Functional Polymer Electrolytes for Multidimensional All-Solid-State Lithium Batteries

BING SUN
Abstract

Pressing demands for high power and high energy densities in novel electrical energy storage units have caused reconsiderations regarding both the choice of battery chemistry and design. Practical concerns originating in the conventional use of flammable liquid electrolytes have renewed the interests of using solvent-free polymer electrolytes (SPEs) as solid ionic conductors for safer batteries.

In this thesis work, SPEs developed from two polymer host structures, polyethers and polycarbonates, have been investigated for all-solid-state Li- and Li-ion battery applications. In the first part, functional polyether-based polymer electrolytes, such as poly(propylene glycol) triamine based oligomer and poly(propylene oxide)-based acrylates, were investigated for 3D-microbattery applications. The amine end-groups were favorable for forming conformal electrolyte coatings onto 3D electrodes via self-assembly. In-situ polymerization methods such as UV-initiated and electro-initiated polymerization techniques also showed potential to deposit uniform and conformal polymer coatings with thicknesses down to nano-dimensions.

Moreover, poly(trimethylene carbonate) (PTMC), an alternative to the commonly investigated polyether host materials, was synthesized for SPE applications and showed promising functionality as battery electrolyte. High-molecular-weight PTMC was first applied in LiFePO$_4$-based batteries. By incorporating an oligomeric PTMC as an interfacial mediator, enhanced surface contacts at the electrode/SPE interfaces and obvious improvements in initial capacities were realized. In addition, room-temperature functionality of PTMC-based SPEs was explored through copolymerization of ε-caprolactone (CL) with TMC. Stable cycling performance at ambient temperatures was confirmed in P(TMC/CL)-based LiFePO$_4$ half cells (e.g., around 80 and 150 mAh g$^{-1}$ at 22 °C and 40 °C under C/20 rate, respectively). Through functionalization, hydroxyl-capped PTMC demonstrated good surface adhesion to metal oxides and was applied on non-planar electrodes. Ionic transport behavior in polycarbonate-SPEs was examined by both experimental and computational approaches. A coupling of Li ion transport with the polymer chain motions was demonstrated.

The final part of this work has been focused on exploring the key characteristics of the electrode/SPE interfacial chemistry using PEO and PTMC host materials, respectively. X-ray photoelectron spectroscopy (XPS) was used to get insights on the compositions of the interphase layers in both graphite and LiFePO$_4$ half cells.

Keywords: Polymer electrolyte, Li-battery, 3D-microbattery, Functionalization, Polyether, Polycarbonate, Copolymer

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To the wandering time and those comforting my heart
List of Papers

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I. Solid polymer electrolyte coating from a bifunctional monomer for three-dimensional microbattery applications
Sun, B., Liao, I-Y., Tan. S., Bowden, T., Brandell, D.

II. Electrodeposition of thin poly(propylene glycol) acrylate electrolytes on 3D-nanopillar electrodes
Sun, B., Rehnlund, D., Lacey J. M., Brandell, D.

III. Hydroxyl-functionalized poly(trimethylene carbonate) electrolytes for 3D-electrode configurations
Mindemark, J., Sun, B., Brandell, D.
Submitted to Polymer Chemistry.

IV. Fabrication of 3D microbatteries using solid polymer electrolytes
Sun, B., Brandell, D.
In manuscript.

V. Polycarbonate-based solid polymer electrolytes for Li-ion batteries
Sun, B., Mindemark, J., Edström, K., Brandell, D.

VI. Realization of high performance polycarbonate-based Li-ion polymer batteries
Sun, B., Mindemark, J., Edström, K., Brandell, D.
VII. **High-performance solid polymer electrolytes for lithium batteries operational at ambient temperature**
Mindemark, J., Sun, B., Törmä, E., Brandell, D.
Submitted to *Chemistry of Materials*.

VIII. **Ion transport in polycarbonate-based solid polymer electrolytes: experimental and computational investigations**
Sun, B., Mindemark, J., Morozov, E., Costa, L., Fang, Y., Bergman, M., Johansson, P., Furó, I., Brandell, D.
In manuscript.

IX. **Interface layer formation in solid polymer electrolyte lithium batteries: an XPS study**
Xu, C., Sun, B., Gustafsson T., Edström, K., Brandell D., Hahlin, M.

X. **At the polymer electrolyte interfaces: the role of the polymer host for interphase layer formation in Li-batteries**
Sun, B., Xu, C., Mindemark, J., Gustafsson, T., Edström, K., Brandell, D.
Submitted to *Journal of Materials Chemistry A*.

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Papers not included in the thesis

Tailoring the conductivity of PEO-based electrolytes for temperature-sensitive printed electronics
Sun, B., Tehrani, P., Robinson, N., Brandell, D.

Electrochemical elaboration of electrodes and electrolytes for 3D structured batteries
Valvo, M., Roberts, M., Oltean, G., Sun, B., Rehnlund, D., Brandell, D., Nyholm, L., Gustafsson, T., Edström, K.

Polymer-ionic liquid ternary systems for Li-battery electrolytes: molecular dynamics studies of LiTFSI in an EMIM-TFSI and PEO blends
Costa, L., Sun, B., Jeschull, F., Brandell, D.
Submitted to *Journal of Chemical Physics*.

