_3 particles into a PEO/ LiTFSI electrolyte more than doubled the conductivity of this system at 100 °C. CHOUDHARY et al. [87] used MMT as fillers in PEO/ LiX polymer electrolytes. Enhancements in ionic conductivity were between a half to a full order of magnitude for the different systems. The cycling performances of $\text{Li}/\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cells with PEO/ LiTFSI composite polymer electrolytes using BaTiO_3 , TiO_2 , and Al_2O_3 fillers were compared by LI et al. [88]. In these studies, the best results were achieved for the cells with BaTiO_3 fillers in the electrolyte.

- (ii) **Active ceramic fillers:** Classical representatives of this group are γLiAlO_2 and LiN_2O_3 . Different studies on γLiAlO_2 fillers in polymer electrolytes have been reported: BORGHINI et al. [89] characterized the properties of a PEO/ LiTFSI electrolyte with and without γLiAlO_2 particles. The use of these fillers reduced the crystallization rate and led to enhanced interface

stabilities. APPETECCHI et al. [90] also stated an increase of ionic conductivity upon addition of γLiAlO_2 fillers to PEO based electrolytes with LiBF_4 and LiCF_3SO_3 salts. The introduction of LiN_2O_3 to poly(ethylene oxide)-grafted polymethacrylates with the lithium salts LiCl_4 and LiCF_3SO_3 was investigated by MORITA et al. They showed enhanced ionic conductivity and mobility when these fillers were added to the system [91].

(iii) Other fillers: Different fillers have been studied for composite polymer electrolytes. For example, the use of cellulose was suggested as a reinforcing agent to enhance mechanical strength of the electrolyte. SAMIR et al. [92] investigated cellulosic whiskers in a PEO/LiTFSI system and indeed found a reinforcing effect while ionic conductivity was retained. Furthermore, carbon based materials as fillers were investigated to increase conductivity and interfacial stability. In fact, APPETECCHI et al. [93] were the first to propose the use of carbon powders as filler materials in polymer electrolytes. IBRAHIM et al. [94, 95] studied carbon nanotubes in PEO/LiPF₆ system plasticized with EC and stated a rise in ionic conductivity.

2.2.7 Fabrication

The literature suggests different fabrication methods for the polymer electrolyte. Although exact conditions and procedures are varying, the approaches can generally be separated to a solvent-based and solvent-free method. In both approaches, all solid components used in the fabrication process of the electrolyte are dried for a sufficient amount of time at an elevated temperature beforehand. Also, the steps are primarily carried out in a dry argon or nitrogen environment to avoid moisture contamination. If processing in open air is required, the materials are placed in a sealed envelope before bringing them out of the dry box.

Solvent-based method

The solvent-based approach is the traditional method for fabricating the polymer electrolyte. In this process, the LiTFSI and PEO are dissolved in a suitable solvent under magnetic stirring. Most common solvents are acetone, acetonitrile, tetrahydrofuran (THF) or methanol. Typically, the dissolution of the two components is done separately and the solutions are mixed together. To ensure salt complexation in the polymer host, the stirring process is done for up to 24 hours. During this step, possible additives are inserted [25, 33, 96, 97, 98]. The downstream processing of the resulting clear and viscous mixture differs in the literature. In most cases it is poured into a high surface area cavity, usually a Petri dish or PTFE-mold. Here, the film formation takes place by slow evaporation of the solvent. This step is often accelerated by pulling vacuum or raising the temperature to up to 120 °C. To ensure complete solvent evaporation, the drying is done for up to one week [25, 33, 96, 97]. In other procedures, the mixture is heated to evaporate the solvent and then hot pressed at 90 °C, leaving behind the polymer electrolyte film [98].

Solvent-free method

This method presents an alternative to fabricate the polymer electrolyte without the use of any solvent. In its original proposal by GRAY et al. [99], dry powders of the polymer, complexing salt and possible additives are physically mixed by ball milling. The homogeneous powder is then heated slightly over the melting temperature of the polymer under continuous mixing to ensure salt complexation. The soft and sticky mixture is then placed between Mylar sheets and hot pressed at elevated temperatures and pressures: First, 5 mm pellets are obtained by hot pressing at a temperature between 70 °C and 110 °C. After the cooling of the pellets, the second step is performed. Here, a pressure of 19 MPa is applied at

room temperature, followed by hot pressing at 7.6 MPa and 70 °C to 110 °C. According to GRAY et al, the procedure results in homogeneous, 150-300 μm thick polymer electrolyte films [25, 99].

This hot pressing method was adopted by many research groups with slight modifications in the procedure and conditions of the individual fabrication steps: After mixing the powders in a mortar instead of a ball mill for two minutes, CAPIGLIA et al. pressed the powder mixture overnight at 80 °C with a hot press, skipping the heating step beforehand [100]. APPETECCHI et al. cooled the polymer electrolyte films in liquid nitrogen after pressing them at 110 °C with a pressure of 820 N/cm⁻² for 10 min and 1640 N/cm⁻² for further 15 min. Finally they dried the films at 55 °C under vacuum for 48 h [90, 101]. SHIN et al. mixed the powders in a mortar and then vacuum sealed the resulting homogeneous mixture in an aluminum bag. After annealing overnight at 90 °C, the electrolyte films were produced by pressing them at 110 °C for 20 min [102]. The fabrication procedure performed by PORCARELLI et al. represents a faster method compared to the one originally proposed, which consists of grinding the powders at 70 °C for several minutes before hot pressing them at 90 °C for 15 minutes [103].

Several advantages of this new approach over the solvent-based method have been stated: It is a faster procedure compared to the traditional approach. As no solvent is used, this method ensures a complete solid state of the electrolyte film. Enhanced mechanical properties for the solvent-free fabricated polymer electrolytes have been obtained in comparison to the solvent-based method. Furthermore, a higher conductivity of the electrolyte films has been observed when fabricated with this hot pressing technique [25, 99].

2.3 Electrode Materials

This chapter reviews the most frequently used electrode materials in LIBs. After the basic structure of the composite electrodes is introduced in the beginning, an overview of the conventional anode and cathode active materials is given. Here, a specific focus is attributed to lithium titanate (LTO) and lithium iron phosphate (LFP), which represent the electrode materials in this work.

2.3.1 Basic Structure

A schematic structure of the composite electrodes in LIBs is shown in Figure 2.8:

Figure 2.8: Schematic structure of the composite electrodes in LIBs adapted from [15]

In general, the electrode's coating is based on a mixture of active material, binder and conductive fillers. With mass fractions around 90 wt%, the active material forms the major part in this composition. They determine the capacity and potential of anode and cathode. The binder is needed for a good cohesion between the electrode particles and sufficient adhesion to the current collector (metal foil). Classical representatives are polymers such as polyvinylidene fluoride (PVDF) or

styrene butadiene rubber (SBR). Since electrons have to be transported through the electrode structures for the redox reactions to occur, conductive fillers are inserted to enhance the electrical properties of anode and cathode. Carbon black is the most popular representative of this group. The amount of these inactive additives in the electrodes depends on the energy- and power requirements of the battery. Generally, a high power design utilizes a high proportion of binder and carbon black, whereas for high energy applications the active material proportion is maximized. The electrode coating is placed on thin metal foils, the current collectors. Typically, aluminum is used for the cathode side due to good electrical conductivity, low cost and weight, as well as sufficient electrochemical stability in the potential range of the cathode. For the lower potential anode, aluminum would form lithium alloys, which is why copper is generally used on this side as an alternative [15].

2.3.2 Anode Active Materials

Pure lithium metal was originally investigated as an anode material for LIBs. It exhibits the highest specific capacity (3861 mAh/g) and best standard potential of all proposed alternatives so far. However, metallic lithium proved to be hazardous for rechargeable batteries as it leads to dendrite formation on the anode's surface during charging, increasing the risk of internal short circuiting, subsequent thermal run-away and explosion. Major efforts have been undertaken to enable the use of lithium metal in rechargeable batteries. For example, solid electrolytes might provide a possible solution to prevent the safety risks since their great mechanical robustness can suppress the formation of lithium dendrites. In spite of that, the use of lithium metal as the anode's active material is still restricted to primary (non-rechargeable) LIBs at the present state. In the following section, an overview of the most popular alternatives is given first. Special focus is then attributed to lithium titanate, which represents the anode active material in this work [104].

2.3.2.1 Overview

An overview of the most studied anode active materials including their characteristic capacities and potentials is shown in Figure 2.9:

Figure 2.9: Potential as a function of gravimetric capacity for popular anode active materials [105]

In general, they can be categorized based on their reaction mechanism into intercalation, alloy or conversion materials.

- (i) **Intercalation materials:** Intercalation describes the reversible insertion of molecules or ions into interstitial vacancies of the parent material. In this process, no covalent bonds are formed or broken [106]. The most popular intercalation hosts are carbon based. Commercially, graphite is the most frequently deployed anode material due to a great combination of properties: Graphite provides a high standard potential that is close to lithium metal (0.125 V vs Li/Li⁺). It shows good mechanical, thermal, chemical and electrochemical stability, resulting in better safety when compared to lithium metal. A favorable reversibility of the intercalation reactions results in moderate cycling stability. Also, it shows high lithium diffusivity and electrical conductivity, as well as acceptable volume changes during lithiation/delithiation.

Finally, the easy availability implies low-cost and consequently makes it very attractive from a commercial standpoint [104, 105]. The most striking disadvantage of graphite is its limited capacity of 372 mAh/g. Other carbon based materials are currently being investigated to improve the specific energy. These include “hard” carbons with a random alignment of small crystallites such as carbon nanotubes, carbon fibers, porous carbon, or graphene [107]. Another popular group of intercalation materials are titanium based oxides, which show favorable properties for high safety applications. A typical representative of this group is lithium titanate, which is extensively studied in Section 2.3.2.2 [106].

(ii) Alloy materials: Alloys describe the combination of metals with the characteristic metal bonding. In LIBs, alloy anode materials build compound phases with lithium. The great advantage of this group is the enormous specific capacity, theoretically resulting in a breakthrough regarding the specific energy of LIBs. However, all alloy materials share the same major drawback: a colossal volumetric expansion of the material upon lithiation. This leads to high mechanical stress on the active material particles, resulting in particle self-pulverization and thus, loss of electrical contact. Moreover, this triggers damage to the solid electrolyte interphase (SEI) on the anode’s surface (for an explanation on the SEI formation, see section 2.4.1) and thus a high irreversible capacity loss in the first cycles. For example, the most investigated representative of the alloy anode materials is silicon, which provides a high theoretical specific capacity of 4200 mAh/g, but a volume expansion of over 400 %. Other alloy materials such as germanium or tin oxide exhibit a similar behavior. Different strategies have been proposed to circumvent the described difficulties. One of the most popular approaches is alloying composites with

active or inactive materials. In this case, the inactive/active materials serve as a buffer that provides free volume for the expansion of the active material particles. Highly investigated representatives of this group are carbon-silicon composites. Second, it is proposed to reduce the active material particle size from micro- to nanoscale. This would induce more homogeneous lithiation/delithiation and minimize differential expansion, thus reduce particle pulverization. Other strategies attempt to stabilize the SEI by encapsulating the alloying material particles using electrolyte additives or inserting binders into the electrodes, which increase the mechanical stability [104, 105].

(iii) Conversion materials: Conversion anode materials are characterized by an exchange reaction during lithiation/delithiation. The reduction/oxidation of a transition metal M in a transition metal compound M_xN_y ($M=\text{Fe, Co, Cu, Mn, Ni}$; and $N=\text{O, P, S, N}$) is accompanied by the composition/decomposition of a lithium compound Li_zN_y [106]:

Classical representatives include iron oxides, cobalt oxides and metal phosphides, sulphides and nitrides. The advantages of such materials can be summarized with high theoretical capacities, environmental abundance, and low material costs. However, similar to the alloy anode materials, they suffer from large volumetric expansions, resulting in poor capacity retention. The additional large potential hysteresis keeps this group from penetrating the commercial market at the present state [105].

2.3.2.2 Lithium Titanate

Lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$), also referred to as lithium titanium oxide and abbreviated as LTO, has emerged as a promising anode active material. This spinel

structured material belongs to the group of intercalation anode materials. Based on the underlying redox couple $\text{Ti}^{3+}/\text{Ti}^{4+}$, LTO exhibits a working potential of 1.55 V vs. Li/Li^+ . When charged/discharged in the potential range of 1 to 3 V, the electrochemical reaction can be expressed as

which results in a theoretical specific capacity of 175 mAh/g [108].

The advantages of this material can be summarized as the following: The non-toxicity and high operating potential of LTO results in favorable safety characteristics. Also, the anode’s operating potential is above the SEI formation potential caused by electrolyte reduction of the anode’s surface, minimizing continued electrolyte decomposition. Yet it should be noted that a complete absence of an SEI is not experimentally verified at the present state. This is due to the possibility that oxidation products from the cathode can migrate to and deposit on the anode surface. Nevertheless, the irreversible capacity loss due to electrolyte decomposition in the first cycles is tremendously reduced. Furthermore, LTO exhibits a negligible volume change upon lithiation/delithiation, resulting in an excellent cycling stability of this material. The constant particle volume minimizes mechanical strain (LTO is also called “zero-strain material”) of the active material and the SEI, leading to less particle fraction and SEI self-pulverization. In addition to these favorable electrochemical properties, the elements of LTO show a relative environmental abundance, resulting in low material costs and enabling commercialization [106, 109].

The favorable safety and stability of this material due to the high operating potential is contrasted by low power- and energy densities. Further difficulties

that have to be surmounted are a low electrical conductivity ($\sim 10^{-8}$ to 10^{-13} S/cm) and poor lithium-ion diffusivity ($\sim 10^{-8}$ to 10^{-13} cm²/s), limiting the charge/discharge rate performance. Different strategies have been proposed to overcome these drawbacks, including anion or cation doping, surface modification with conductive coatings and nanostructuring [109, 110].

One attempt to illustrate the unique cubic spinel structure of LTO in the form $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is shown in Figure 2.10(a). The oxygen atoms arrange approximately as a cubic closed packing (ccp), located at the 32e Wyckoff-position. Lithium-ions sit in the tetrahedral 8a sites of the lattice, whereas the first half of the octahedral 16d sites are randomly occupied by $1/6$ Li^+ and $5/6$ Ti^{4+} . The second half of the octahedral 16c sites remain empty though play a fundamental role during lithium intercalation [110].

Figure 2.10: Schematic LTO lattice structure and illustrated lithium insertion/extraction mechanism [110]

When the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ structure is lithiated to $\text{Li}_7\text{Ti}_5\text{O}_{12}$, it is believed that the additional lithium-ions occupy the 16c octahedral sites. Driven by electrical

repulsion, the same number of Li^+ present on the tetrahedral $8a$ sites simultaneously hop to the octahedral $16c$ sites. Thus, the total number of lithium-ions that can be inserted equals half of the empty $16c$ octahedral sites. This results in the rock-salt phase of $\text{Li}_7\text{Ti}_5\text{O}_{12}$ once all $8a$ sites are empty and all $16c$ sites are occupied. The insertion/extraction mechanism is illustrated in Figure 2.10(b). Remarkably, the lattice parameter remains nearly constant during lithium intercalation, which is attributed to the similar size of the lithium-ions to the $8a$ and $16c$ intercalation sites. In fact, the lattice parameters only change from $a = 8.3595 \text{ \AA}$ to $a = 8.3538 \text{ \AA}$ upon lithiation, which is equivalent to a negligible volumetric contraction of only 0.2% [108, 110].

2.3.3 Cathode Active Materials

For conventional LIBs, the cathode represents the most expensive and highest weight component, justifying extensive research on next-generation cathode materials in the past years. A broad overview of these is given in the first part of this section, followed by a more detailed characterization of lithium iron phosphate as the cathode material utilized in this work.

2.3.3.1 Overview

An overview of the currently most investigated cathode materials is shown in Figure 2.11, comparing their characteristic potential range and gravimetric capacity. The commercialized and most frequently investigated next-generation cathode materials belong to the group of intercalation materials. Here, classical representatives can be categorized into layered, spinel and olivine structures, however new intercalation compounds have been proposed in the past years. Recently, conversion cathode materials have attracted attention.