Copolymers of trimethylene carbonate and ε-caprolactone as electrolytes for lithium-ion batteries
Mindemark, J., Törmä, E., Sun, B., Brandell, D.

LiTFSI-PMMA:PEGMA graft copolymer electrolytes for high temperature Li-battery applications
Bergman, M., Bergfelt, A., Sun, B., Bowden, T., Brandell, D., Johansson, P.
My contribution to the appended papers

I. Involved in planning, performed major part of the experiments, major contribution to discussions and writing of the manuscript.

II. Major contributions to planning, all experiments, involved in all discussions and writing of the manuscript.

III. Involved in planning, performed parts of the characterizations, involved in discussions and writing of the manuscript.

IV. Major contributions to planning, performed all experiments, major involvement in discussions and writing of the manuscript.

V. Involved in planning, performed characterization and electrochemical measurements, involved in discussions and writing of the manuscript.

VI. Major contributions to planning, experiments, involved in all discussions and writing of the manuscript.

VII. Involved in planning, performed electrochemical measurements, involved in discussions and writing of the manuscript.

VIII. Major contributions to planning, performed electrochemical measurements, major involvement in discussions and writing of the manuscript.

IX. Involved in planning and experiments, discussions and writing of the manuscript.

X. Major contributions to planning, experiments, discussion and writing of the manuscript.

Disclaimer: Part of this thesis is based on my licentiate thesis entitled Fabrication of Polymer Electrolytes for 3D-Microbatteries (Uppsala University, 2013).
Contents

1. Introduction ........................................................................................................... 15

2. Polymer Electrolytes .......................................................................................... 19
   2.1 Ionic conduction in polymer electrolytes .............................................. 20
   2.2 Li-ion polymer batteries ..................................................................... 24
   2.3 From 2D to 3D battery designs ......................................................... 27
   2.4 Polycarbonate as an alternative polymer host .................................... 32
   2.5 At the electrode/polymer electrolyte interfaces .................................. 34

3. Methodology ........................................................................................................... 37
   3.1 Polymer functionalization ..................................................................... 37
      3.1.1 Functional side-groups ................................................................ 37
      3.1.2 Copolymerization ..................................................................... 39
   3.2 Fabrication of solid polymer electrolytes ............................................. 40
      3.2.1 Solution-casting ......................................................................... 41
      3.2.2 UV-initiated polymerization ..................................................... 41
      3.2.3 Electro-initiated polymerization ............................................... 42
   3.3 Materials Characterization ....................................................................... 44
      3.3.1 Vibrational spectroscopy ............................................................ 44
      3.3.2 Nuclear Magnetic Resonance spectroscopy ................................ 45
      3.3.3 Electrochemical impedance spectroscopy .................................. 47
      3.3.4 Cyclic voltammetry .................................................................... 49
      3.3.5 Thermal analysis ....................................................................... 50
      3.3.6 Morphological analysis .............................................................. 50
      3.3.7 X-ray photoelectron spectroscopy .............................................. 51

4. Results and Discussion ....................................................................................... 54
   4.1 Solid polymer electrolytes for 3DMBs (Papers I-IV) ......................... 54
      4.1.1 In-situ polymerized electrolytes on 3D substrates ...................... 54
      4.1.2 Polymerization conditions and cell assembly ............................. 57
      4.1.3 Functionalized polycarbonates ............................................... 60
   4.2 Polycarbonate-based thin-film Li-batteries (Papers V-VIII) ............... 63
      4.2.1 Poly(trimethylene carbonate) homopolymers ........................... 63
      4.2.2 Copolymers of poly(trimethylene carbonate) ........................... 65
   4.3 Interfacial chemistry of polymer electrolytes (Papers IX-X) .......... 66
      4.3.1 SEI formation at anode/polymer electrolyte interfaces ............. 67
      4.3.2 SPI formation at cathode/polymer electrolyte interfaces .......... 68
Abbreviations and symbols