Figure 2.11: Potential as a function of gravimetric capacity for popular cathode active materials [105]

(i) **Layered compounds:** Layered structured cathode materials with the chemical formula LiMO_2 ($\text{M} = \text{Co}, \text{Mn}, \text{Ni}$) represent the most commercialized group for conventional LIBs. Their schematic lattice structure is illustrated in Figure 2.12(a): The oxygen atoms build a ccp lattice structure, hosting the transition metal and lithium cations in the octahedral lattice sites. The lithium/transition metal ratio for this group is unity or less. In 1980, LiCoO_2 (abbreviated LCO) was proposed as the first cathode material, and it has been widely used in portable electronics ever since. However, high cost due to limited cobalt resources, toxicity, safety concerns and low specific capacity made other cathode materials necessary. Alternatives include the partial or full replacement of the toxic and rare cobalt with manganese and nickel, resulting in various representatives of the so-called NMC (or NCM) cathode materials with the structural formula $\text{LiCo}_x\text{Mn}_y\text{Ni}_{1-x-y}\text{O}_2$. This research is motivated by idealized combination of the high capacity of LiNiO_2 , stable crystal structure of LiCoO_2 , and good environmental compatibility and safety of LiMnO_2 . However, the introduction of nickel induces the partial

Figure 2.12: Schematic lattice structure of classical cathode materials [111]

blocking of lithium-ion diffusion paths by the nickel atoms, limiting rate capability [111, 112].

- (ii) **Spinel compounds:** The lattice structure of the spinel group with the chemical formula LiM_2O_4 is illustrated in Figure 2.12(b). Similarly to the layered structure, the oxygen atoms build a ccp lattice while the transition metal and lithium ions occupy the octahedral crystal sites. However, in contrast to the former, $1/4$ of the M-cations are located in the lithium-ion layer, leaving $1/4$ of the sites in the transition metal layer empty. This results in a three-dimensional framework of MO_2 , providing three-dimensional lithium-ion diffusion paths. One of the classical representatives of the spinel group is LiMn_2O_4 (abbreviated LMO), which exhibits excellent rate capability, high safety, environmental compatibility, low cost, high operating potential and thus, good specific energy. Unfortunately, due to dissolution of Mn^{2+} -ions into the electrolyte and phase transformations during cycling, severe capacity fading is observed especially at higher temperatures. Strategies to prevent this mainly involve the doping of these materials with various metal ions. Extensive research has led to considerable improvements of their cycling performance. Currently, the main disadvantages of this group include limited

specific capacity as well as electrolyte decomposition in the first cycles due to the high operating potential of this material [111, 113].

(iii) Olivine compounds: The olivine structure of these compounds with the chemical formula LiMXO_4 ($X = \text{S, P, Si, As, Mo, W}$) is illustrated in Figure 2.12(c). The large polyanion XO_4^{3-} increases the redox-potential and stabilizes the lattice of these materials. Of such materials, most popular representative is LiFePO_4 , and its structure, advantages and disadvantages are examined in greater detail in the following Section 2.3.3.2 [104].

(iv) New intercalation compounds: Recently proposed cathode intercalation compounds include silicates (Li_2MSiO_4 , $M = \text{Fe, Mn}$), borates (LiMBO_3 , $M = \text{Fe, Co, Mn}$) and tavorite (LiMPO_4F , $M = \text{Al, Fe, V}$): Silicate compounds have attracted attention because of their potential to extract two lithium-ions per formula unit, leading to a high theoretical specific capacity of 333 mAh/g. Unfortunately, experimentally achieving this proved to be difficult with intrinsically low electrical conductivities remaining unsurmounted. Investigations of borate active materials are motivated due to their lightest polyanion group BO_3 , also resulting in an improved theoretical specific energy. However, their performance is limited at the present state by kinetic polarization and moisture sensitivity. The most striking advantage of the tavorite compounds are their great thermal stability due to the strong oxygen-phosphorus bond. Nevertheless, a poor energy density requires more research for this derivative of the olivine group [104, 113].

(v) Conversion compounds: Conversion or alloying cathode materials are proposed as an high energy density alternative to the intercalation compounds. However, the arising products of the underlying conversion reactions can

change the structure and chemistry of the electrode with the reaction mechanisms often remaining unknown [114]. Classical representatives of this group include fluorine and chlorine compounds, sulfur and lithium sulfide, selenium and tellurium, as well as iodine [104].

2.3.3.2 Lithium Iron Phosphate

Lithium iron phosphate, with the chemical formula LiFePO_4 and abbreviated as LFP, attracted attention as a possible next-generation cathode material for power tools, electric vehicles and stationary energy storage. It belongs to the group of olivine structured cathode materials and provides an OCV of 3.4 V vs. Li/Li^+ . Based on the redox couple $\text{Fe}^{2+}/\text{Fe}^{3+}$, the electrochemical insertion/extraction reaction is expressed as

which results in a specific capacity of 170 mAh/g.

Research in LFP is motivated by several advantages: It provides a characteristic flat discharge curve and great cycling performance due to good reversibility of the insertion/extraction reaction. The olivine structure benefits from higher safety compared to LCO and thermal stability up to 400 °C. Relative abundance of its elements results in low material costs which make it attractive for commercialization. Furthermore, the non-toxicity and environmental compatibility of LFP results in a 'green' alternative to other cathode chemistries [115].

Major limitations include the low electrical conductivity ($\sim 10^{-9}$ to 10^{-11} S/cm) and lithium-ion diffusivity coefficient ($\sim 10^{-11}$ to 10^{-13} cm^2/s), resulting in poor rate performance. Different strategies were proposed to surmount these drawbacks,

such as conductive material coatings, decreasing the LFP particle size or doping LFP with cations to improve intrinsic conductivity [116]. Another disadvantage is the low tap density of LFP: nanosized LiFePO_4 shows a tap density of $0.6 - 1 \text{ g/cm}^3$, which is much less compared to 2.6 g/cm^3 for commercial LCO. In spite of the reasonable gravimetric capacity, this reduces the volumetric energy density, increasing cell size. In order to overcome this disadvantage, new synthesis methods are proposed to control morphology and improve homogeneity of the LFP particles [115].

The complex olivine structure of LFP is illustrated in Figure 2.12(c). The oxygen-anions build an hexagonal close packed (hcp) framework. Half of the octahedral sites are occupied by iron-ions, and one sixth by lithium-ions. Since the oxygen-atoms are bonded to iron- and lithium-ions (LiO_6 is edge-shared and FeO_6 is corner-shared), this results in a highly stable crystal structure [111]. Upon charging/discharging, the lattice parameters change from $a = 10.33 \text{ \AA}$, $b = 6.01 \text{ \AA}$ and $c = 4.69 \text{ \AA}$ in the completely lithiated state ($V = 291.3 \text{ \AA}^3$) to $a = 9.81 \text{ \AA}$, $b = 5.79 \text{ \AA}$ and $c = 4.78 \text{ \AA}$ ($V = 271.5 \text{ \AA}^3$) in the fully delithiated state. This is equivalent to a volume contraction of 6.77 % [115].

2.4 Electrode/Electrolyte Interface

It is generally accepted that the performance of lithium-ion batteries is not only dependent on the electrode and electrolyte, but also on the properties of the electrode/electrolyte interface. Besides the limited ionic conductivity of the polymer electrolyte, high interfacial resistance is known to be one of the two major drawbacks in ASLIBs. This is due to various reasons: Most important, the active surface area at the interface is much less compared to conventional cells, where the liquid electrolyte soaks into the pores of the electrodes and provides enhanced active material contact. This is not the case for a solid electrolyte, which greatly increases the interfacial resistance. Furthermore, since the interface is between two solids, electrode volumetric changes during lithiation and delithiation cycles lead to increased damage to this area [14]. In spite of the fact that polymer electrolytes exhibit a much higher electrochemical stability window compared to liquid electrolytes, a surface layer formation was also observed for ASLIBs. This surface layer can substantially increase the interfacial resistance. In the following section, the understanding of the surface layer formation in polymer electrolyte based ASLIBs is described. Based on this, different attempts for decreasing resistance at the electrode/electrolyte interface are presented.

2.4.1 Surface Layer Formation

In liquid electrolyte cells, a so-called solid electrolyte interphase (SEI) forms during the first charge/discharge cycles on the surface of the negative electrode. This is due to the mismatch of the anode's electrochemical potential and the electrochemical stability window of the liquid electrolyte. As a consequence, the electrolyte is reduced when in contact with the active material of the anode, inducing its decomposition. Finally, this results in the deposition of the reduction

products on the electrode's surface and formation of the SEI, which schematic structure is shown in Figure 2.13:

Figure 2.13: SEI formation on the anode's surface in liquid electrolyte cells [117]

The evolution of this thin and solid layer can be observed by an irreversible capacity loss in the first cycles of the battery. It is well known today that a good and controlled formation of the SEI is of major importance for the cell's performance. The film is insulating to electrons, but permeable to lithium-ions. Therefore, the layer shows properties of a solid electrolyte, hence the name. Furthermore, these properties allow for spatial separation of the electrons and lithium ions in the anode, which is crucial for the operating principle of the battery. In addition to that, the SEI prohibits physical contact between the electrode and electrolyte, preventing ongoing electrolyte decomposition and protecting the electrode from exfoliation. Due to the importance of this layer in the battery's performance, a tremendous amount of research on the SEI has been carried out. Overall, this led to a decent understanding of the layer's composition and formation mechanism [118, 6].

Compared to liquid electrolyte cells, the interfacial chemistry in ASLIBs has been explored much less. This might be due to a theorized higher chemical

and electrochemical stability of the polymer electrolyte. In addition, the film is ideally well attached to the electrode, making investigations of the interface between the two solid layers more difficult. Nevertheless, the presence of an interfacial resistance has been observed after cell assembly based on electrochemical impedance spectroscopy (EIS). Several studies attributed this to the formation of a passivation film on the surface of the electrodes: In 1984, FAUTEX [119, 120] described the formation of an ionically conducting passivation film between a lithium electrode and a PEO/LiCF₃SO₃ electrolyte, stating that this film would act as a solid electrolyte interphase similar to liquid electrolyte systems. They supported their results with EIS studies, in which they attributed the higher frequency semicircle in the impedance data to the electrolyte resistance R_e and the lower frequency circle to the interface resistance R_i , as shown in Figure 2.14 (a).

Figure 2.14: Impedance diagrams for an Li-PEO/LiCF₃SO₃-Li system with electrolyte resistance (R_e) and interface resistance (R_i) [119]

As expected, both arcs decreased with temperature. However, the time dependency differed, as shown in Figure 2.14 (b): a slight reduction of the high frequency arc was observed after cell assembly, which was attributed to a small creepage of the polymer electrolyte film leading to a decrease of its bulk resistance. In contrast, the low frequency semicircle greatly increased with

time. This evolution of interfacial resistance would indicate the growth of an ionically conducting surface film at open-circuit conditions. Subsequent investigations [121, 122] similarly described the development of a resistive layer on the anode.

Attempts at characterizing the film formation mechanism and composition followed. However, it is worth noting that both are still not well understood yet. Besides, the surface layer is highly influenced by the processing conditions and specific chemistry of the investigated system. Most of the research has concentrated on the interface between a lithium anode and PEO-based electrolyte, while literature on the formation of a passivation layer on other electrode materials is rare [86]. Thus, the following explanations have to be taken within this in mind.

PELED et al. [123] suggested that the layer builds due to reaction of lithium with water, salt anions and other impurities. They proposed a schematic of the Li/PE interface, which is shown in Figure 2.15(a).

Figure 2.15: Schematic illustration of the Li/PE interface and composition of the passivation layer [123]

Because of the rough surface of the stiff polymer electrolyte film, voids are generated between the anode and electrolyte. The passivating film would form at the interface where the polymer electrolyte is contacting the native oxide layer, or when polymer electrolyte spikes penetrate to the metallic lithium. Aside from that, they described the surface layer to be a heterogeneous film consisting of a mosaic of individual particles, as shown in Figure 2.15(b). The exact composition depends on the specific chemistry of the cell, including the utilized polymer host, salt, present impurities and possible additives. LE GRANVALET-MANCINI et al. [124] investigated the formation of a passivation layer at the interface of a lithium anode and PEO-lithium triflate electrolyte with atomic force microscopy (AFM) and EIS. Based on their results, they stated that the layer composed of crystallites and noted the presence of CF_3 radicals and Li-O-R compounds. The radicals would induce chain scission of the polymer host. Furthermore, low conductivity of the passivating films was concluded. ISMAIL et al. [125] analyzed the composition of the passivation layer at the interface of a lithium electrode and PEO-based electrolyte with LiTFSI or LiBF_4 as the salt. Based on X-ray photoelectron spectroscopy results, they stated that LiF was formed due to reaction of lithium with impurities in the electrolyte and the native oxide layer. In addition to that, the system with LiTFSI led to thin and low porosity surface films, whereas the passivation layer in the cell with the PEO/ LiBF_4 electrolyte was thicker and highly porous. Using XPS measurements, XU et al. characterized the electrode/electrolyte interfaces in Li/graphite half-cells with PEO/LiTFSI polymer electrolytes and compared the passivation films with the respective SEI in liquid electrolyte systems. After showing that the PEO based electrolyte contains several ppm of water, their results ended in the schematic illustration of the investigated interfaces shown in Figure 2.16.

Figure 2.16: Schematic illustration of the Li/PE interface and composition of the passivation layer in a polymer and liquid electrolyte cell [123]

For the graphite/PE interface, a high formation of LiOH was observed, which was assigned to reactions of water with lithium ions. Besides that, they found LiTFSI decomposition on the graphite surface. The newly developed species at the Li/PE interface were mainly based on lithium fluorides and lithium alkoxides. In contrast, the SEI of respective liquid electrolyte system was based on decomposition products of the electrolyte such as carbonate species or PEO-type polymer.

2.4.2 Reduction of the Interfacial Resistance

Different attempts for decreasing the interfacial resistance have been proposed. One of the most popular is the introduction of filler particles into the polymer electrolyte. The resulting composite polymer electrolyte was introduced in Section 2.2.6, and the enhancing effect of filler particles on the ionic conductivity was explained. Besides improving electrical properties of the bulk electrolyte, fillers were investigated to decrease interfacial resistance. For example, Figure 2.17(a) shows the effect of BaTiO₃, TiO₂ and Al₂O₃ particles in a PEO/LiTFSI electrolyte

on the developing interfacial resistance in a Li-PE-Li cell after assembly:

Figure 2.17: Effect of filler particles on the interfacial resistance of a PEO/LiTFSI polymer electrolyte and Li anode at 80 °C [126]

The introduction of all three fillers leads to a significant reduction of the interfacial resistance. The best results are obtained for the BaTiO₃ filler while a more detailed study of the effect of these particles for different sizes (0.1 μm and 0.5 μm) and weight percentages (1.5 wt%, 10 wt% and 15 wt%) is shown in Figure 2.17(b). This study illustrates that an introduction of only 1.5 wt% of 0.1 μm sized BaTiO₃ particles can reduce the interfacial resistance to around 15 % compared to the filler-free system. As stated previously, surface film formation is believed to be induced by reactions of lithium with water and other impurities. It is assumed that filler particles might absorb the water, therefore suppressing the reactions between lithium and the water. This would result in a stabilizing effect of the interface [126]. Many other studies show the positive effect of various fillers on the interfacial resistance for various electrode/polymer electrolyte chemistries [83, 90, 127, 128].

A further attempt to inhibit surface layer formation was proposed by MASONA et al. They placed a self-assembling monolayer (SAM) of copolymer

molecules with the formula $\text{H}(-\text{CH}_2)_{32}(-\text{CH}_2\text{CH}_2\text{O}-)_{10}\text{H}$ onto the surface of the polymer electrolyte films. The PEO like head of the molecules would absorb into the polymer system, leaving the nonpolar tail for self-assembling. This SAM surface structure, which is illustrated in Figure 2.18(a), was confirmed with FTIR spectroscopy. Investigating the interfacial resistance development with EIS, they found a much slower formation of the passivation layer compared to untreated polymer electrolytes as shown in Figure 2.18(b). It is suggested that the hydrocarbon tails "hide" the lithium anode from water or other impurities in the electrolyte and therefore hinder surface layer formation [129].

Figure 2.18: Self-assembled monolayer (SAM) on the polymer electrolyte to inhibit passivation at the Li/electrolyte interface [129]

Besides inhibiting a surface layer formation, increasing the contact between the electrode's active material particles and the polymer electrolyte would reduce the interfacial resistance. In order to do this, temperature and pressure can be tuned. However, this is limited by the mechanical properties of the polymer electrolyte and the application environment. To increase the specific surface area between the solid electrolyte and the electrodes, thin films of the respective electrodes are used. Nevertheless, charge transport to deep active material particles remains one of the major challenges in the field of ASLIBs [130].