ATR  attenuated total reflectance
BETI  bis(perfluoroethylsulfonyl)imide
BSE  backscattered electron
CE  counter electrode
CL  ε-caprolactone
CPE  composite polymer electrolyte
CV  cyclic voltammetry
DSC  differential scanning calorimetry
DMC  dimethylene carbonate
EC  ethylene carbonate
EDS  energy-dispersive X-ray spectroscopy
EIS  electrochemical impedance spectroscopy
ESCA  electron spectroscopy for chemical analysis
ESW  electrochemical stability window
EO  ethylene oxide
FEA  finite element analysis
FTIR  fourier-transform infrared spectroscopy
FTO  fluorine-doped tin oxide
GP  galvanostatic polarization
GPE  gel polymer electrolyte
HPE  hybrid polymer electrolyte
LiBOB  lithium bis(oxalato)borate
LiPON  lithium phosphorous oxynitride
Li-poly  Li-ion polymer battery
LiTFSI  lithium bis(trifluoromethanesulfonyl)imide
LSV  linear sweep voltammetry
NMR  nuclear magnetic resonance
MB  microbattery
MD  molecular dynamics
MEMS  microelectromechanical
Mw  molecular weight
PAN  poly(acrylonitrile)
PANI  polyaniline
PCL  poly(ε-caprolactone)
PE  polyethylene
PEA  glycercyl poly(oxypropylene) triamine
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>PEGDME</td>
<td>poly(ethylene glycol) dimethyle ether</td>
</tr>
<tr>
<td>PEO</td>
<td>poly(ethylene oxide)</td>
</tr>
<tr>
<td>PGSE</td>
<td>pulsed-gradient-spin-echo</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly(methylmethacrylate)</td>
</tr>
<tr>
<td>PO</td>
<td>propylene oxide</td>
</tr>
<tr>
<td>PP</td>
<td>polypropylene</td>
</tr>
<tr>
<td>PPGDA</td>
<td>poly(propylene glycol) diacrylate</td>
</tr>
<tr>
<td>PPO</td>
<td>poly(propylene oxide)</td>
</tr>
<tr>
<td>PTMC</td>
<td>poly(trimethylene carbonate)</td>
</tr>
<tr>
<td>PVdF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>rf</td>
<td>radio frequency</td>
</tr>
<tr>
<td>RDF</td>
<td>radical distribution function</td>
</tr>
<tr>
<td>RE</td>
<td>reference electrode</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>RVC</td>
<td>reticulated vitreous carbon</td>
</tr>
<tr>
<td>SEI</td>
<td>solid electrolyte interphase</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SPE</td>
<td>solid polymer electrolyte</td>
</tr>
<tr>
<td>SPI</td>
<td>solid permeable interphase</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMC</td>
<td>trimethylene carbonate</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>$V_{OC}$</td>
<td>open circuit voltage</td>
</tr>
<tr>
<td>VTF</td>
<td>Vogel-Tammann-Fulcher</td>
</tr>
<tr>
<td>WE</td>
<td>working electrode</td>
</tr>
<tr>
<td>WLF</td>
<td>Williams-Landel-Ferry model</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>surface area</td>
</tr>
<tr>
<td>a</td>
<td>asymmetric vibration</td>
</tr>
<tr>
<td>B</td>
<td>activation energy</td>
</tr>
<tr>
<td>$B_0$</td>
<td>magnetic field</td>
</tr>
<tr>
<td>$C_{dl}$</td>
<td>double-layer capacitance</td>
</tr>
<tr>
<td>$C_g$</td>
<td>electrolyte capacitance</td>
</tr>
<tr>
<td>$D_+,$</td>
<td>ionic diffusion coefficient</td>
</tr>
<tr>
<td>$E_a,$</td>
<td>activation energy</td>
</tr>
<tr>
<td>$E_k,$</td>
<td>kinetic energy</td>
</tr>
<tr>
<td>$E_b,$</td>
<td>binding energy</td>
</tr>
<tr>
<td>$I_0,$</td>
<td>initial current</td>
</tr>
<tr>
<td>$I_{ss}$</td>
<td>steady-state current</td>
</tr>
<tr>
<td>$l,$</td>
<td>thickness</td>
</tr>
<tr>
<td>j</td>
<td>imaginary number</td>
</tr>
</tbody>
</table>
\( r \) \quad \text{hydrodynamic radius}
\( R_b \) \quad \text{bulk resistance}
\( R_0 \) \quad \text{initial resistance}
\( R_{ss} \) \quad \text{steady-state resistance}
\( R_t \) \quad \text{decoupling index}
\( t^\pm \) \quad \text{transference number}
\( T_c \) \quad \text{crystalline temperature}
\( T_D \) \quad \text{decomposition temperature}
\( T_g \) \quad \text{glass transition temperature}
\( T_m \) \quad \text{melting temperature}
\( T_1 \) \quad \text{spin-lattice relaxation}
\( T_2 \) \quad \text{spin-spin relaxation}
\( Z'' \ (Z_{lm}) \) \quad \text{imaginary impedance}
\( Z' \ (Z_{Re}) \) \quad \text{real impedance}
\( \Delta H_m \) \quad \text{heat of fusion from a crystalline phase}
\( \Lambda \) \quad \text{molar conductivity}
\( \Phi \) \quad \text{working function}
\( \nu \) \quad \text{stretching vibration}
\( \delta \) \quad \text{bending vibration}
\( \sigma \) \quad \text{conductivity}
\( \varepsilon \) \quad \text{dielectric constant}
\( \mu_i \) \quad \text{mobility of charge carriers}
\( \mu^\pm \) \quad \text{ion mobility}
\( c_i \) \quad \text{concentration of charge carriers}
\( q_i \) \quad \text{charge}
\( \eta \) \quad \text{viscosity}
\( \tau \) \quad \text{time duration}
\( \tau_{\sigma} \) \quad \text{conductivity relaxation time}
\( \tau_s \) \quad \text{structural relaxation time}
\( w_i \) \quad \text{weight fraction}
1. Introduction

*All the art of living lies in a fine mingling of letting go and holding on.*  
-Henry Ellis

Electrical energy storage has become one of the major issues in renewable and sustainable energy research for many different applications, ranging from small-scale microelectronics to large-scale electric supply for vehicles and stationary grids. As a key pathway to limit petroleum consumption and carbon dioxide emissions, political incentives and R&D initiatives now aim for advanced energy storage solutions optimized for grid-ready storage by the years 2015-2016 in the near term, and to tackle the worldwide energy crisis in the longer term.\(^1\)