2.5 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy, also called AC Impedance Spectroscopy and abbreviated EIS, is an analytical characterization tool for electrochemical systems. It represents a non-destructive method to analyze electrochemical processes in batteries and is the most popular instrument for measuring ionic conductivity in polymer electrolytes [6].

Figure 2.19 illustrates the operating principle of EIS. In general, the investigated system is excited by a sinusoidal current (galvanostatic EIS) or voltage (potentiostatic EIS), causing a respective sinusoidal voltage or current response. EIS assumes linearity of the investigated system. In the case of batteries, the characteristic non-linear current-voltage curve is therefore linearized by only applying a small excitation amplitude. Thus, this pseudo-linear system responds with a current/voltage of the same frequency but different amplitude and phase shift. By measuring both and evaluating the data with a fast FOURIER transform (FFT), the system's impedance (compare Section 2.1.3) can be calculated. This process is

Figure 2.19: Pseudo-linearity and operating principle of EIS

repeated for many different excitation frequencies, resulting in an impedance curve, which is typically presented in the form of a NYQUIST-plot [132, 131].

This NYQUIST-plot represents the basis for the subsequent data analysis. In general, an equivalent-circuit model (ECM) can be built to fit the obtained impedance spectra. In doing so, the investigated system is modeled with a combination of electrical elements, such as resistors, capacitors and inductors. These are then assigned to electrochemical processes in the system and used to interpret the experimental data [133].

Figure 2.20(a) illustrates an example of an ECM and the respective impedance curve for an ASLIB consisting of two lithium-metal electrodes and a PEO/LiTFSI polymer electrolyte proposed by BOUCHET et al. [134].

Figure 2.20: Nyquist-Plot and ECM for (a) a symmetric ASLIB consisting of a polymer electrolyte (PE) sandwiched between two lithium metal electrodes and (b) a polymer electrolyte (PE) sandwiched between two ideal blocking electrodes (IBE)

The ECM for the Li/PE/Li cell starts with an inductor and resistor to describe electrical connections of the system, followed by a series of four different sections which are related to single cell components or electrochemical processes: Section (I) represents the bulk electrolyte and is modeled with a parallel connection of an ohmic resistance R_b and capacitance C_b . This combination results in the characteristic high frequency arc of the impedance curve. The second arc in the NYQUIST-plot in Section (II) is assigned to a passive layer forming on the lithium metal electrodes. It is described by a parallel connection of an ohmic resistance (R_i), combined with a constant phase element (CPE_i) instead of a pure capacitance due to the slightly depressed form of the semicircle. At medium frequencies in Section (III), another small impedance is observed in the experimental data, again modeled with the parallel connection of an ohmic resistance R_e and a constant phase element CPE_e . However, this impedance behavior is stated to not be reproducible and thus makes electrochemical interpretation difficult. Finally, Section (IV) is related to the transport of charged particles, described with a typical WARBURG-element [134].

Besides the electrochemical analysis of batteries, EIS is also most commonly used instrumentation for measuring ionic conductivity of polymer electrolytes. Here, the thin polymer/salt films are contacted by two blocking electrodes, usually made of stainless steel. Ideal blocking electrodes (IBE) exhibit the behavior of ideal capacitors, thus no electron-transfer reactions take place. The simplest ECM for such an IBE/PE/IBE setup is shown in Figure 2.20(b). The electrical double layer at the electrode/electrolyte interface is represented with a capacitor C_{DL} while the bulk electrolyte is modeled with a parallel connection of an ohmic resistance R_b and capacitance C_b . In reality, a power-law frequency dependence has been observed for the double layers in solid electrolyte systems instead of a pure capacitance.

Thus, the capacitors in the ECM are often replaced by constant phase elements. Furthermore, non-ideal behavior of the blocking electrodes due to partial charge adsorption can take place at the electrode/electrolyte interface. Cations in the electrolyte can be neutralized by electrons in the electrode. This results in a further complication of the ECM. MARZANTOWICZ et al. [135] stated different ECMs for electrolyte cells depending on the measuring temperature and polymer/salt ratio. In general, it is convention to take the lower frequency minimum in the impedance curve as the bulk electrolyte resistance. From this, the electrolyte's ionic conductivity can be calculated by knowing the electrode/electrolyte contact area A and polymer electrolyte thickness t (see Equation 3.1) [135, 136].

CHAPTER 3

Manufacturing the Polymer Electrolyte

3.1 Introduction

The polymer electrolyte is the major component differentiating ASLIBs from conventional liquid electrolyte cells. The extent of optimization regarding its electrical and mechanical properties will influence how much ASLIBs can penetrate the battery market: The polymer electrolyte exhibits a lower ionic conductivity compared to conventional electrolytes, hindering high power applications. Additionally, mechanical properties of the polymer/salt complex determine the functionality of the ASLIB. It has to be robust enough to avoid physical contact between the electrodes, prevent hazardous dendrite growth on the anode's surface and remain structurally stable during processing and cell assembly. On the other hand, good contact at the electrode/electrolyte interface requires a soft electrolyte layer, leading to a difficult problem to solve.

The objective of this chapter is to implement a suitable fabrication procedure for the polymer electrolyte, and optimize its electrical and mechanical properties afterwards. In order to do that, electrochemical impedance spectroscopy is used to compare the ionic conductivity of the electrolyte films. Different fabrication procedures are investigated, and the most promising one is chosen for the preparation of the LTO/LFP cells. The salt concentration in the two component polymer-salt system is optimized to obtain the best combination of processability, interface wettability and ionic conductivity. The chapter ends with the testing of nanosized BaTiO₃ filler particles as a possible additive for this specific PEO/LiTFSI chemistry.

3.2 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is the standard for measuring ionic conductivity in solid electrolytes. To obtain reproducible results, this section introduces a consistent way of measuring ionic conductivity by testing different setups and excitation amplitudes at several measurement temperatures.

3.2.1 Experimental

Figure 3.2 shows the two investigated setups. In setup A, the circular polymer electrolyte coin is sandwiched between two stainless steel electrodes, which are then contacted to the potentiostat for the EIS measurements. Setup B additionally envelopes the electrodes and polymer electrolyte with a coin cell covering that consists of a stainless steel top and bottom held together by an electrically isolating gasket.

Figure 3.1: Investigated setups for measuring the ionic conductivity in polymer electrolyte films with electrochemical impedance spectroscopy

The ionic conductivity σ of the polymer electrolyte can be calculated from the bulk electrolyte's resistance R_b , the film's thickness t_e and the electrode/electrolyte contact area A :

$$\sigma = \frac{t_e}{R_b A} \quad (3.1)$$

The bulk electrolyte resistance R_b is represented by the lower frequency minimum in the Nyquist plot of the cell's impedance curve and is therefore determined by EIS. For the two shown setups, the thickness of the polymer electrolyte is evaluated by measuring the thickness of the single stainless steel parts (electrodes and/or covering), and subtracting them from the setup's total thickness, which is taken before each EIS measurement. The thickness of the stainless steel parts is measured only once at room temperature before each setup is put together, and are assumed to be constant for all subsequent measurements.

Various simplifications have to be noted at this point. First, a thermal expansion of the stainless steel is neglected. With a coefficient of linear thermal expansion for stainless steel in the order of $\alpha_{L,SS} \sim 15 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ [137], a total thickness of all stainless steel parts of around 2 mm and a maximum temperature change in the measurements of 40 $^\circ\text{C}$, the theoretically occurring expansion is in the order of $\sim 1 \text{ } \mu\text{m}$. This is minor compared to the total electrolyte thickness of around 300 μm . Secondly, it is supposed that all layers can be stacked perfectly onto each other, and thus the contact area between the two electrodes and the electrolyte therefore matches their full diameter. Finally, it is assumed that the polymer electrolyte coin is of a uniform thickness.

EIS measurements are performed with a VersaSTAT 3 from PRINCETON APPLIED RESEARCH in the potentiostatic setting, meaning that the polymer electrolyte is excited with an alternating voltage and the current response is measured to evaluate the cell's impedance. A DC voltage of 1 V is applied to reduce any impact of external noise. Excitation amplitudes between 1 mV and 30 mV are tested at 20 $^\circ\text{C}$, 40 $^\circ\text{C}$ and 60 $^\circ\text{C}$ with a frequency range from 1 MHz, which represents the upper limit of the potentiostat, to 2 Hz.

3.2.2 Results

Figure 3.2 shows the impedance curves for the two setups, measured with different excitation amplitudes at 20 °C, 40 °C and 60 °C. As stated, all measurements are performed with a frequency range from 1 MHz to 2 Hz, and the plots are adjusted to show the most important range of the data.

Figure 3.2: EIS results for the two setups at 20, 40 and 60 °C

Several important observations can be made from these plots:

- (1) In both setups, an amplitude of 1 mV leads to scattering of the data, clearly visible in the zig-zag-like impedance curve for the respective measurements at 20 °C (Figure 3.2(a) and (d)). This is due to a bad signal-to-noise ratio: a

low excitation amplitude only induces a small current, which can easily be impacted by external noise.

- (2) Compared to the measurements with small voltage amplitudes, an excitation of 20 mV or 30 mV leads to a drop of the impedance at lower frequencies. This results in the observed variation of impedances from the characteristic 45° straight line at low frequencies for these measurements. The effect is caused by the nonlinearity of the system: EIS assumes linearity by only taking into account the first harmonic frequency response. However, especially at lower frequencies, the system reacts with higher frequency harmonic signals, which fails to satisfy the assumption of pseudo-linearity.
- (3) A frequency shift in the measurements occurs when changing the temperature. This becomes visible with the change of the characteristic lower frequency minimum (indicated with Δ) that is taken as R_b the ionic conductivity calculation. As a consequence, the lower frequency semicircle attributed to the resistance and capacitance of the bulk electrolyte is not visible anymore. This cannot be adjusted by changing the frequency range of the measurements due to the upper limit of the potentiostat of 1 MHz. However, the frequency shift does not impact ionic conductivity measurements, since only the lower frequency minimum of the semicircle is needed for the calculation, and it can still be approximated from these curves.

Ionic conductivity is evaluated for all measurements and summarized in Figure 3.3. For both setups and at all temperatures, the calculated ionic conductivity is negligibly affected by the excitation amplitude. At 20 and 40 °C, differences in the values for the two different setups are insignificant, considering also that two different polymer electrolyte coins were investigated. In contrast to that, a difference in the ionic conductivity with these two setups is observed at 60 °C. This is due to

Figure 3.3: Evaluated ionic conductivity for different setups, excitation amplitudes and temperatures

the melting of the polymer electrolyte. The melting temperature of pure PEO is 65 °C and it decreases when salt is introduced. The melting results in a density and mechanical robustness change of the polymer/salt system. Some flattening was observed for setup A, and in both cases the total setup thickness decreased dramatically. Consequently, the assumptions of a uniform thickness and good contact between electrodes and electrolyte are not fulfilled anymore, leading to the differing of ionic conductivity values for these two setups at this temperature.

3.2.3 Conclusion

To establish a consistent way for measuring the ionic conductivity of the polymer electrolyte, two different setups were tested with several excitation amplitudes and temperatures. A bad signal-to-noise ratio at low excitation amplitudes and nonlinearity of the system at high amplitudes leads to the choice of 10 mV for the subsequent EIS measurements. No significant differences in the results for the two different setups are observed. In both cases, reproducible measurements can only be performed below the melting of the polymer/salt complex, which occurs around 60 °C. Due to simplicity, setup A is chosen for following ionic conductivity measurements.

3.3 Implementation of the Fabrication Method

Figure 3.4 shows some of the difficulties that can occur during the fabrication of the polymer electrolyte. When solvent is evaporated or the polymer/salt system is melted and mixed, bubbles may form and end up in the electrolyte films (Figure 3.4(a)). This not only impacts electrical properties, but also limits reproducibility. In addition, the polymer electrolyte is highly sensitive to the environmental and processing conditions, such as moisture and air contact or processing temperatures. The PEO/LiTFSI mixture is of a hygroscopic nature, thus contact with air during the fabrication can hinder drying of the electrolyte (Figure 3.4(b)). Processing at high temperatures in an oxygen or nitrogen environment can induce overoxidation or thermal degradation of the PEO chains (Figure 3.4(c)).

Figure 3.4: Several difficulties during the fabrication of the polymer electrolyte

The objective of this section is to implement a fabrication method that leads to reproducible results and optimal mechanical and electrical properties of the obtained polymer electrolyte films. As stated in Section 2.2.7, two general approaches have been suggested in the literature, and both are investigated in the following: a classical solvent-based procedure and a solvent-free method. For the latter, an annealing step at a temperature above the melting point of the polymer is often

performed to help salt complexation to the PEO chains. However, this step is time consuming as the polymer electrolyte is typically annealed for no less than 24 hours. Therefore, the actual effect of the annealing step on the electrical properties of the polymer electrolyte is determined by also testing the solvent-free method without the annealing step.

3.3.1 Experimental

The classical solvent-based approach (method A), the completely solvent-free procedure with an annealing step (method B) and without one (method C) are summarized in Figure 3.5.

(a) Method A: Solvent based fabrication

(b) Method B: Solvent free fabrication with annealing

(c) Method C: Solvent free fabrication without annealing

Figure 3.5: Investigated fabrication procedures of the polymer electrolyte

For all methods, PEO with a molecular weight of 10^5 g/mol is supplied from Sigma Aldrich and dried at 50 °C for 24 h under vacuum. Equivalently, LiTFSI is also obtained from Sigma Aldrich and dried with the same procedure but at a temperature of 120 °C. The components are stored and handled in a nitrogen glove box. The polymer and salt are weighted to obtain an ethylene oxide (EO)/ LiTFSI molar ratio of 18:1.

Method A (see Figure 3.5(a)) continues with the separate dissolution of the PEO and LiTFSI in appropriate amounts of tetrahydrofuran (THF). Subsequently, the solutions are poured together and stirred overnight. The cap is removed, so that the solvent can be evaporated slowly to minimize bubble formation. This is carried out by placing the mixture on a heating plate and raising the temperature from room temperature to 70 °C (which is above both, the boiling point of 66 °C for THF and melting temperature of 65 °C for PEO) in ~ 20 °C intervals, resting for at least 2 hours at each step. To get rid of any last traces of solvent and help the salt complexation in the polymer matrix, the polymer/salt blend is annealed in a vacuum oven at 70 °C for 24 hours. The resulting homogenous, quasi-transparent and highly viscous mixture is then placed between two Mylar sheets, sealed in a plastic bag and heat pressed at again 70 °C in a two-step procedure: first, the mixture is warmed up by heat pressing with hand pressure for 1 min; secondly, a pressure of 4 MPa is applied to obtain thin polymer electrolyte films of around 200 to 300 μm , which usually takes around 20 seconds. After the polymer electrolyte has cooled and is brought back into the glovebox, the Mylar sheets can be removed and the polymer electrolyte is punched into circular coins of suitable diameters. To eliminate any remaining traces of oxygen or water contamination, these polymer electrolyte discs are dried in a vacuum oven at room temperature for 24 hours.

The dry fabrication procedures (methods B and C, see Figure 3.5(b) and (c)) start with the careful grinding of the lithium salt to obtain a very fine powder using a mortar and pestle. Subsequently, the polymer powder is added and physically mixed with the salt. This is done by carefully mixing the powders with a spatula rather than grinding with a mortar, as the sticky polymer powder does not allow proper mixing at room temperature when grinded. The mortar is placed on a heating plate and brought up to a temperature of 70 °C under continuous mixing so that the molten polymer dissolves the salt. Method B continues with the additional annealing of the polymer/salt blend at 70 °C for 24 hours in a vacuum oven whereas method C skips this step. Equivalent to the solvent-based method A, the mixture is then hot pressed into thin polymer electrolyte films, subsequently punched into appropriate sizes and then dried at room temperature for 24 hours under vacuum.

EIS is performed on the polymer electrolyte coins with setup A in Figure 3.1(a) from Section 3.2. A stationary voltage of 1 V, frequency range of 1 Mz to 2 Hz and voltage amplitude of 10 mV is used for these measurements. Based on the impedance results, the ionic conductivity can be determined as explained previously. For each fabrication procedure, three polymer electrolyte coins are investigated, and the average, minimum and maximum ionic conductivity are stated.

3.3.2 Results

Figure 3.6 shows the fully processed polymer electrolyte coins which are obtained from the three different fabrication procedures.

Figure 3.6: Obtained polymer electrolyte coins from the three different fabrication procedures

The optical differences of the fabricated polymer electrolytes can be ascribed to the thickness variations of the three coins. The thicker the electrolyte film, the more its color will change from a cloudy to a more saturated white. As it is difficult to produce polymer electrolytes with identical thickness, a distribution in the color is typical. However, the processability in terms of a high mechanical robustness was comparable for all obtained films.

The measured bulk electrolyte resistances obtained from EIS and film thicknesses for the investigated polymer electrolyte coins are shown in Appendix B.1. Figure 3.7 illustrates the evaluated ionic conductivity for the polymer electrolytes obtained from the three fabrication methods.

The diagram reveals the following results:

- (1) For all polymer electrolytes, the conductivity curve shows a nearly linear temperature dependence in the semi-logarithmic diagram, indicating ARRHENIUS-behavior. This corresponds with the expectations from the VTM-model in Equation 2.9: for the evaluated temperature range, the prefactor $T^{-0.5}$ is close to constant, and the VTM-model results in the ARRHENIUS-equation. The ionic conductivity increases with temperature due to the rise in mobility

Figure 3.7: Ionic conductivity for the three fabrication methods at several temperatures. The curves represent the average values and the error bars the obtained minimum and maximum based on measurements of three polymer electrolyte coins per fabrication method.

of both polymer chains and coordinated ions. Consequently, both major conduction mechanisms are increasing, vehicular diffusion and hopping of lithium ions between complexation states (see Section 2.2.4), resulting in the observed conductivity rise.

- (2) The scattering of the measured ionic conductivity values increases with temperature, which can be observed in the larger error bars at higher temperatures. As already stated in Section 3.2, this effect is due to the measuring setup: A higher temperature causes a softer polymer/salt system. Since the electrolyte film is sandwiched between two stainless steel electrodes under slight pressure (compare Figure 3.1(a)), this leads to some electrolyte squeezing out of the sides. Consequently, this induces a deterioration of the electrode/electrolyte contact and a non-uniform thickness. As a result, the variability of the data increases.

- (3) The dry method does not lead to a decrease in ionic conductivity compared to the solvent-based procedure. In fact, the solvent-free method produces a slightly higher ionic conductivity in the polymer electrolyte based on this data. However, this statement has to be taken with some uncertainty due to the high scattering of the conductivity values at high temperatures. Nevertheless, taking into account that the solvent-free method is less complex and more time efficient, it can be concluded that the dry method shows advantages over the solvent-based one.
- (4) The polymer electrolytes that were fabricated with Method B and C only exhibit a negligible difference in the ionic conductivity. Consequently, it can be stated that the annealing step in the dry fabrication method has no substantial effect on the ionic conductivity of the polymer electrolyte. This is an important result, as an additional annealing step would increase processing time and complexity.

3.3.3 Conclusion

Three different fabrication methods were investigated: a solvent-based approach as well as a solvent-free method with and without an annealing step. The ionic conductivity for polymer electrolytes from each fabrication procedure was measured in the temperature range from 20 to 50 °C. The temperature dependence on ionic conductivity matches the expectations from the VTM-model. Furthermore, the less complex and more time efficient solvent-free method does not lead to a decreased ionic conductivity compared to the solvent-based procedure. In addition to that, results show no major differences when the polymer electrolyte is annealed. As a consequence, the dry method without the annealing step is chosen for the subsequent processing of the polymer electrolyte.

3.4 Optimization of the Salt Concentration

This section seeks to find the best salt concentration for the two component PEO/LiTFSI mixture. This is not only important to maximize the ionic conductivity of the system, but also to optimize the mechanical properties of the thin electrolyte films: they have to be mechanical robust enough for a good processability, but soft enough for a good contact at the electrode/electrolyte interface.

3.4.1 Experimental

Polymer electrolyte coins with a PEO molecular weight of 10^5 g/mol are fabricated with several salt concentrations r using the solvent-free procedure without the annealing step (= Method C) from Section 3.3 in a nitrogen glove box. Here, r represents the molecular ratio of lithium ions to ethylene oxide repeat units. With the molecular weight for ethylene oxide and LiTFSI of 44.03 g/mol and 287.06 g/mol, respectively, the conversion from molecular ratio r to weight ratio x can be calculated. Table 3.1 shows the several investigated salt concentrations and further lists the quantities of LiTFSI used to fabricate the respective polymer electrolytes with a constant 2.5 g of PEO.

Table 3.1: Investigated salt concentrations in molecular and weight ratio

r [$\text{mol}_{\text{Li}^+}/\text{mol}_{\text{EO}}$]	x [$\text{g}_{\text{Li}^+}/\text{g}_{\text{PEO}}$]	m_{PEO} [g]	m_{LiTFSI} [g]
0.035	0.186	2.500	0.570
0.040	0.207	2.500	0.652
0.045	0.227	2.500	0.734
0.050	0.246	2.500	0.815
0.055	0.264	2.500	0.897
0.060	0.281	2.500	0.978
0.065	0.298	2.500	1.060
0.070	0.313	2.500	1.141
0.080	0.343	2.500	1.304

EIS is performed on the fully fabricated polymer electrolyte coins at 20 and 40 °C with setup A from Section 3.2. A stationary voltage of 1 V, excitation amplitude of 10 mV and frequency range of 1 MHz to 2 Hz is used for these measurements. Again, three polymer electrolytes are investigated per salt concentration, and the obtained maximum, minimum and calculated average is evaluated.

3.4.2 Results

Figure 3.8 shows the obtained polymer electrolyte coins for the different salt concentrations.

Figure 3.8: Obtained polymer electrolyte films for the different salt concentrations

The mechanical robustness of the polymer electrolyte decreases with larger amounts of salt, leading to stiff films at low salt concentrations and softer films as r is increased. At molecular ratios around $r = 0.07$, the polymer/salt mixture becomes so soft that it cannot be peeled off the Mylar sheet anymore (compare Figure 3.8 for $r = 0.07$). For even higher r values, the films are not solidifying at room temperature anymore, as illustrated in Figure 3.8 for a salt concentration of $r = 0.08$.

The observed behavior is expected due to the fact that a higher salt concentration decreases the melting temperature of the polymer/salt system. In order to find the best mechanical properties for the polymer electrolytes, a compromise has to be found: From the processing perspective, a high mechanical robustness would be favorable to easily peel off the polymer electrolyte film from the Mylar sheet, and furthermore to punch out the coins and assemble the cell without damaging the polymer electrolyte. In contrast, a soft sheet will increase contact at the electrode/electrolyte interface, resulting in a decreased interfacial resistance.

The evaluated EIS results and the film thicknesses of the polymer electrolyte coins with the different salt concentrations are shown in Appendix B.2. Figure 3.9 illustrates the ionic conductivity versus salt concentration calculated from this data.

Figure 3.9: Ionic conductivity of the polymer electrolyte versus salt concentration. The curves represent the average values and the error bars the obtained minimum and maximum based on measurements of three polymer electrolyte coins per salt concentration.

In general, the diagram shows an increase in the ionic conductivity with increasing r values especially at small salt concentrations. The curve reaches a maximum ionic conductivity of $\sigma = 4.6 \cdot 10^{-6}$ S/cm at 20 °C and of $\sigma = 5.3 \cdot 10^{-5}$ S/cm at 40 °C for a salt concentration of $r = 0.060$. At higher values of r , the ionic conductivity stops increasing and even drops slightly at a molecular salt-to-polymer ratio of $r = 0.065$.

The described behavior can be explained by the following opposing effects: On the one hand, a high salt concentration leads to an increase in available charge carriers, which has a positive effect on ionic conductivity and leads to the rise of σ at low salt concentrations. On the other hand, high quantities of salt can aggravate its dissociation, leading to the formation of ion clusters. Furthermore, the glass transition temperature of the polymer electrolyte increases with r , resulting in the decrease of the amorphous parts in the polymer/salt system. As stated previously, both conduction mechanisms, vehicular diffusion and lithium-ion hopping between complexation sites, are based on having mobile PEO chains, which only occur in the amorphous part of the electrolyte. Consequently, the ionic conductivity decreases at high salt concentrations.

3.4.3 Conclusion

Polymer electrolytes were fabricated with different molecular ratios of salt-to-ethylene oxide repeat units from $r = 0.035$ to $r = 0.080$ and investigated regarding their mechanical and electrical properties. The stiffness of the films decreases with an increasing amount of salt, leading to a favorable processability at low values of r . However, uniform polymer electrolyte films can still be obtained for salt quantities of up to $r = 0.055$. Minimal resistance at the electrode/electrolyte

interface is expected at high salt concentrations due to a softer PEO/LiTFSI system, though the processability decreases. For a temperature of 40 °C, a maximal ionic conductivity is obtained at $r = 0.060$. In regard to all these results, a salt concentration of $r = 0.055$ is chosen for the PEO/LiTFSI electrolyte to optimize its electrical and mechanical properties at a temperature of 40 °C.

3.5 Testing BaTiO₃ Filler Particles

The striking disadvantages of ASLIBs with polymer electrolytes are the poor ionic conductivity and high interfacial resistance especially at moderate temperatures. Considerable research efforts were undertaken to bring down the operating range of the polymer electrolyte to room temperature. To improve the electrolyte's ionic conductivity and suppress a surface layer formation, the introduction of nano- or micro-sized filler particles into the polymer/salt system has proven to be successful. The most striking enhancements for these composite polymer electrolytes (CPE) were summarized in the Sections 2.2.6 and 2.4.2.

One of the most popular fillers are ferroelectric BaTiO₃-nanoparticles. Ferroelectricity describes the ability of materials to undergo a reversible and spontaneous electric polarization induced by an external electric field. Different conductivity enhancing mechanisms have been proposed based on this characteristic: The spontaneous polarization of the BaTiO₃ particles might increase the dipole moment of the ether groups in the PEO chains. Thus, the increased polarity of the PEO chains would facilitate salt dissociation. In addition, the ferroelectric nanoparticles might provide a high ion-conduction interface due to their permanent dipole. Furthermore, an increase in the amorphous regions of the polymer electrolyte due to the introduction of the BaTiO₃ particles has been suggested. Acting as

nucleation centers, they would lead to a higher nucleation rate, resulting in an accelerated solidification [138, 139].

In this section, the effect of barium titanate (BaTiO_3) nanoparticles on the ionic conductivity of a PEO/LiTFSI system is investigated. CPEs with different BaTiO_3 weight fractions are fabricated with both, the solvent-based and solvent-free procedure.

3.5.1 Experimental

BaTiO_3 with a particle size of <100 nm is supplied from Sigma Aldrich and dried at 150°C for 24 h prior to use. The CPEs are produced with different weight percentages of BaTiO_3 , a constant salt concentration of $r = 0.055$ and the same PEO molecular weight of 10^5 g/mol in a nitrogen glove box. Both major fabrication approaches from Section 3.3 are carried out, the solvent- and annealing-free procedure (= Method C) and the solvent-based method (= Method A): For the dry fabrication method, the ceramic fillers are added to the salt powder prior to the grinding step. For the solvent-based method, the nanosized filler particles are inserted to the salt/THF solution and magnetically stirred for 12 hours, before the PEO/THF solution is added. Once the BaTiO_3 powder is introduced in the described way, the two fabrication methods follow the respective procedures from section 3.3.

EIS is performed on the CPE coins with the different weight percentages of BaTiO_3 obtained from the two fabrication methods. Once more, a stationary voltage of 1 V, frequency range of 1 MHz to 2 Hz and voltage amplitude of 10 mV is used for these measurements, and the bulk electrolyte resistance is taken from

the lower frequency minimum in the impedance curves and used to calculate the ionic conductivity of the several CPE coins.

3.5.2 Results

Figure 3.10 shows the CPE coins for several BaTiO_3 mass fractions x obtained from the two different fabrication methods.

Figure 3.10: CPE coins for several BaTiO_3 mass fractions x obtained from the solvent-free and solvent-based fabrication

The figure reveals significant differences in the results for the two procedures: For the solvent-based method, an introduction of the nanosized BaTiO_3 filler particles changes the electrolyte films from a quasi-transparent-like color to a opaque white. This effect is expected for homogeneously displaced BaTiO_3 particles in the polymer matrix since the original color of the ceramic filler powder is also white. However, for the solvent-free method, no change of the bulk electrolyte's color is obtained. In fact, on closer inspection of the CPE coins fabricated with the solvent-free approach, some BaTiO_3 particles can be detected even by eye. Most likely, this is due to an insufficient stabilization of the nanosized BaTiO_3 particles, resulting in particle agglomeration. The dry method dissolves the filler particles during the heating step of the electrolyte's fabrication procedure in the melted polymer/salt system. However, the polymer matrix exhibits a high viscosity,

hindering complete dissolution of the particles and promoting agglomeration.

The ionic conductivity as a function of the BaTiO_3 weight fraction x for the solvent-based and solvent-free procedure at 20 °C and 40 °C is illustrated in Figure 3.11. The respective EIS impedance data evaluated to obtain these conductivity values can be found in Appendix B.3.

Figure 3.11: Ionic conductivity as a function of the BaTiO_3 weight fraction in the PEO/LiTFSI electrolyte with a constant salt concentration of $r = 0.055$. The solvent-free and solvent-based fabrication procedures are investigated at 20 °C and 40 °C.

The diagram gives rise to the following results:

- (1) For the solvent-free method, a decrease in the ionic conductivity is observed when the BaTiO_3 powder is introduced. Supported by the visual results from Figure 3.10, this can be attributed to an agglomeration of these ceramic nanoparticles. BaTiO_3 is insulating by its nature. Since all proposed conductivity enhancing mechanisms in the polymer/salt environment are based

on the nano- or microsize of this filler, an introduction of larger, insulating particles results in a decrease of the conductivity.

- (2) If the CPEs are fabricated with the solvent-based method, a small enhancing effect on ionic conductivity is observed. However, this increase is negligible compared to the superior ionic conductivity of the solvent-free procedure without any BaTiO_3 . There are different possible reasons for why these results do not match the enhancement of ionic conductivity stated in the literature [86, 138, 139, 140, 141]: Most likely, the carried out solvent-based fabrication procedure could not fully prevent agglomeration. ZHANG et al. [139] investigated the influence of the BaTiO_3 particles size on the ionic conductivity. Comparing sizes between 5 nm and 500 nm, they stated an increasing ionic conductivity with a decreasing particle size. As a result, the effect of 500 nm filler particles was small, matching the obtained results from Figure 3.11. The supposed agglomeration of the BaTiO_3 could be due to differences in the system's chemistry and fabrication procedure. Here, the pure BaTiO_3 particles were dissolved in THF for the solvent-based procedure. In contrast to that, ZHANG et al. coated the BaTiO_3 powder with a titanate coupling agent (TCA-K38S) by stirring in acetonitrile. The coupling agent bonds the dissimilar inorganic filler particles and the organic polymer electrolyte together, avoiding separation and subsequent agglomeration. In addition, it is also worth noting at this point that data on exactly the same salt concentration of $r = 0.055$ in the PEO/LiTFSI system and the low temperatures (20 °C and 40 °C) is rare, making it difficult to compare the results in full detail.

3.5.3 Conclusion

CPEs with different weight fractions of BaTiO₃ (<100 nm) were fabricated with the solvent-free and solvent-based procedure. For an increasing weight fraction of BaTiO₃, the results show a decreasing effect on the ionic conductivity for the solvent-free method and only a small conductivity enhancement for the solvent-based procedure, which does not match the results stated in the literature. It is suggested that this is due to the agglomeration of the nanosized BaTiO₃ particles, as no coupling agents are used in both proposed procedures in contrast to other investigations. The agglomeration is visually supported for the CPEs obtained from the solvent-free method.

CHAPTER 4

Cycling Behavior of LTO-PEO/LiTFSI-LFP Cells at 40 °C

4.1 Introduction

In the following, first cycling results are presented for the LTO-PEO/LiTFSI-LFP cell chemistry. It is important to highlight that all cell testing is performed close to the body temperature at 40 °C. This assures solid-state of this specific cell chemistry but induces higher bulk electrolyte and interfacial resistance, and thus prohibits comparison to frequent investigations at temperatures of 70 to 100 °C from the literature. As a basis for further optimization, several experiments are performed to relate the obtained capacity behavior to electrochemical phenomena: First, the cell's impedance is investigated during both, cell cycling and storage. Next, LTO-PEO/LiTFSI-Li and LFP-PEO/LiTFSI-Li half-cells are cycled with the goal to separate LTO- or LFP-specific effects. Finally, Li-PEO/LiTFSI-Li symmetric cells are built in order to study the bulk polymer electrolyte.