![Figure 1. Comparison of different commercial rechargeable batteries in terms of the gravimetric power and energy densities. Redrawn from ref. 2.](image)

If comparing the rechargeable battery chemistries on the commercial market (illustrated in Fig. 1), the superior gravimetric and volumetric energy densities of Li-ion batteries have established their dominating role in consumer electronics.\(^2-5\) In recent years, pressing demands to power electric vehicles and smart grids have been generating a new development towards batteries with improved safety and more reliable overall performance.\(^4-6\) New commercial electrode materials (*e.g.*, with lithium titanate anodes and lithium-iron phosphate cathodes) have indeed prompted commercial batter-
ies with largely improved cycling stability at high charge/discharge rates.\(^7,^8\)

Also high-voltage batteries, using for example lithium-nickel-manganese-cobalt or lithium-nickel-cobalt-aluminum oxide cathodes, are attractive for high energy supplies.\(^9\) In parallel, development of electrolytes with improved safety, stability and compatibility with a wide range of electrodes are frontier demands for the next generation of batteries.\(^3,^6,^10,^11\) Since safety hazards are generally associated with the flammable and volatile liquid components in conventional liquid electrolytes, extensive interest has been focused on the development of battery systems using inflammable electrolytes or introducing functional additives (e.g., flame retardant, solid electrolyte interphase stabilizer) to suppress unwanted side-reactions.\(^12–^16\) In addition to intrinsically stable battery components, formation of stable passivation layers at the electrode/electrolyte interfaces has shown to be critical for capacity retention and long-term stability\(^17,^18\).

Table 1. A comparison of different electrolyte systems for commercial Li-ion batteries.

<table>
<thead>
<tr>
<th>Category</th>
<th>Liquid electrolyte(^15,^19)</th>
<th>Gel electrolyte(^20)</th>
<th>Ceramic electrolyte(^10)</th>
<th>Solvent-free polymer electrolyte(^11,^21,^22)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical stability window (oxidation)</td>
<td>Up to 4-5V Down to 1.3V</td>
<td>Up to 4-5V Down to 1.0V</td>
<td>Up to 8V Down to -1V</td>
<td>Up to 5V Down to 0.5V</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>Poor</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Mechanical stability</td>
<td>Poor</td>
<td>Poor</td>
<td>Hard, brittle</td>
<td>Flexible, ductile</td>
</tr>
<tr>
<td>Flexibility</td>
<td>Low</td>
<td>Low-medium</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Ionic conductivity at room temperature</td>
<td>High</td>
<td>Medium-high</td>
<td>Medium-high</td>
<td>Low</td>
</tr>
<tr>
<td>Example</td>
<td>LiPF(_6) in EC:DMC 1:1</td>
<td>LiClO(_4) in EC/PC soaked in PMMA</td>
<td>Li(_2)S-P(_2)S(_5)</td>
<td>PEO/LiTFSI (+SiO(_2))</td>
</tr>
<tr>
<td>Remark on practical use (safety)</td>
<td>Flammable</td>
<td>Flammable</td>
<td>Non-flammable</td>
<td>Non-flammable</td>
</tr>
</tbody>
</table>

Light-weight and cost-effective materials with simple fabrication approaches for manufacturing are necessary for commercialization of rechargeable batteries. The development of solid-state and flexible ionic conductors constitutes a great potential to generate a significant step forward towards safe batteries with flexible designs.\(^23–^25\) As indicated in Table 1, solvent-free polymer electrolytes are strong candidates for building all-solid-state batteries which offer a simplified design with good dimensional stability and durability for practical use. Given their promising properties in terms of electrochemical and thermal stability, the ionic conductivity at ambient temperature in solid polymer electrolytes remains a challenging obstacle. Most of their applications have therefore been intended for high temperature,
high voltage or low-current battery applications, also with niche implementations for Li metal batteries.\textsuperscript{26–31} It is worth to note that another class of solid electrolytes, ceramic electrolytes (e.g., ß-Alumina, Li\textsubscript{2}S-P\textsubscript{2}S\textsubscript{5}), has also drawn great interests, especially for high-temperature battery applications.\textsuperscript{11,32} Considering the brittleness in ceramics and glasses, however, the inferior flexibility of these materials have to be tackled to accommodate the volume changes in the electrodes or against an external shock.

Demands for battery down-scaling to micro-dimensions for miniature portable electronics, such as micro-electromechanical systems (MEMS), smart cards, micro-medical implants and remote sensors, address new challenges in battery design and fabrication.\textsuperscript{33–35} To catch up with the successful development of novel micro-devices, growing attention has been drawn to materials fabrications for new batteries with multidimensional architectures. The realization of microbatteries (MBs) provides a test bed for 3D architectures as novel battery designs. Several reviews of the field presents a great variety of inspirational ideas on component design and manufacturing.\textsuperscript{34–43} As demonstrated in Fig. 2, conventional Li-ion batteries containing liquid electrolytes commonly employ thin-film battery components in a 2D (planar) design. There are, however, great possibilities to achieve more than 10 times higher areal capacities in 3DMBs than in 2D design, enabling a multifold increase in both power and energy densities via enhancement of the active surface area of the electrodes.\textsuperscript{43,38,44} The transition from 2D to 3D architectures promises great technical progress not only for powering micro-sized devices, but may also result in discoveries and innovations transferable to applications of more conventional dimensions.\textsuperscript{45} But challenges remain in the development of suitable electrolytes and appropriate routes to integrate the respective cell component into all-solid-state 3D configurations.

Figure 2. Schematic illustrations of a conventional 2D battery design using liquid electrolyte (left) and an all-solid-state 3D battery design using solid electrolyte (right).

The scope of this thesis work has been to develop suitable solid polymer electrolytes (SPEs) which can function in all-solid-state Li and Li-ion batteries, from small-scale to large-scale applications. The research strategies employed here have primarily focused on three aspects: synthesizing novel
functional monomers and polymer electrolytes (Paper I, III, VII, VIII), exploring optimized approaches for electrolyte fabrication (Paper II, IV-VI) and revealing the interfacial chemistry at the electrode/SPE interfaces in Li polymer batteries (Paper IX, X).

Section 2 in this thesis addresses the key features in polymer electrolytes, in particularly SPEs, and some major concerns for their implementation to the emerging Li polymer batteries (Section 2.2) and 3D-microbatteries (Section 2.3). A promising polymer host material, polycarbonate, has been explored as an alternative to the dominating polyether host materials for solid ion conductors (Section 2.4). Moreover, the formation of passivation layers at the electrode/SPE interfaces, which may restrict cycling stability and capacity retention, have been addressed in Section 2.5.

In Section 3, the major methodologies utilized in the included papers for polymer electrolyte design, characterization and fabrication are presented. Targeted for non-planar substrates, i.e., both thin-film composite and 3D electrodes, functionalized monomer and polymers derived from either poly(propylene oxide) (PPO) or poly(trimethylene carbonate) (PTMC) polymer backbones have been developed (Section 3.1). Thin and uniform polymer electrolyte coatings with thicknesses ranging from micro- to nano-regimes could be achieved via in-situ polymerization methods (Section 3.2). Characterization techniques employed for polymer electrolyte analysis and cell investigations are described in Section 3.3.

Key results from the included papers are summarized in Section 4, divided according to the different research focuses. Section 4.1 describes the solvent-free polymer electrolyte systems which have potential application in 3DMBs (Paper I-IV). The studies comprising SPEs intended for the broader application area of thin-film Li polymer batteries, i.e., using PTMC and/or its derivatives (e.g., oligomer PTMC or copolymers of TMC and ε-caprolactone), are summarized in Section 4.2. Here, cell optimization for enhanced cycling performance at both elevated and room temperatures are realized (Paper V-VIII). Finally, the results of the investigations at the electrode/SPE interfaces are presented in Section 4.3. A brief comparison is made between poly(ethylene oxide) (PEO) and PTMC-based SPE system for LiFePO₄ and graphite cells after short-term electrochemical cycling (Paper IX, X).
2. Polymer Electrolytes

*The farther backward you can look, the farther forward you can see.*
-Winston Churchill

Polymers, which are derived from their subunits – monomers – are found widely in nature but can also be artificially synthesized for a wide range of applications in the fields of bioscience, materials chemistry and engineering. In contrary to small molecules in liquid and gas phases, polymers are composed of long chains of covalently bonded repeating units, generating macromolecules. Due to their high molecular weight, polymers generally behave like solids, but do as such display unique characteristics in for example toughness and viscoelasticity, generating great flexibility and durability in processing and practical use. The chemical and physical properties of polymers could be significantly influenced by the chemical composition of the repeating unit and the functional end groups, the number of chemically active sites, as well as the shape of the polymer chains. Therefore, this allows great possibilities to tailor polymers with multi-functionality through controlled polymer synthesis and chemical modifications.

After ionic conduction in oligomer-salt complexes was first discovered in a (CH$_2$CH$_2$O)$_n$-HgCl$_2$ complex in the 1960s,$^{46}$ pioneering studies on polymer electrolytes was initiated by P. V. Wright et al. and M. Armand et al. on macromolecular complexes of PEO and alkali metal salts in 1970s.$^{47,48}$ Polymer electrolytes span a wide range of materials, very different in chemical and physical nature depending on the applications they are made for.$^{49-51}$ For example, there are significant differences in polymer electrolytes for batteries and for fuel cells, where the latter are loaded with solvent, generally highly acidic and forms tough membranes. The major differences among polymer electrolytes depend on the most crucial properties of interest. In most cases, ionic conductivity is of highest importance, while polymer electrolytes for fuel cells also have to fulfill major requirements on tolerance towards gas permittivity and water retention.$^{49}$ There are also related systems, generally referred to as polyelectrolytes, which comprise complexes with charged and immobilized cations or anions covalently bonded with the polymer.$^{49}$ In this thesis work, the focus is primarily on Li-ion conductive polymer electrolytes, i.e., a Li salt dissolved in a polymer matrix.