4.2 Experimental

Lithium titanate oxide (LTO) and lithium iron phosphate (LFP) are ordered from MTI CORPORATION, carbon black (Super C65) from TIMCAL, N-methyl-2-pyrrolidone (NMP) from ALFA AESAR and poly(ethylene oxide) (PEO, $M_W = 100,000$ g/mol), poly(vinylidene fluoride) (PVDF, $M_W = 534,000$ g/mol) as well as bis(trifluoromethane)sulfonimide (LiTFSI) from SIGMA ALDRICH. All dry powders (LiTFSI, active materials, PVDF, carbon black and PEO) are dried in a vacuum oven overnight at suitable temperatures (150 °C, 110 °C, 110 °C, 110 °C and 50 °C respectively) and stored in the inert environment of a nitrogen filled glovebox until processing.

4.2.1 Electrolyte Preparation

PEO/LiTFSI based polymer electrolytes are manufactured in a nitrogen-filled glove-box with a solvent-free fabrication method (see Section 3.3) and salt concentration of $r = 0.055$ (compare Section 3.4). The procedure results in $\sim 300 \mu\text{m}$ thick films, which are subsequently dried in a vacuum oven overnight at room temperature and transferred to an argon-filled glovebox. Here, these films are hand-punched into polymer electrolyte coins of 19 mm diameter and stored until cell assembly.

4.2.2 Electrode Preparation

LTO anode and LFP cathode films are prepared with a conventional solution casting method which is summarized in Figure 4.1. A solvent-based procedure was chosen due to the ease of processing and superior homogeneity of the mixed electrode slurries.

Figure 4.1: Schematic illustration of the LTO/LFP electrode fabrication procedure

The electrode fabrication starts in a nitrogen-filled glovebox by grinding lithium salt in a mortar and pestle. The resulting fine powder is added to a solution of PEO and PVDF in suitable amounts of N-methyl-2-pyrrolidone (NMP), which is stirred until the LiTFSI is completely dissolved in the polymer solution. In parallel, the LTO or LFP active material and conductive carbon additive are thoroughly ground together in a mortar and pestle. They are then added in small increments to the NMP solution of lithium salt, PEO and PVDF and mixed until completely homogenized. This is supported by stirring at a high shear rate in an homogenizer. Next, the anode and cathode slurries are brought out of the glovebox and coated on copper and aluminum foils, respectively, using a doctor-blade technique. Here, coating thicknesses are varied to match the anode-to-cathode capacity ratio of the electrode coins in the end. The NMP solvent is slowly evaporated at room temperature, followed by the calendaring of the anode and cathode sheets. Subsequently, these are punched into 15 mm diameter anode and 14 mm diameter cathode discs. Finally, a second drying step at 60 °C in a vacuum oven overnight ensures complete solvent evaporation and minimizes possible moisture contamination. The obtained electrode discs are brought and stored in an argon filled glovebox prior to cell assembly.

The composition of the LTO and LFP composite electrodes for the experiments of this chapter are summarized in Table 4.1. The active material particles form the major part of the anode and cathode. Binder (PVDF) is added for good cohesion between the electrode particles and adhesion to the current collector. Carbon black is needed for increasing the electrical conductivity of the electrodes. Finally, PEO is inserted to improve the charge transport of lithium-ions from the polymer electrolyte to the active material particles in the bulk electrode.

Table 4.1: Composition of LTO and LFP composite electrodes

LTO or LFP	PVDF	Carbon black	PEO
89.5 wt.%	5 wt.%	3 wt.%	2.5 wt.%

Lithium metal electrode chips (16 mm diameter, 0.6 mm thickness) are obtained in vacuum sealed Aluminum cans from MTI CORPORATION and stored in an argon-filled glovebox. Before cell assembly, the lithium chips are brushed to remove the passivation layer on the electrode surface.

4.2.3 Cell Assembly

A schematic of the produced CR2032 coin cells is shown in Figure 4.2(a). They are assembled using the stacking procedure shown in Figure 4.2(b).

Figure 4.2: Coin cell schematic and cell assembly with the stacking procedure

The assembly procedure takes place in the inert atmosphere of an argon filled glovebox (MBRAUN LABmaster 130, O_2 and H_2O content < 0.1 ppm). First, the coated side of the cathode (A) is carefully pressed on a polymer electrolyte disk (B).

This combination (C) is added, polymer-side-up, to the positive casing (D). Next, a gasket is put in the coin cell (E), which not only ensures good contact of the pressed cathode-electrolyte sheets to the casing, but also avoids physical contact between the stainless steel and conducting coin cell parts, thus preventing short-circuiting. Subsequently, the anode is pressed on top of the cathode-electrolyte system (F), followed by a stainless steel spacer and spring (G). Finally, the negative case of a CR2032 coin cell is pressed on top of the setup (H) and crimped closed with 1 ton of pressure. In the conclusion of these steps, an all-solid lithium-ion battery is obtained, which is brought out of the argon environment for cell testing.

4.2.4 EIS Measurements and Cell Cycling

The cells are cycled with a BT-2000 Battery Tester from ARBIN INSTRUMENTS at a temperature of 40 °C, which is held constant with an Incubator 6858 from FISHER SCIENTIFIC. Cells containing at least one composite electrode are cycled with a constant rate charge/discharge. Suitable cutoff voltages are chosen depending on the combination of electrodes used and the C-rates are quantified based on the cell's theoretical capacity. The latter is calculated from the measured weight of the limiting electrode (cathode) and the respective active material percentage. Cycling procedures for symmetric cells with lithium-metal electrodes on both sides are explained later.

EIS measurements are performed with a VersaSTAT 3 from PRINCETON APPLIED RESEARCH. After resting all cells for a sufficient amount of time before each measurement to ensure steady-state, they are excited with a voltage amplitude of 10 mV at OCV through a frequency range of 1 MHz to 10 mHz. An Incubator 6858 from FISHER SCIENTIFIC keeps the cells at a temperature of 40 °C.

4.3 First Cycling Results and Impedance Investigation

4.3.1 Experiment Motivation and Description

This section presents the first cycling data obtained for the LTO-PEO/LiTFSI-LFP cells at 40 °C. EIS is a powerful instrument to assign impedance changes to electrochemical processes. Thus, the cell's impedance behavior is investigated during cycling in order to relate capacity changes to electrochemical phenomena. Furthermore, in order to separate between calendar and cycling induced effects, uncycled cells are also investigated over storage time.

Six LTO-PEO/LiTFSI-LFP cells are fabricated as explained previously. Three cells are cycled with a charge/discharge current of $C/20$, their cell specifications (including capacity ratios and active material amounts) used to calculate the respective currents are listed in Appendix C. EIS is performed in the completely discharged state ($SOC = 0\%$) every five cycles. Before each impedance measurement, the cell is rested for 24 h to ensure steady-state. Both, cycling and impedance measurements are performed at 40 °C. The other three cells are stored at 40 °C without any cell cycling and EIS is performed over time.

4.3.2 Results

Figure 4.3 presents the cell cycling results for the three LTO-PEO/LiTFSI-LFP cells. The experimental procedure is illustrated in the voltage profile (Figure 4.3(a)), which is shown for only one of these cells. Capacity and coulombic efficiency is evaluated in Figure 4.3(b) and (c). The curves present the obtained averages of the three cells while the error bars state minimum and maximum values. Most important observations can be summarized as follows:

Figure 4.3: Cell cycling results for LTO-PEO/LiTFSI-LFP cells

- (i) **Voltage Profile:** The LTO-PEO/LiTFSI-LFP cells successfully charge/discharge with a rate of C/20 at 40 °C for 15 cycles.
- (ii) **Specific capacity:** All three cells show reproducible capacity behavior. The capacity is continuously increasing in the first 5 cycles, in average from around 15 mAh/g_{LFP} to 47 mAh/g_{LFP}, which is equivalent to a capacity change of over 300 %. This drastic increase is followed by a tremendous capacity drop to about half of the maximum value at cycle number 6 and then a slower decrease to about 13 mAh/g_{LFP} after 15 cycles. Comparing the obtained specific capacity to the theoretical one, a low capacity has to be concluded. With a theoretical capacity for LFP of 170 mAh/g_{LFP}, the average maximum capacity after cycle 5 is equivalent to the lithiation of only ~ 27 % of the available cathode active material.

(iii) **Coulombic efficiency:** For all three cells, the coulombic efficiency is below unity. This is especially the case after each impedance measurement, where cells are not cycled for at least 24 h.

EIS results for the three cycled and three stored cells are summarized in Figure 4.4. Impedance curves are shown for one of the cycled (Figure 4.4(a)) and one of the stored cells (Figure 4.4(b)). As an indicator of the cells' resistance, R_{cell} evaluates the real impedance part of the lower frequency minimum for the cycled cells. For the stored cells, the lower frequency minimum diminishes with time. Here,

Figure 4.4: Impedance investigation of LTO-PEO/LiTFSI-LFP cells. EIS is performed with an excitation of 10 mV around OCV at 40 °C. R_{cell} evaluates $\text{Re}(Z)$ for the lower frequency minimum (cycled cells) or $\text{Re}(Z)$ for 864 Hz (stored cells).

the real part of the cells' impedance at a constant frequency of 864 Hz is evaluated for R_{cell} . Figure 4.4 (c) compares the cells' resistance over cycling and storage.

For the cycled cells, a tremendous impedance drop is observed from the measurements before cycling to after cycle five. This is followed by the formation and widening of a medium and high frequency arc in the impedance spectra, resulting in a moderate increase of the cells' resistance. For the stored cells, the impedance strongly decreases in the first 20 hours of storage and remains constant at low resistances afterwards.

Based on these impedance results, different hypotheses for the obtained capacity behavior of the cycled cells can be formulated:

- (i) **Capacity increase (cycle 1 - 5):** The capacity increase of over 300 % in the first cycles is related to a drastic impedance decrease in the cycled cells. However, the impedance drop is observed in the first 20 hours of storage for the uncycled cells as well. Thus, the capacity behavior might be due to a combination of two effects: First, improved contact at the electrode/electrolyte interface may result in a decreased interfacial resistance. The soft and highly viscous polymer electrolyte at 40 °C might need time, based on the impedance results of the stored cells around 20 hours, to penetrate the pores of the electrodes. However, since the capacity increase continues after the first 20 hours of charging/discharging, a second phenomena has to exist, which must be cycling induced. It is proposed that this is due to the formation of lithium-ion pathways into the bulk electrodes. With the increased number of pathways, the lithium-ions would lithiate a larger share of the active material particles after the first cycles, thus resulting in a rise of capacity.

(ii) Drastic capacity drop (cycle 6): It is difficult to relate the capacity collapse after six cycles to the cells' impedance, since there are no measurements directly before and after this drop. Consequently, based on this data, it is left to interpretation. Both active materials, LFP and LTO, suffer from low electrical conductivity ($\sim 10^{-8}$ to 10^{-13} S/cm [116, 110]) and limited lithium-ion diffusivity ($\sim 10^{-8}$ to 10^{-13} cm²/s [116, 110]). Consequently, electrons or lithium-ions might accumulate in the electrodes and side reactions can occur. This would not only lead to a loss of charge carriers, but could also induce the blocking of lithium-ion diffusion paths and particle isolation, all resulting in the capacity drop of the cells. A second root cause for the capacity failure could be a gas evolution in the LTO anode. Gassing of LTO has been reported especially at elevated temperatures [142]. This could induce a worsening of the contact at the electrode/electrolyte interface, and thus lead to the obtained capacity drop.

(iii) Moderate capacity decrease (cycle 6 - 15): The moderate capacity decrease until cycle 15 is related to the formation and widening of a medium and high frequency arc in the impedance spectra. This can be interpreted with several electrochemical phenomena, however the assignment of these processes to the arcs is difficult due to the lack of equivalent circuit models for LFP-PEO/LiTFSI-LTO cells. Possibilities for these phenomena include: (1) hindered lithium-ion diffusion in the bulk electrodes due to the blockage of pathways by the formation of side products; (2) worsened charge transport at the PEO-LiTFSI/active material interface based on blocked surface area by these side products; (3) aluminum current collector corrosion by an attack of TFSI anions, or (4) surface layer formation on the electrodes. For the latter, it is important to note that the film formation would have to be

cycling induced, since no arcs are observed for the stored cells. This does not match the proposed surface layer formation mechanism in the literature which is based on the reaction of lithium with impurities such as water, independent of cycling.

(iv) Generally low capacity: In the best state of the cell after cycle five, still only 27 % of the cathode active material is lithiated. The obtained cell resistance R_{cell} for the LTO-PEO/LiTFSI-LFP ASLIBs at that state is around 2000 Ω . This is much higher compared to the liquid electrolyte equivalents. The generally high resistance and low capacity is due to the two major drawbacks in the field of ASLIBs: first, the polymer electrolyte's lower bulk ionic conductivity; secondly, a high interfacial resistance is present due to insufficient contact between the solid electrolyte and the electrodes' active material particles.

4.3.3 Conclusion

LTO-PEO/LiTFSI-LFP cells were investigated over cycling and storage at 40 °C. For a constant rate charging/discharging at C/20, results show an increase of the average specific capacity to a maximum value of around 47 mAh/g_{LFP} after 5 cycles, followed by a drastic drop and then a moderate capacity decrease to 13 mAh/g_{LFP} after 15 cycles. The obtained capacity behavior was related to the cells' impedance during cycling and storage. The generally low capacity of 27 % of the theoretical one, equivalent with insufficient lithiation of the active material particles, is due to low conductivity of the polymer electrolyte and limited contact at the electrode/electrolyte interface. The capacity increase in the beginning is explained by a combination of two effects: first, an improvement of contact at the electrode/electrolyte interface until 20 hours after cell assembly; secondly, a

deeper penetration of lithium-ions into the bulk electrode via the formation of diffusion pathways during the first cycles. Furthermore, two different phenomena are proposed for explaining the rapid capacity decrease: on the one hand, the well-known poor electrical conductivity and lithium-ion diffusivity of both active materials could result in the accumulation of lithium-ions and/or electrons in the electrodes, thus inducing the formation of performance reducing side-products; on the other, outgassing of LTO might occur and lead to a worsening of contact at the electrode/electrolyte interface. In the literature, a surface layer formation is often stated to be a reason for the increase of interfacial resistance. The formation mechanism is described to be based on reactions of impurities with lithium, and thus would be cycling-independent. However, no surface layer formation is observed based on EIS investigations on stored cells even 200 h after cell assembly.

4.4 LTO and LFP Half-Cells

4.4.1 Experiment Motivation and Description

LTO-PEO/LiTFSI-Li and LFP-PEO/LiTFSI-Li cells (referred to as LTO- or LFP-half-cells respectively) are investigated in order to separate LTO- or LFP-specific effects from the cycling behavior described in the LTO-PEO/LiTFSI-LFP full-cells. The well-understood lithium metal electrodes do not contain any carbon black, binder or other additives. Consequently, their use simplifies the cell setup as well as the occurring electrochemical processes, and thus facilitates interpretation of the cycling results: Electrical conductivity and lithium-ion diffusion issues can be eliminated when using these lithium electrodes since lithium is highly electrically conducting and no lithium-ion diffusion into the bulk electrode takes place during cycling. Furthermore, no current collector is needed for lithium-metal electrodes. Three LTO-half-cells and three LFP-half-cells are fabricated as explained previously.

Their specifications can be found in Appendix C. The cells are cycled with a C-rate of C/40 in the first 5 cycles and C/20 in the following 20 cycles at a temperature of 40 °C.

4.4.2 Results

Figure 4.5 summarizes the cycling results for the LTO-half-cells. The experimental procedure is illustrated in the voltage profile (Figure 4.5(a)), which is shown for only one of these cells. The specific capacity and coulombic efficiency are illustrated in Figure 4.5(b) and (c). Out of the three assembled ASLIBs, one short circuited prior to cycling, indicating failure in the process of manufacturing. Thus, the presented plots only evaluate the remaining two cells.

Figure 4.5: Cell cycling results for LTO-PEO/LiTFSI-Li cells

The qualitative capacity behavior of the LTO-half-cells matches the cycling results obtained for the LTO-PEO/LiTFSI-LFP full-cells: A capacity increase is followed by a drastic drop and then a slower decrease of the specific capacity. Quantitatively, a much higher maximum capacity is obtained ($\sim 80 \text{ mAh/g}_{\text{LTO}}$ after cycle three). However, this difference can be explained not only by the “quasi-infinite” amount of available charge carriers due to the use of metallic lithium as one of the electrodes, but also ascribed to a difference in the cycling procedure: in the first five cycles, a C-rate of C/40 is used instead of C/20, resulting in a higher capacity at the beginning of the cycling procedure. Similarly to the full-cells, the coulombic efficiency stabilizes at around 90 % when cycling at C/20 after the first 5 cycles. However, no major capacity drops take place here. This is due to the fact that EIS is not performed and the cells are cycled non-stop.