The key components in a polymer electrolyte are a polymer host and a salt. A polymer with a high dielectric constant – and a good electronic insu-
lator – behaves as an ‘immobile solvent’, and should be capable of strong coordination with the relevant cations (e.g., Li\(^+\), Na\(^+\), Mg\(^{2+}\)). Polyethers, polyesters and polyamines are typical examples of polymer hosts used for polymer electrolytes. The choice of salt should favor those which promote fast ion conduction in the polymer matrix. This requires an understanding of the interactions in polymer-salt complexes (i.e., polymer-ion and ion-ion interactions). Apart from the more conventional ‘salt-in-polymer’ electrolytes, ‘polymer-in-salt’ electrolytes also possess functionality in many electrochemical systems. The materials explored in this thesis are, however, based on the salt-in-polymer concept.

Polymer electrolytes can be generally divided into three major categories: solid polymer electrolytes (SPEs), composite polymer electrolytes (CPEs) and gel polymer electrolyte (GPEs). SPEs refer to solvent-free electrolytes based only on a solid polymer and a salt. An SPE with addition of inorganic nanoparticles (e.g., Al\(_2\)O\(_3\), SiO\(_2\)) is generally classified as a CPE, which often can display improvements in mechanical properties and conductivity. GPE is a hybrid of both liquid and solid electrolytes, and is sometimes also called a hybrid polymer electrolyte (HPE). GPEs are highly conductive polymer electrolytes, commonly comprising liquid plasticizers (often above 50 wt.%) embedded in a solid matrix. This is also the type of polymer electrolyte utilized in current commercial Li-ion polymer batteries. However, a compromise between mechanical properties, electrochemical stability and ionic conductivity of the polymer electrolyte must be considered. A mechanically rigid electrolyte may be a poor ionic conductor as compared to a plasticized electrolyte. On the other hand, the addition of plasticizers (e.g., linear and cyclic carbonate solvents) often results in great loss in mechanical strength, stability and safety.

For practical use, a polymer electrolyte should basically exhibit two functions: allowing shuttling of ions between the electrodes and acting as a mechanical separator to prevent short-circuits between them. This renders a simplification in product design as compared to liquid electrolytes, since SPEs can eliminate the use of both the liquid battery components and the separator. New challenges, arising from the evolution in battery design, also demand great considerations in material design and fabrication methods.

### 2.1 Ionic conduction in polymer electrolytes

Different from ionic transport in the liquid phase, a so-called ‘hopping’ mechanism is commonly used to explain ionic conduction in polymer electrolytes which are based on the salt-in-polymer concept. It is also generally considered that the ionic conduction in polymers takes place along the flexible and randomly aligned chains in the amorphous phase, rather than in the rigid and orderly packed crystalline phase.\(^{49}\) **Fig. 3** briefly illustrates a com-
comparison of the different arrangements of polymer chains in crystalline and amorphous regions in a PEO-based semicrystalline electrolyte.

Figure 3. Schematic illustration of the crystalline and amorphous regions in a semicrystalline PEO-based electrolyte.

For vitreous electrolytes, the ionic conductivity could be described by Arrhenius law (see Eq. 1 below). In the amorphous domains of polymer electrolytes, however, the temperature-dependent behavior of the ionic conductivity is better described by the Vogel-Tammann-Fulcher (VTF) model (which can also be extended to the Williams-Landel-Ferry model, WLF), shown in Eq. 2. This model reflects how ions being complexed with a polymer are transported using the free volume (i.e., vacancies) at temperatures above the glass-transition temperature \( T_g \).\(^{49}\) \( T_g \) is an important parameter which defines the temperature limit for the phase transition in a polymer material from a hard and brittle to a molten or rubber-like state. At temperatures above \( T_g \), the polymer chain segments possess more freedom in movement accompanying the volume expansion at elevated temperatures, thereby generating more free volume and facilitating ionic conduction. Commonly, the lower \( T_g \) the polymer has, the more flexible is the material.

\[
\sigma = \sigma_0 \exp \left( \frac{-E_a}{RT} \right) \tag{1}
\]

\[
\sigma = \sigma_0 \exp \left( \frac{-B}{R(T - T_0)} \right) \tag{2}
\]

In the equations above, \( \sigma \) is the ionic conductivity of the polymer electrolyte, \( T \) is the absolute temperature, \( E_a \) and \( B \) are activation energies and \( T_0 \) is associated with the glass-transition temperature under an infinitesimally slow cooling rate.

A coupling between chain relaxation and ion transport has been evidenced in both experimental and modeling studies of polyether-based electrolytes.\(^{53-}\)
The decoupling index ($R_\tau$) is defined as the ratio between a structural relaxation time ($\tau_s$) and a conductivity relaxation time ($\tau_\sigma$), as shown in Eq. 3:

$$R_\tau = \frac{\tau_s}{\tau_\sigma}$$  \hspace{1cm} (3)

Here, the relation between the viscosity or segmental relaxation (represented by $\tau_s$) and the conductivity (inversely correlated with $\tau_\sigma$) is described by the decoupling index ($R_\tau$).