Figure 4.6 shows the cycling results obtained for the LFP/PEO-LiTFSI/Li cells. Again, a voltage profile for one of these cells is presented in Figure 4.6(a). The specific capacity and coulombic efficiency are evaluated for each individual cell in Figure 4.6(b) and (c).

All three cells short-circuited within the first five cycles, indicated by the scattering of the voltage profile at the end of each procedure. In all cases, the failure occurs during the charging step, which suggests the short-circuit is due to dendrite formation in the cells. The risk of dendrite formation is aggravated when using lithium metal instead of a composite electrode. This is due to the fact that lithium-ions are not intercalating in but plating on the lithium metal anode during cycling. The failure of all cells after the first five cycles makes a comparison with the capacity behavior of the full-cells and LTO-half-cells difficult. Qualitatively,

Figure 4.6: Cell cycling results for LFP-PEO/LiTFSI-Li cells

the capacity curve of the LFP-half-cells looks similar compared to the full-cells: the specific capacity increases until the short-circuiting of the cells. The coulombic efficiency in the first cycles of the LFP-half-cells is about 95 %, which is slightly closer to unity compared to both, LTO-half-cells and full-cells. This could be an indicator of more reversible charging/discharging processes in the LFP cathode compared to the LTO anode. However, this remains inconclusive since only five cycles can be evaluated. Moreover, it has to be considered that a quasi-infinite amount of charge carriers is available due to the half-cell chemistry. Thus, the lithium metal electrode can make up for any occurring irreversible capacity losses in the next cycle. Consequently, the statement of higher charging/discharging reversibility in the LFP cathode compared to the LTO anode is very ambiguous.

4.4.3 Conclusion

LTO-PEO/LiTFSI-Li and LFP-PEO/LiTFSI-Li half-cells were investigated to separate electrode specific behavior from the cycling results obtained for the LTO-PEO/LiTFSI-LFP full-cells. The qualitative behavior of the LTO-half-cells matches the results obtained for the full-cells. Quantitative differences can mainly be ascribed to a different cycling procedure in the first five cycles. All LFP-half-cells short-circuit within the first five cycles during the charging step, indicating failure due to lithium dendrite growth. Until then, the capacity behavior looks similar but coulombic efficiency is closer to unity compared to the full-cells and LTO-half-cells. This might indicate superior reversibility in the LFP cathode. However, this statement is ambiguous due to the fact that only five cycles were investigated and that a quasi-infinite amount of charge carriers is available in the half-cell, which can replace any irreversible capacity losses. All in all, it can be concluded: first, the phenomena inducing the capacity increase in the first cycles occurs in both electrodes; and secondly, the phenomena leading to the rapid capacity decrease occur in the LTO electrode while the LFP electrode could not sufficiently be investigated.

4.5 Symmetric Cells

4.5.1 Experiment Motivation and Description

In order to investigate the bulk polymer electrolyte during cycling, Li-PEO/LiTFSI-Li symmetric cells are tested. Again, the use of lithium metal electrodes simplifies the occurring electrochemical processes due to the absence of any electrode additives. Thus, interfacial and bulk electrolyte phenomena dominate the cycling behavior, facilitating data interpretation.

The lithium stripping/plating procedure for the testing of symmetric cells differs

from the conventional cycling of LIBs with at least one composite electrode. Due to the quasi-infinite amount of available charge carriers in both lithium metal electrodes, a completely lithiated/deliathiated state is not reached during cycling. Thus, a natural voltage range for cell cycling does not exist. Consequently, instead of defining cut-off voltages, cell testing is performed with a constant charge/discharge capacity: cycling occurs with a specified current and polarity is switched in constant time intervals. In doing so, each electrode alternately acts as a source (with lithium stripping from the surface) and as a sink (with lithium plating on the surface). The voltage at the end of each cycling step is then characteristic for the cell resistance.

In the following, symmetric cells are tested with two different cycling procedures. First, stripping/plating occurs with a current of $25\ \mu\text{A}$ (equivalent to a current density of about $12.5\ \mu\text{A}/\text{cm}^2$) for 10 h, which approximately mimics conditions in the half- and full-cells when tested at a C/40-rate. Secondly, the same current of $25\ \mu\text{A}$ is applied but for a significantly shorter time of only 2 h. EIS is performed before, during and after the cell cycling to evaluate the cells' impedance behavior, specifically in terms of the bulk electrolyte resistance.

4.5.2 Results

Figure 4.7(a) presents the voltage profile for the cycling of a symmetric cell with a constant current of $25\ \mu\text{A}$ and stripping/plating time intervals of 10 h. Obtained EIS results after each cycle are shown in Figure 4.7(b).

The voltage curve shows a disproportionately high increase during the first charging step to over 0.5 V and a decrease of the potential difference during the subsequent first discharge. The following plating/stripping steps exhibit the expected voltage

Figure 4.7: Voltage profile and EIS results for the galvanostatic lithium stripping/plating test of a Li-PEO/LiTFSI-Li symmetric cell at 40 °C. A current of 25 μA was applied for 10 h.

behavior: an abrupt rise/drop when changing current direction due to existing overpotentials in the cell is followed by a moderate increase of the potential difference induced by the formation of concentration gradients. In the end of the fourth charging step, a sudden and significant voltage drop close to 0 V occurs and this behavior repeats in the following cycling steps. This indicates the short circuiting of the cell due to dendritic growth of metallic lithium.

EIS results relate the described voltage behavior to the cell's impedance. The tremendous voltage increase in the first cycle is related to a high interfacial resistance, indicated by a wide semicircle in the EIS results before cycling. This could be explained by bad contact at the electrode/electrolyte interface uneven lithium metal and polymer electrolyte surfaces directly after cell assembly. After electrode surface wetting took place and the interface homogenized, the cell's interfacial impedance drops significantly and remains nearly constant for the measurements from cycles 2 to 5. For all EIS results, the bulk electrolyte resistance is consistently between 500 and 800 Ω . No continuous increase/decrease is observed, indicating that these differences can likely be related to data scattering rather than to ongoing electrochemical phenomena.

In order to prevent the cell's from short-circuiting and to investigate the bulk polymer electrolyte after a higher number of cycles, another symmetric cell was investigated with stripping/plating time intervals of only 2 h. The testing results in terms of the obtained voltage profile and impedance curves are summarized in Figure 4.8.

Figure 4.8: Voltage profile and EIS results for the galvanostatic lithium stripping/plating test of a Li-PEO/LiTFSI-Li symmetric cell at 40 °C. A current of 25 μA was applied for 2 h in both directions.

The voltage profile shows a successful plating/stripping of the lithium-metal electrodes at the given conditions for over 50 cycles without short circuiting of the symmetric cell. After a slight increase of the plating/stripping end-voltages until cycle 3, the cell resistance is exponentially decreasing and before remaining nearly constant from cycle 35 to the end of cell testing.

The impedance measurements relate the resistance changes predominantly to a change of the medium frequency arc in the obtained impedance curves: the slight increase of end-voltages in the beginning of cycling is related to a widening of the respective semicircle, and the subsequent exponential decrease due to a contraction of this arc. Again, changes in this interfacial resistance can be

ascribed to an ongoing surface wetting of the electrodes and homogenization of the electrode/electrolyte interface. For all EIS measurements, the bulk electrolyte resistance is nearly identical. This indicates that no accumulation of charge carriers or irreversible side reactions occur in the bulk electrolyte.

4.5.3 Conclusion

Li-PEO/LiTFSI-Li cells were built and cycled with two different procedures to study the behavior of the bulk polymer electrolyte under charging/discharging. First, galvanostatic plating/stripping of the lithium metal electrodes was performed with $25\ \mu\text{A}$ for 10 h, representing cycling conditions used for the LTO-PEO/LiTFSI-LFP full-cells. This procedure induced short-circuiting of the symmetric cell after four cycles due to dendrite growth of the metallic lithium. In the second testing procedure, the same current of $25\ \mu\text{A}$ was used for the lithium plating/stripping but the step time was reduced to only 2 h, which successfully prevented short circuiting. EIS was performed alongside the cycling of these cells to separate the bulk electrolyte resistance from interfacial impedances. Most importantly, the impedance curves show that the bulk electrolyte resistance is not changing during cycling. Thus, it can be concluded that the observed capacity changes in the LTO-PEO/LiTFSI-LFP full-cells are not due to electrochemical phenomena in the bulk polymer electrolyte. Furthermore, EIS relates resistance changes of the symmetric cells predominantly to effects at the electrode/electrolyte interface. An improving contact and homogenization at the electrode/electrolyte interface is proposed to explain this behavior.

CHAPTER 5

Investigating the Electrode Composition and Cell Assembly Method

5.1 Introduction

As shown in the previous chapter, insufficient contact at the electrode/electrolyte interface is a major drawback for the LTO-PEO/LiTFSI-LFP cells at the investigated temperature of 40 °C. In this chapter, two approaches are presented for improving the electrode/electrolyte interface. First, it is proposed to put small quantities of polymer electrolyte into the electrodes. Secondly, a different cell assembly procedure is tested by not stacking the several layers together, but melting the polymer electrolyte on the electrode surface in order to improve contact.

5.2 Electrode Composition

In conventional LIBs, electrode pores are soaked with liquid electrolyte, facilitating lithium-ion migration into the bulk electrode. In contrast to that, this is not the case for ASLIBs, since the rigid structure of the solid electrolyte prohibits its penetration into the small electrode pores. In order to circumvent this and end up with a comparable electrode structure, it is proposed to put small quantities of polymer electrolyte into anode and cathode during electrode processing. This would provide continuity at the electrode/electrolyte interface and diffusion pathways for lithium-ions into the electrode, thus facilitating access to a larger portion of active material particles and consequently increasing cell capacity.

5.2.1 Experimental

Table 5.1 shows the three electrode compositions investigated in the following. Composition 1 does not contain any lithium salt but does consist of 2.5 wt.% PEO.

Electrode composition 2 exhibits the same amount of polymer but also consists of 0.9 wt.% LiTFSI. This is equivalent to a molecular ratio of salt to ethylene oxide repeating units of $r = 0.055$, representing the found to be optimal salt concentration for the polymer electrolyte at the given conditions (see Section 3.4). In composition 3, the amount of polymer electrolyte in the electrode is doubled. Carbon black and binder weight percentages are held constant, such that the rise of PEO or lithium salt content is compensated by a decrease of the active material content.

Table 5.1: Composition of LTO and LFP composite electrodes

Comp. #	LTO or LFP	PVDF	Carbon black	PEO	LiTFSI
1	89.5 wt.%	5 wt.%	3 wt.%	2.5 wt.%	0 wt.%
2	88.6 wt.%	5 wt.%	3 wt.%	2.5 wt.%	0.9 wt.%
3	85.2 wt.%	5 wt.%	3 wt.%	5 wt.%	1.8 wt.%

The electrode and polymer electrolyte processing as well as LTO-PEO/LiTFSI-LFP cell assembly was explained in Section 4.2. Three cells are tested per electrode composition. In order to allow a proper surface wetting at the electrode/electrolyte interface, all cells are rested at 40 °C for three days prior to constant rate charging/discharging at C/30.

As a reference, liquid electrolyte cells (LECs) are built with the three different electrode compositions. The liquid electrolyte is based on 1 M LiTFSI in a EC/EMC 3:7 (v/v) solution. Physical contact of the electrodes is prohibited by a glass microfiber filter (15.6 mm, Whatman GF/D) separator, soaked in 100 μ L of the liquid electrolyte. Apart from replacing the polymer electrolyte coin with a liquid salt solution and separator film, the coin cell setup for the LECs is equivalent

to the ASLIBs from Figure 4.2(a). Due to the possibility of an SEI formation, cell cycling starts with one C/40 and two C/20 constant rate charge/discharge cycles. Afterwards, cell testing is performed by cycling with C/5. All LECs are kept at a constant temperature of 20 °C during cycling.

5.2.2 Results

Figure 5.1 shows the cycling results obtained for the LECs with the three different electrode compositions for charging/discharging at C/5 and 20 °C. The voltage profile is shown for a LEC with electrode composition 1.

Figure 5.1: Cycling results for LTO-EC/EMC/LiTFSI-LFP liquid electrolyte cells with three different electrode compositions

For all LECs, a constant capacity behavior with only slight fading is obtained. The LEC containing electrodes of composition 1 exhibit the highest specific capacity of up to 142 mAh/g_{LFP}, which is equivalent to 85 % of the theoretical. Composition 2 leads to a maximum capacity of 118 mAh/g_{LFP} while composition 3 only shows values of up to 100 mAh/g_{LFP}, the worst of these three cells. In all cases, the coulombic efficiency is close to unity throughout the cell cycling.

The presented results prove general functioning of the electrodes. Differences in the cycling behavior for the three different electrode compositions can be explained as follows: Compositions 1 to 3 contain increasing amounts of PEO/LiTFSI, with the lowest portion in composition 1 and the highest in composition 3. For LECs, this extraneous addition of PEO/LiTFSI is not needed for proper cell functioning. As stated previously, liquid electrolyte soaks into the electrode pores. Thus, lithium-ions penetrate via the much lower resistance liquid electrolyte instead of the polymer alternative into the bulk electrode. Consequently, a higher share of unnecessary PEO or LiTFSI in the electrodes worsens the cells' maximum capacity.

Figure 5.2 summarizes the cycling results obtained for the all-solid LTO-PEO/LiTFSI-LFP cells with the three different electrode compositions. Figure 5.2(a) shows the voltage profile for a cell with electrodes of composition 2, illustrating the testing procedure. Figure 5.2(b) and (c) present the obtained average, minimum and maximum capacity and coulombic efficiency, respectively. For all electrode compositions, three cells were tested. However, one cell of composition 2 short circuited prior to cycling, indicating failure during manufacturing. Thus, cycling results of only two cells are evaluated here.

Figure 5.2: Cycling results for LTO-PEO/LiTFSI-LFP cells with three different electrode compositions

Qualitatively, all cells show the same capacity behavior as presented and explained in Chapter 4: The average capacity is low compared to the theoretical one and a fast increase is followed by a rapid capacity drop. Different electrochemical phenomena have been proposed in the previous chapter for explaining this behavior. Comparing the capacity curves for the three electrode compositions gives rise to the following two results: first, composition 2 induces the highest maximum capacity; second, composition 1 leads to the lowest capacity drop. These two findings support the motivation of this experiment as well as the proposed underlying electrochemical phenomenon for the observed capacity drop: By putting small

quantities of PEO and LiTFSI in the electrode (= composition 2), more active material becomes available due to the additional lithium-ion pathways into the bulk electrode. This results in the maximum obtained capacity for this electrode composition. However, it was proposed that the capacity drop might occur due to the accumulation of lithium-ions and/or electrons in the electrodes, resulting in the production of side products. By having only polymer and no LiTFSI in the electrodes (= composition 1), this effect would slow down, resulting in a slower capacity decrease.

5.2.3 Conclusion

For optimizing lithium-ion transport into the bulk electrode, it is proposed to put quantities of PEO and/or LiTFSI in the electrodes. Different PEO and LiTFSI weight percentages in the electrode compositions were tested by cycling LTO/LFP cells with a liquid EC/EMC/LiTFSI electrolyte and solid PEO/LiTFSI alternative. Results for all LECs show good capacity behavior, proving basic functionality of the electrodes. Here, the capacity behavior diminishes when inserting PEO or LiTFSI in the electrodes. This is expected since polymer electrolyte in these cells is unnecessary, as lithium transport into the bulk electrodes occurs via the much lower resistance liquid electrolyte. For the all-solid LTO-PEO/LiTFSI-LFP cells, the insertion of PEO/LiTFSI results in an increase of the maximum capacity, indicating that more active material becomes available due to additional lithium-ion pathways in the electrodes. However, the introduction of LiTFSI simultaneously accelerates the capacity decrease. This could be explained by the accumulation of charge carriers in anode and/or cathode during cycling, which worsens when inserting LiTFSI into the electrodes.

5.3 Assembly Procedure

For optimizing contact at the electrode/electrolyte interface, a melting assembly procedure is proposed. So far, LTO-PEO/LiTFSI-LFP cells were assembled by stacking and pressing the anode/electrolyte/cathode layers together, see Figure 4.2(b) on page 88. However, this procedure allows small gaps to remain at the interface due to the rigid and uneven polymer electrolyte. By melting the polymer/salt mixture on the electrode sheets at an elevated temperature under vacuum conditions, gaps could be minimized and the electrolyte might be able to penetrate the pores, thus improving contact with the active material particles.

5.3.1 Experimental

Polymer electrolyte and electrodes are fabricated as explained in Section 4.2 but without punching them in the respective coins. Thus, electrode and electrolyte sheets result from these procedures. Subsequently, the melting assembly procedure is as follows, illustrated in Figure 5.3.

Figure 5.3: Melting assembly procedure

A polymer electrolyte sheet is put onto the coated anode/cathode foils (A) and melted at 70 °C under vacuum conditions over night (B, C). After letting the polymer electrolyte dry naturally to room temperature under vacuum, the electrode/electrolyte sheets are punched into anode/electrolyte and cathode/electrolyte

coins of suitable diameters (D). Before bringing these into the inert atmosphere of an argon filled glovebox for cell assembly, they are again vacuum dried at room temperature overnight to minimize any moisture and oxygen contamination during punching. Subsequently, cell assembly starts by pressing the cathode/electrolyte coin (E) on the anode/electrolyte disc (F). This sandwich (G) is then put into the positive casing of a CR2032 coin cell (H). After adding a gasket, spacer and spring (I), the setup is closed by pressing a negative casing on top (J). Finally, the whole setup is crimped with 1 ton of pressure to result in the melting procedure assembled LTO-PEO/LiTFSI-LFP coin cell.

This assembly procedure is tested with electrode composition 1 and 2 from Table 5.1 on page 106. Three cells are built and tested per electrode composition. Cell specifications are attached in Appendix C. It is worthwhile mentioning that the electrodes coins cannot be weighted individually, since they are always combined to the melted polymer electrolyte. Thus, averages are taken to back calculate the cells' theoretical capacity and C-rates. To compare the results with the stacking assembly procedure from the previous section, the same cycling procedure is performed. All cells are rested for three days prior to constant rate charging/discharging at C/30 and 40 °C.

5.3.2 Results

Figure 5.4 summarizes the cycling results obtained for the LTO-PEO/LiTFSI-LFP cells with the two different electrode compositions assembled using the melting procedure. The voltage profile is shown once for each electrode composition while the capacity curve represents the average, minimum and maximum values for the three cells.

Figure 5.4: Cycling results for melting procedure LTO-PEO/LiTFSI-LFP cells with two different electrode compositions

The cycling results show the failure of all cells early in the testing procedure. Except for one charge/discharge cycle for electrode composition 1, all cells show steep voltage curves with a high voltage drop when a charge/discharge current is applied. This leads to the premature reaching of the cut-off voltages and thus negligible obtained capacity.

The behavior indicates failure due to a high cell resistance. There are different effects which could have induced this behavior. First of all, when melting the polymer electrolyte on the electrode sheets, the viscous and sticky melted polymer/salt mixture moves due to a change in density. This might have damaged

the electrode/electrolyte interface, since the sticky electrolyte could have separated active material particles from the bulk electrode, inducing particle isolation. Next, it is well-known that gassing of LTO is aggravated by elevated temperatures [142], which might have worsened the electrode/electrolyte contact. Furthermore, the melting of a polymer electrolyte sheet on both electrodes also results in an additional polymer electrolyte/polymer electrolyte interface. This might increase the total resistance of the cell and hinder lithium ion hopping from one electrode to the other. In addition, it is also worth noting that the total polymer electrolyte thickness in this setup is doubled compared to the stacking procedure, since two polymer electrolyte sheets are present in this setup.

5.3.3 Conclusion

For optimizing contact at the electrode/electrolyte interface, it is proposed to melt polymer electrolyte on the electrode sheets. LTO-PEO/LiTFSI-LFP cells were built with this melting assembly procedure and cycled with constant charge/discharge at a C-rate of C/30. The results show early failure of all cells due to a high cell resistance. Different explanations for this were proposed: The sticky melted polymer electrolyte might damage the interface and eventually isolate electrode particles during the fabrication. Additionally, gassing of LTO due to the exposure to higher temperatures might be the issue. Furthermore, the additional polymer electrolyte/polymer electrolyte interface might hinder hopping of lithium-ions from one electrode to the other. Finally, the total electrolyte thickness is doubled, which results in an increased cell resistance and might induce the premature reaching of the cut-off voltages during cycling.

CHAPTER 6

Conclusion

6.1 Summary

To overcome safety concerns and unfavorable stability of liquid electrolytes in conventional LIBs, a unique all-solid chemistry was proposed, consisting of a PEO-based polymer electrolyte with LiTFSI salt, an LTO anode and LFP cathode. This chemistry seems to be tailor-made for biomedical applications, which is why all investigations in this work were performed close to body temperature at 40 °C.

The manufacturing of the polymer electrolyte was investigated in the first part of this work. In order to evaluate the ionic conductivity of the polymer/salt system as one of the critical electrolyte properties, a reproducible way to measure EIS was determined in the beginning. Afterwards, two different approaches for fabricating the polymer electrolyte were tested, a solvent-based procedure and a solvent-free one. Negligible differences in ionic conductivity and mechanical properties between both fabrication methods were obtained. Thus, the less complex and more time efficient solvent-free procedure was taken for the subsequent processing of the polymer electrolyte. Next, the salt concentration in the two component polymer/salt blend was optimized. Polymer electrolyte coins with several molecular ratios of ethylene oxide repeat units to lithium-ions (r) were fabricated. They were investigated regarding their ionic conductivity, processability and assumed wettability at the electrode/electrolyte interface. Based on that, the optimal salt concentration at a temperature of 40 °C was found to be $r = 0.055$. As a possible additive for improving ionic conductivity and mechanical robustness of the polymer electrolyte, nanosized BaTiO₃ filler particles were investigated.

However, the results do not match the enhancing effects as described in the literature, which is likely due to obtained agglomeration of filler particles in this work.

In the second part of this master's thesis, the cycling behavior of the LTO-PEO/LiTFSI-LFP chemistry was investigated. Again, it is important to highlight the testing temperature of 40 °C. This assures a completely solid cell chemistry, but simultaneously induces a bulk electrolyte and interfacial resistance which are order of magnitudes higher compared to frequent investigations of polymer electrolyte cells at 70 to 100 °C from the literature. In spite of these drawbacks, the LTO-PEO/LiTFSI-LFP cells were successfully charged/discharged for more than 25 cycles with a C-rate of C/20. However, the obtained specific capacity of these cells is below 50 mAh/g_{LFP}, which is low compared to the theoretical capacity of 170 mAh/g_{LFP}. Also, all cells show a significant capacity increase in the beginning, followed by a rapid drop. In order to relate this behavior to electrochemical phenomena, further experiments were performed: An impedance investigation on both cycled and stored LTO-PEO/LiTFSI-LFP cells showed that high interfacial resistance due to poor contact at the electrode/electrolyte interface is a major drawback to obtaining higher capacity. Furthermore, it suggests that the capacity increase in the beginning is due to a combination of two phenomena: first, an ongoing surface wetting at the electrode/electrolyte interface until 20 hours after cell assembly; and secondly, deeper penetration of lithium-ions into the bulk electrode due to the formation of additional lithium-ion diffusion pathways during the first cycles. Moreover, it is proposed that the observed capacity drop could either be due to the accumulation of charge carriers in the electrodes, resulting in performance reducing side products, or gassing of LTO, which could damage

the electrode/electrolyte interface. To separate electrode specific effects from the capacity behavior, LTO-PEO/LiTFSI-Li and Li-PEO/LiTFSI-LFP half-cells were investigated. The cycling results show that the phenomena inducing the capacity increase occurs in both electrodes. LTO-half-cells also exhibit the capacity drop, however the short-circuiting of all LFP-half-cells within the first five cycles due to dendritic lithium growth hinders further conclusions. To investigate the bulk electrolyte during cycling, Li-PEO/LiTFSI-Li were tested next. Based on this, it was found that the bulk electrolyte resistance remains unchanged during cycling, proving basic functionality of the polymer electrolyte.

Two approaches for improving the electrolyte/electrode interfacial resistance were proposed in the third part of this work. First, it was suggested to put small quantities of PEO and/or LiTFSI in the electrodes to increase charge transport into the bulk electrode. Results with 2.5 wt.% of PEO and 0.9 wt.% of LiTFSI ($r = 0.055$) showed the highest maximum capacity, but also an accentuated capacity drop compared to electrode equivalents without lithium salt. The maximum capacity was attributed to the increased portion of available active material particles due to additional lithium-ion diffusion pathways in the bulk electrode. However, the insertion of LiTFSI may simultaneously aggravate accumulation of charge carriers in the electrodes, which was proposed to be the underlying phenomena for the capacity drop. Secondly, melting the polymer electrolyte onto the electrode sheets instead of only stacking them together was tested to improve the electrode/electrolyte contact. However, all cells failed early in the cycling procedure. Several explanations for this were suggested, including the increased gassing of LTO at elevated temperatures or the isolation of active material particles during the melting of the polymer electrolyte on the electrodes.

All in all, LTO-PEO/LiTFSI-LFP cells were manufactured by implementing fabrication methods, optimizing compositions for the components and refining an assembly procedure. The ASLIBs successfully cycle at a temperature of 40 °C, but show need for further optimization due to a low and inconsistent capacity. The cycling behavior of these cells was related to several electrochemical phenomena based on impedance measurements and investigations on respective half- and symmetric-cells. In the end, a unique electrode composition and assembly procedure was proposed to optimize interfacial resistance.

6.2 Outlook

In the following, I present my personal recommendations on how to proceed in fabricating the polymer electrolyte, the electrodes and assembling the components together.

For the polymer electrolyte, the solvent-free fabrication procedure with a salt concentration of $r = 0.055$ results in a promising combination of ionic conductivity and mechanical properties for applications at 40 °C. From the results in this work, it seems that the major drawback is interfacial resistance due to poor contact at the electrode/electrolyte interface and not the bulk electrolyte resistance. Although not a priority, further minimizing the electrolyte's resistance would still optimize the system. In order to do that, I would recommend investigating electrolyte additives. For this, two groups should be mentioned: First, small amounts of liquid plasticizers cannot only enhance ionic conductivity, but more importantly, improve contact at the electrode/electrolyte. However, this no longer guarantees a complete solid-state battery. Secondly, filler particles can lead to enhanced ionic conductivity and mechanical robustness while maintaining the unique solid-state characteristic.

The investigation of the electrode composition in this work indicated the potential benefit of having small amounts of polymer electrolyte in the electrode structure. However, inserting electrically insulating PEO/LiTFSI quantities into the electrode simultaneously decreases the already poor electrical conductivity of the LTO and LFP based electrodes. My recommendations for circumventing this issue would be the following, in this order: First, increasing the amount of carbon black in the electrodes. This would be the most straightforward solution. However, raising the weight percentage of one component simultaneously decreases others, possibly requiring other solutions. Second, reducing the electrode thickness would increase electrode/electrolyte contact and decrease lithium-ion diffusion distances. Nevertheless, energy requirements would have to be evaluated since decreasing the electrode coating thickness also reduces cell capacity. Third, nanosizing the active material particles would induce both improved contact and reduced diffusion distances, but complicate fabrication due to their tendency to agglomerate. Finally, active material coatings could enhance the electrical conductivity of the electrodes.

The assembly method is of major importance to reduce interfacial resistance. The used stacking procedure shows advantages in simplicity, but leads to limited electrode/electrolyte contact. As shown, melting the polymer electrolyte on the electrodes leads to other difficulties. Consequently, I would recommend testing a different procedure: assembling the cells by producing a polymer electrolyte solution with the solvent-based fabrication procedure presented in this work, then casting it on the electrode sheets by doctor blading and drying it afterwards. This could result in improved contact at the electrode/electrolyte interface.

APPENDIX A

Modeling Resistive Heating of the Polymer Electrolyte

When a current is passing a battery, heat is generated. This phenomena is referred to as resistive heating of the cell. Due to the high temperature sensibility of polymer electrolytes (PEs), this might influence the performance of ASLIBs. In order to estimate the temperature distribution in the PE film during cell cycling, the resistive heating of the polymer electrolyte film is modeled for a highly simplified battery structure. Although out of the scope of this master's thesis, the results are significant for this project, which is why this modeling work is attached to this thesis.

A.1 Problem Specification

The general layered structure of an ASLIB is shown in Figure A.1(a). For the subsequent modeling, this structure is simplified to consist only of a PE film, as shown in Figure A.1(b). Obviously, this simplification is not close to reality, as

Figure A.1: General and simplified structure of the ASLIB

there is no battery consisting only of a polymer electrolyte. Nevertheless, compared to the other layers of the battery, the PE exhibits lowest electrical as well as thermal conductivity and is the thickest layer in the described set up. This justifies the given simplification to obtain a first estimation of the resistive heating of the polymer electrolyte, as most heat will be generated in this part of the battery. To further specify this heat transfer problem, the polymer electrolyte is described to be a circular disc of thickness $2b$ and diameter d . It is surrounded by air with a constant temperature T_∞ , which is also the initial temperature throughout the polymer electrolyte.

A.2 Calculation

The general energy equation is given by

$$\rho c_v \left[\left(\frac{\partial T}{\partial t} \right) + \mathbf{v} \cdot \nabla T \right] = \hat{r} - \nabla \cdot \mathbf{q} - T \left(\frac{\partial P}{\partial T} \right)_v \nabla \cdot \mathbf{v} + \nabla \mathbf{v} : \underline{\boldsymbol{\tau}} \quad (\text{A.1})$$

where ρ is the material's density, c_v the isochoric heat capacity, T the temperature, $\mathbf{v}$ the velocity, $\hat{r}$ the internal heat generation, $\mathbf{q}$ the specific heat, P the pressure and $\underline{\boldsymbol{\tau}}$ the sheer stress tensor. In the following, it is assumed that the diameter of the PE is large compared to it's thickness ($b \ll d$), and that the heat flux over the cylindrical areas of the PE (at $r = d/2$) is negligible compared to the heat flux over the flat surfaces of the PE (at $x = 0$ and $x = b$). As a consequence, the temperature profile becomes independent of the radius and only depends on the spatial coordinate x and time t , $T = T(x, t)$. In the specified problem, convective heat transport can be neglected, an no compressible work or viscous dissipation takes place. Taking these considerations into account, and also evaluating FOURIER's law

$$\mathbf{q} = -k \nabla T \quad (\text{A.2})$$

where k is the thermal conductivity, the energy equation simplifies to:

$$\rho c_v \frac{\partial T}{\partial t} = \hat{r} + k \frac{\partial^2 T}{\partial x^2} \quad (\text{A.3})$$

The internal heat generation $\hat{r}$ caused by the resistive heating can be described by

$$\hat{r} = \frac{RI^2}{V} = \frac{16I^2}{\pi^2 d^2 \sigma} \quad (\text{A.4})$$

where the material's electrical resistance R is expressed with the ionic conductivity σ to $R = \frac{4b}{\sigma \pi d^2}$, and the PE's volume is $V = \frac{\pi}{4} d^2 b$. To solve the partial, inhomogeneous differential Equation A.3, the temperature profile $T(x, t)$ is separated into a steady state solution $T_{ss}(x)$ and unsteady state part $\theta(x, t)$:

$$T(x, t) = T_{ss}(x) + \theta(x, t) \quad (\text{A.5})$$

The specified problem in Figure A.1(b) is of a symmetric nature. Therefore, the temperature profile is going to show a maximum at $x = 0$. At $x = b$, NEWTON's law of cooling can be evaluated, which then leads to the following two boundary conditions:

$$\text{B.C. 1 (at } x=0\text{):} \quad \frac{\partial T}{\partial x} = 0 \quad (\text{A.6})$$

$$\text{B.C. 2 (at } x=b\text{):} \quad -k \frac{\partial T}{\partial x} = h(T(b) - T_\infty) \quad (\text{A.7})$$