In most polymer electrolytes, $\tau_s$ and $\tau_\sigma$ are closely related (i.e., $R_\tau$ approaching unity). This signifies a similar mechanism in ionic conduction and polymer relaxation. To achieve fast ion conduction in SPEs, common strategies in molecular design are therefore either to promote the polymer dynamics via suppressing the crystalline domains and designing low $T_g$ polymers (e.g., incorporating hyperbranched side-chains $^{62-65}$ and comonomer units $^{66-68}$), or to increase the amount of dissociated charge carriers. $^{63,69-73}$ On the other hand, loss of polymer mechanical strength often accompanying a reduction in $T_g$ should be taken into account. Approaches to decouple the ionic motion from polymer dynamics has been realized in some more rigid polymer/salt complexes $^{74-76}$ and also those based on the polymer-in-salt concept. $^{52,64,77}$

The overall ionic conductivity in polymer electrolytes can be determined from Eq. 4:

$$\sigma(T, P) = \sum_i c_i q_i \mu_i$$  \hspace{1cm} (4)

in which the key parameters are the amount of charge carriers ($c_i$), their charge ($q_i$) and their mobility ($\mu_i$) as a function of system temperature. Both cations and anions can contribute to ion conduction in a polymer electrolyte. One example of the ion conduction processes in PEO-LiX complexes (X=PF$_6$, BF$_4$, ClO$_4$, N(CF$_3$SO$_2$)$_2$; the latter often abbreviated ‘TFSI’) is illustrated in Fig. 4, in which each Li cation can be coordinated by about five ether oxygens. $^{78}$ The cations migrate between the coordination sites of the polymer chains assisted by the segmental motion of the polymer matrix. The two important parameters, the amount of charge carrier and ion mobility, are often reversibly correlated. The free anions can form ion-pairs and/or charged clusters with the cations being coordinated to the polymer chains. Neutral ion pairs have no contribution to the molar conductivity (often denoted as $\Lambda$, i.e., conductivity per unit of salt concentration), even though the total amount of charge carriers increases with the rise in salt concentration. Ionic conductivity is thus promoted by suppressing the formation of ion-
pairs, which may be achieved by using a highly dissociable salt. It has been found that a reduction of the amount of ion-pairs and salt aggregates can be achieved by using anions with low lattice energies, such as TFSI and \( \text{N(SO}_2\text{CF}_2\text{CF}_3\text{)}_2^- \) (BETI).\(^49,79\) This is due to that the ‘bulky’ anions are energetically favorable for dissociation of ionic aggregates with small cations, especially at low salt concentrations.

![Figure 4. Illustration of ion-polymer interactions in a PEO/LiX polymer electrolyte.](image)

**Figure 4.** Illustration of ion-polymer interactions in a PEO/LiX polymer electrolyte.

![Log \( \sigma \) vs. [Li\(^+\)]/[EO] graph](image)

**Figure 5.** Illustration of the influence of the salt concentration on the ionic conductivity in the PEO/LiX systems (e.g., LiClO\(_4\), LiTf, LiTFSI).\(^49,50\)

**Fig. 5** illustrates the common trend in the transition of ionic conductivity with increasing salt concentration, which is typical for PEO-LiX complexes. Generally, a plasticizing effect on the polymer can be expected with the addition of a low-concentration salt (while the number of charge carriers increases), which leads to a decrease in viscosity (usually a reduction in \( T_g \) of the polymer), thereby facilitating ion transport. However, as the addition of salt increases, crosslinks are formed by intermolecular bonds between ions and the coordination sites at the polymer chains, which may reduce the polymer segmental motions and stiffen the system. This can result in an abrupt reduction of ionic conductivity after reaching a maximum value at a certain
salt concentration, accompanied with a distinct increase in $T_g$. At increasing temperatures, better solvation of the Li salt in the polymer matrix and faster polymer motions are expected, which would generally lead to higher ionic conductivity.

Other parameters which are commonly addressed to evaluate the electrolyte properties are the transference number ($t^\pm$) and the ion mobility ($\mu^\pm$):

$$t^+ = \frac{\mu_+}{\mu_+ + \mu_-}, t^+ + t^- = 1$$

$$\mu^\pm = \frac{D^\pm}{RT}$$

The transference number is defined as the fraction of charge carried by the cation or anion. Eq. 5 applies when the salt is completely dissociated. In an ideal case, when only cation migration occurs and no concentration gradient is built up, a cationic transference number is equal to one. Otherwise, the sum of the cationic and anionic transference numbers is one. A high cationic transference number is favorable in Li-batteries to minimize concentration polarization and to facilitate Li intercalation/deintercalation processes. SPEs are, however, non-ideal electrolytes which often experience a concentration gradient and long-range interactions. Dominating anionic movement is commonly observed. For example, in the frequently studied PEO-LiTFSI and PPO-LiTFSI systems, a cationic transference number in the range of 0.1 – 0.5 at 80 °C can be observed depending on the salt concentration. Immobilization of the anions to the polymer chains (rendering a polyelectrolyte, or a single-ion conductor) can enable a cationic transference number close to unity. However, a decreased overall ionic conductivity could then be expected since contributions from free anions or charged ion-clusters to ion conduction in SPEs are excluded in these materials. The ionic mobility in high molecular weight polymer electrolytes is proportional to the inverse of the segmental relaxation time. The ionic mobility can be related to the diffusion coefficient ($D_+$ and $D_-$) by Eq. 6.