The PE layer is defined to be at the constant environment temperature T_∞ in the beginning, and the initial condition therefore becomes:

$$\text{I.C. (t=0):} \quad T(x, 0) = T_\infty \quad (\text{A.8})$$

A.2.1 Steady State Solution

For the steady state solution, the time derivative in Equation A.3 equals zero. Therefore, the ordinary differential equation

$$\frac{\partial^2 T}{\partial x^2} = -\frac{\hat{r}}{k} = A \quad \text{with: } A = -\frac{16I^2}{\pi^2 d^2 \sigma k} \quad (\text{A.9})$$

needs to be solved, where the cluster of constants A is introduced to shorten writing. After integrating twice, the steady state solution

$$T_{ss} = \frac{A}{2}x^2 + C_1x + C_2 \quad (\text{A.10})$$

is obtained. The constants C_1 and C_2 are calculated by evaluating the boundary conditions given in Equations A.6 and A.7, which gives $C_1 = 0$ and $C_2 = -\frac{kAb}{h} - \frac{Ab^2}{2} + T_\infty$. As a result, the steady state temperature profile of the specified problem is obtained:

$$T_{ss} = \frac{A}{2}x^2 - \frac{kAb}{h} - \frac{Ab^2}{2} + T_\infty \quad \text{with: } A = -\frac{16I^2}{\pi^2 d^2 \sigma k} \quad (\text{A.11})$$

A.2.2 Unsteady State Solution

To obtain the differential equation for the unsteady state solution $\theta(x, t)$, the partial differential Equation A.3 is evaluated with the approach $T(x, t) = T_{ss}(x) + \theta(x, t)$ from Equation A.5:

$$\rho c_v \frac{\partial T}{\partial t} = \hat{r} + k \left(\frac{\partial^2 T_{ss}}{\partial x^2} + \frac{\partial^2 \theta}{\partial x^2} \right) \quad (\text{A.12})$$

where $\frac{\partial^2 T_{ss}}{\partial x^2} = -\frac{\hat{r}}{k}$. As a consequence, a homogeneous partial differential equation is resulting for the unsteady state part of the solution:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 \theta}{\partial x^2} \quad \text{with: } \alpha = \frac{k}{\rho c_v} \quad (\text{A.13})$$

Furthermore, the boundary conditions from Equation A.6 and A.7 can be evaluated using the same approach, which then gives:

$$\text{B.C. 1 (at } x=0\text{): } \left. \frac{\partial \theta}{\partial x} \right|_{x=0} = 0 \quad (\text{A.14})$$

$$\text{B.C. 2 (at } x=b\text{): } \left. \frac{\partial \theta}{\partial x} \right|_{x=b} = -\frac{h}{k} \theta \Big|_{x=b} \quad (\text{A.15})$$

As both spatial boundary conditions are homogeneous, a separation of variables can be used to solve for the unsteady state part of the temperature profile

$$\theta(x, t) = \hat{T}(t) \cdot \hat{X}(x) \quad (\text{A.16})$$

and the partial differential equation becomes:

$$\hat{X} \frac{d\hat{T}}{dt} = \alpha \hat{T} \frac{d^2 \hat{X}}{dx^2} \quad (\text{A.17})$$

If both sides of this equation are divided by $\hat{T}\hat{X}$, the left side only varies with time t and the right side only with position x . This is why both sides have to equal a constant and the functions $\hat{T}(t)$ and $\hat{X}(x)$ can be calculated separately:

$$\frac{1}{\hat{T}} \frac{d\hat{T}}{dt} = \frac{\alpha}{\hat{X}} \frac{d^2 \hat{X}}{dx^2} = -C^2 \quad (\text{A.18})$$

First, the location dependent term $\hat{X}(x)$ with the relative ordinary differential equation

$$\frac{d^2 \hat{X}}{dx^2} + C^{*2} \hat{X} = 0 \quad \text{with: } C^{*2} = \frac{C^2}{\alpha} \quad (\text{A.19})$$

is solved for. The general solution for this equation is

$$\hat{X}(x) = A_k \sin(C^* x) + B_k \cos(C^* x) \quad (\text{A.20})$$

and the constants A_k , B_k and C^* need to be found. Using the separation of variables from Equation A.16, the boundary conditions for the unsteady state solution become:

$$\text{B.C. 1 (at } x=0\text{): } \left. \frac{\partial \hat{X}}{\partial x} \right|_{x=0} = 0 \quad (\text{A.21})$$

$$\text{B.C. 2 (at } x=b\text{): } \left. \frac{\partial \hat{X}}{\partial x} \right|_{x=b} = -\frac{h}{k} \hat{X} \Big|_{x=b} \quad (\text{A.22})$$

Evaluating Equation A.21 with the derivative of the location dependent part of the unsteady state solution

$$\frac{d\hat{X}}{dx} = C^* A_k \cos(C^* x) - C^* B_k \sin(C^* x) \quad (\text{A.23})$$

gives:

$$A_k = 0 \quad (\text{A.24})$$

Taking this into account and evaluating the second boundary condition from Equation A.22 then leads to

$$\tan(C^* b) = \frac{h}{kC^*} \quad (\text{A.25})$$

where both sides can be plotted over C^* and the intercepts will give different solutions C_n^* to this equation:

Figure A.2: Both sides of Equation A.25 plotted over C^* . The intercepts of these curves will give the solutions C_n^* .

Because the constants C_n^* will show up in the exponential term of the total temperature solution (equation A.33), the smallest values for C_n^* will impact the total solution the most. In the following, the smallest five C_n^* are calculated numerically and taken into account for the following calculations. The location dependent part

of the unsteady state solution $\hat{X}(x)$ is therefore approximated by

$$\hat{X}(x) = \sum_{n=1}^5 B_n \cos(C_n^* x) \quad (\text{A.26})$$

It is important to note, that this location dependent term still depends on the constants B_n , and the initial condition needs to be evaluated after setting the total solution together to eliminate it.

Second, the time dependent part $\hat{T}(t)$ of the unsteady state solution needs to be calculated with the differential equation

$$\frac{d\hat{T}}{dt} + \hat{T}C^2 = 0 \quad \text{with: } C^2 = \alpha C_n^{*2} \quad (\text{A.27})$$

After separating the two variables $\hat{T}$ and t , both sides of this equation can be integrated, which then gives:

$$\hat{T}(t) = \sum_{n=0}^{\infty} D_n \exp(-\alpha C_n^{*2} t) \quad (\text{A.28})$$

Replacing the product of the constants B_n and D_n with E_n and only accounting for the first five terms, the unsteady state part of the solution can be described by:

$$\theta(x, t) = \sum_{n=1}^5 E_n \exp(-\alpha C_n^{*2} t) \cos(C_n^* x) \quad (\text{A.29})$$

The initial condition of the unsteady state solution is obtained by evaluating Equation A.8 with the solution approach $T(x, t) = T_{ss}(x) + \theta(x, t)$:

$$\text{I.C. (t=0):} \quad \theta(x, 0) = T_{\infty} - T_{ss}(x) \quad (\text{A.30})$$

Using the relation for the unsteady state solution to evaluate $\theta(x, 0)$ and inserting the steady state solution T_{ss} , the equation becomes

$$\sum_{n=0}^{\infty} E_n \cos(C_n^* x) = -\frac{A}{2}x^2 + \frac{kAb}{h} + \frac{Ab^2}{2} \quad (\text{A.31})$$

By multiplying both sides of this equation with $\cos(C_n^*x)$ and integrating from 0 to b, the summation term can be simplified to the integral of $E_n \cos^2(C_n^*x)$ from 0 to b. Dividing through this integral then gives the formulas for E_n :

$$E_n = \frac{\int_0^b \left(-\frac{A}{2}x^2 + \frac{kAb}{h} + \frac{Ab^2}{2} \right) \cos(C_n^*x) dx}{\int_0^b \cos^2(C_n^*x) dx} \quad (\text{A.32})$$

A.2.3 Total Solution

The total solution is obtained by summing up the steady state solution from Equation A.11 with the unsteady state solution from Equation A.29. Only accounting for the first five terms, this then gives

$$T(x, t) = \frac{A}{2}x^2 - \frac{Ab}{2}x - \frac{kAb}{2h} + T_\infty + \sum_{n=1}^{\infty} E_n \exp(-\alpha C_n^{*2}t) \cos(C_n^*x) \quad (\text{A.33})$$

where E_n can be found from Equation A.32, C_n from numerically solving for the intercepts in Figure A.2 and $A = -\frac{16I^2}{\pi^2 d^2 \sigma k}$.

A.3 Simulation

The calculated equations are implemented and then simulated with Matlab[®]. Table A.1 summarizes the different assumed parameter values for a system with a polymer electrolyte that is based on poly(ethylene oxide) (PEO) as the polymer backbone and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt. Due to a lack of experimental data, different inaccuracies of the chosen parameter values have to be mentioned. The isochoric heat capacity was assumed based on a study by VILLANNO et al. [143] that investigated the isobaric heat capacity of a PEO/LiBETI polymer electrolyte. Therefore, the influence of the different salt chemistry and the difference between isochoric and isobaric heat capacity is neglected here. The heat transfer coefficient of air is dependent on the exact cooling conditions in the experiment and is assumed to be 10 W/m² K in this

Table A.1: Parameters for a system with a PEO/LiTFSI polymer electrolyte (PE) at 313.15 K

parameter	symbol	value	unit
isochoric heat capacity of the PE	c_v	1700 ^[143]	J/kg K
heat transfer coefficient of air	h	10 ^[144]	W/m ² K
thermal conductivity of the PE	k	0.1626 ^[145]	W/m K
ionic conductivity of the PE	σ	10 ⁻⁴	S/cm
density of the PE	ρ	900	kg/m ³

specific problem. The thermal conductivity of the PE is chosen based on a study of SONG et al. [145] for a PEO/LiTFSI system. The electrical conductivity and density of the polymer electrolyte were measured at the temperature of 40 °C in own experiments.

The geometry of the polymer electrolyte and cycling conditions for the first simulation are summarized in Table A.2. They are chosen to represent the experimental conditions in this master's thesis.

Table A.2: Geometry and cycling conditions for the system, representing experimental conditions in this master's thesis

parameter	symbol	value	unit
thickness of the PE	b	300	μm
diameter of the PE	d	15	mm
current	I	0.05	mA
surrounding air temperature	T_∞	313.15	K

The steady state solution gives a quadratic temperature profile with a maximum in the middle of the polymer electrolyte, as shown in Figure A.3(a). The total temperature profile at different time points is plotted in Figure A.3(b).

Figure A.3: Temperature profile for the experimental conditions from this master's thesis specified in Table A.2

Qualitatively, the quadratic profile of the steady state solution is expected, as heat is generated throughout the polymer electrolyte, but cooling only takes place at the edges of the film. Quantitatively, only a negligible temperature increase is observed compared to the constant environment temperature of $T_{\infty}=313.15$ K for the given parameters. This is due to the very low chosen current of $I=0.05$ mA, which is why the heat production in the extremely thin polymer electrolyte sheet is small. The total solution starts at the initial temperature $T_{\infty} = 313.15$ K, and then converges against the steady state solution with increasing time. Although the temperature profiles seem to be straight lines on the first view in this figure, it is important to note that the curves are of a quadratic nature for $t > 0$.

Figure A.4 shows the steady state solution for the variation of several parameters. A higher current increases the resistive heating and consequently rises the temperature profile (Figure A.4(a)). One possible way to counteract a rising temperature at a high current is to decrease the thickness of the polymer electrolyte film, as shown in Figure A.4(b). As illustrated in this diagram, a thinner

Figure A.4: Steady state solution for the variation of several parameters. The values of the not varied parameters are $I=10$ mA, $b=150$ μm , $\sigma=10^{-4}$ S/cm and $T_{inf}=40$ $^{\circ}\text{C}$

polymer electrolyte would reduce the heat production and therefore decrease the temperature curve inside the film. Figure A.4(c) underlines the sensitivity of the temperature profile to the ionic conductivity of the polymer electrolyte: A higher conductivity would decrease the electrical resistance of the electrolyte and therefore reduce the heat generation. The surrounding air temperature determines the average values of the temperature profiles (Figure A.4(d)).

A.4 Conclusion

The temperature profile in the polymer electrolyte of a cycling ASLIB was modeled. In order to reduce complexity of the system, the battery's structure was simplified to only consist of the polymer electrolyte film. The general approach of the calculation is based on the unsteady state energy equation with an internal heat generation term due to resistive heating. This gives an inhomogeneous partial differential equation, which is solved by separating the total temperature profile in a steady state and unsteady state part. Simulations were performed in Matlab[®] with estimated parameters for a PEO/LiTFSI polymer electrolyte at 40 °C. The steady state solution is of quadratic nature with a maximum in the middle of the polymer electrolyte, which fits with expectations. For the experimental conditions used in this master's thesis, no significant temperature increase is obtained with this model. However, when the current is raised, the polymer electrolyte is warming up quickly due to increased resistive heating. This effect can be counteracted efficiently by reducing the thickness or increasing the conductivity of the polymer electrolyte sheet.

APPENDIX B

Supplementary Material for the Polymer Electrolyte's Ionic Conductivity Measurements in Chapter 3

The following sections present the measured bulk electrolyte resistances R_b (in form of the lower frequency minimums in the impedance curves obtained from EIS) and the measured film thicknesses. Both are necessary for the calculation of the in Chapter 3 presented polymer electrolyte ionic conductivity curves.

B.1 Supplementary Material for Section 3.3

Figure B.1: Bulk electrolyte resistances obtained from EIS for the different fabrication procedures as a function of temperature

Figure B.2: Film thicknesses for the polymer electrolytes obtained from the different fabrication procedures as a function of temperature

B.2 Supplementary Material for Section 3.4

Figure B.3: Bulk electrolyte resistances obtained from EIS as a function of salt concentration for 20 °C and 40 °C

Figure B.4: Film thicknesses for the polymer electrolyte coins as a function of salt concentration

B.3 Supplementary Material for Section 3.5

Figure B.5: Bulk electrolyte resistances obtained from EIS as a function of BaTiO₃ mass fraction for 20 °C and 40 °C

Figure B.6: Film thicknesses for the polymer electrolyte coins obtained from the different fabrication procedures as a function of BaTiO₃ mass fraction for 20 °C and 40 °C

APPENDIX C

Supplementary Material for the Cell Cycling in Chapter 4 and 5

The following Tables C.1 to C.5 present the cell specifications for Chapter 4 and 5. Consistently, anode diameter is 15 mm and cathode diameter 14 mm. Based on the active material percentage of the electrodes and an average weight of the respective current collector discs, the active material weight in each composite electrode can be back calculated. This is then taken to calculate the cell's theoretical capacity based on the limiting electrode, and the anode-to-cathode capacity ratio. Specific theoretical capacity for LFP is 170 mAh/g and for LTO 175 mAh/g.

Table C.1: Cell specifications for the LTO-PEO/LiTFSI-LFP cells from Section 4.3

cell #	LFP weight / mg	LTO weight / mg	theoretical capacity / mAh	capacity ratio
#1	5.1	5.6	0.867	1.14
#2	5.1	5.8	0.867	1.17
#3	5.1	5.5	0.867	1.12

Table C.2: Cell specifications for the LTO- and LTP-half-cells from Section 4.4

cell #	active material weight / mg	theoretical capacity / mAh
LTO-half-cell #1	5.82	0.99
LTO-half-cell #2	5.82	0.99
LTO-half-cell #3	5.82	0.99
LFP-half-cell #1	5.37	0.91
LFP-half-cell #2	5.37	0.91
LFP-half-cell #3	4.92	0.84

Table C.3: Cell specifications for the LTO-EC/EMC/LiTFSI-LFP liquid electrolyte cells from Section 5.2

electr. comp.	LFP weight / mg	LTO weight / mg	theoretical capacity / mAh	capacity ratio
1	5.1	5.5	0.867	1.12
2	8.3	9.8	1.41	1.21
3	7.0	9.0	1.180	1.30

Table C.4: Cell specifications for the LTO-PEO/LiTFSI-LFP cells with the three different electrode compositions from Section 5.2

electr. comp. / cell #	LFP weight / mg	LTO weight / mg	theoretical capacity / mAh	capacity ratio
1 / #1	7.8	9.0	1.30	1.20
1 / #2	7.9	9.0	1.30	1.18
1 / #3	7.9	9.0	1.30	1.18
2 / #1	7.6	9.5	1.30	1.28
2 / #3	7.6	9.6	1.30	1.29
3 / #1	7.3	9.1	1.25	1.28
3 / #2	7.3	9.1	1.25	1.28
3 / #3	7.6	9.1	1.30	1.22

Table C.5: Specification averages for the LTO-PEO/LiTFSI-LFP cells assembled with the melting procedure from Section 5.3

electr. comp.	LFP weight / mg	LTO weight / mg	theoretical capacity / mAh	capacity ratio
1	7.7	9.3	1.31	1.24
2	7.7	9.5	1.30	1.27

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