2.2 Li-ion polymer batteries

The history of Li-ion polymer batteries (Li-poly) started in the 1980s when solvent-free polymer electrolytes based on PEO and alkali salts were proposed by M. Armand et al. for lithium battery applications. Nowadays, the concept ‘Li-poly’ may refer to both Li-ion batteries and Li-metal batteries using polymer electrolytes – or gels – instead of conventional liquid electrolytes.
A battery is generally a series of coupled electrochemical cells. As illustrated in Fig. 6, the key components in a typical Li-ion polymer battery cell are a positive electrode (cathode) and a negative electrode (anode), both deposited on current collectors (e.g., copper and aluminum foils), and a polymer electrolyte which serves as both an ionic conductive medium and separator. During discharge, \( \text{Li}^+ \) ions are extracted from the anode where oxidation occurs and transported through the electrolyte towards the cathode where reduction takes place. At the same time, electrons flow in the opposite direction via an external circuit. The charging process allows the current to flow in the opposite direction, thereby restoring the electrical energy in the battery. The difference in electrochemical potential of the electrodes determines open circuit voltage (\( V_{OC} \)) and also set an electrochemical stability window (ESW) required for the electrolyte. To eliminate internal current leakage, the electrolyte should be electronically insulating and also electrochemically inert within this window, but at the same time able to transport ions efficiently. The second role of the polymer electrolyte – its ability to act as a mechanical separator – distinguishes it from typical liquid-based electrolytes where another separator material is necessary.

![Figure 6. Schematic illustration of battery components in a Li-poly battery and the principle of a Li-ion battery consisting of a LiFePO\(_4\) cathode and a graphite anode.](image)

The major motivation for using solvent-free polymer electrolytes originates from the needs to solve some critical problems associated with the use of liquid/gel electrolytes:

- Interphase layer formation: the electrolyte decomposition leads to the formation of passivation layers on the electrodes and irreversible capacity loss. Under certain extreme operation conditions (e.g., high temperature), several aging mechanisms associated with SEI growth or destruction may interfere significantly with the cycling stability. 

\(^{84, 85}\)
• Gas evolution: electrolyte oxidation could generate CO₂ gas and vapors evolved from volatile organic solvents. The gas formation may introduce internal pressure in the batteries during cycling and storage, especially at high temperatures, and ultimately destroy the battery packaging.⁸⁶

• Thermal runaway: the volatile and flammable nature of the organic solvents, such as dimethylene carbonate (DMC) and ethylene carbonate (EC), can cause self-ignition and hence fire or explosion under abusive conditions (e.g., overcharging, overheating and short-circuit).

• ‘Cross-talk’: it has been found that the dissolution and precipitation of metallic cations due to the decomposition of the cathode material can shuttle between the two electrodes and accelerate battery aging.⁸⁷

• Deformation of the separator: typical separator materials are composed of polyethylene (PE) sandwiched in polypropylene (PP) layers, which may undergo severe deformation and shrinking.⁸⁸

• Cost: the cost of the separator and the electrolyte attributes to approximately 22 % of the total device cost, which is the second largest next to the cost of the cathode.⁸⁹ Also, a number of electrolyte additives (e.g., flame retardants, redox shuttles and ionic liquids) raise the overall cost.

Considering the inherent chemical and thermal stability of solvent-free polymer electrolytes, gas evolution and thermally runaway can be greatly suppressed by using polymer electrolytes.⁹⁰ The selective ionic diffusion mechanism in polymer electrolytes may also be beneficial to minimize the ‘cross-talk’ effect. As a separator, polymer electrolytes typically show a good tolerance for volume changes during cell operation.⁹¹ The electrochemical inertness in many polymer host materials generally ensures a wide electrochemical window for SPEs, as illustrated in Table 1.

Commonly considered as the major obstacle, the ambient-temperature conductivity of most SPEs still remains too low for practical implementations (e.g., the RT conductivity is in the range of 10⁻⁵ to 10⁻⁸ S cm⁻¹ for polyether-based SPEs).¹¹,²² In commercial Li-ion batteries, the RT ionic conductivity can be largely enhanced with the addition of liquid components, such as liquid carbonates and ionic liquids, but thereby generating a reduction in both safety and mechanical strength. Approaches to resolve these issues include tailoring the ionic conductivity and mechanical properties of SPEs via synthetic modifications (e.g., branched polymer or copolymers)⁹²,⁹³ and novel fabrication approaches (e.g., layer-by-layer deposition).⁶⁹ A few attempts have been made to apply solvent-free polymer electrolytes in ambient-temperature Li-poly batteries,²⁹,³⁰,⁹⁴–⁹⁶ but new approaches for SPE development are still demanded for the materials to be useful for practical application (i.e., >10⁻⁴ S cm⁻¹).²¹ This is also a major motivation to expand the choice of polymer host materials beyond polyethers (see further discussion in Section 2.4). At elevated temperatures, SPEs are superior to liquid electrolytes in terms of safety, stability and battery aging. The ionic conductivity
of SPEs can be significantly enhanced at elevated temperatures, e.g., to around $10^{-3}$ S cm$^{-1}$ at 60 °C and $10^{-2}$ S cm$^{-1}$ at 80–100 °C.$^{11,76}$

The choice of salt in SPEs favor those facilitating ion-pair dissociation and thermally stable (e.g., LiTFSI)$^{84,97}$ and should preferably be chemically inert towards electrode surfaces and the other battery components such as the current collector. Earlier studies showed risks of Al corrosion at voltages above 3.8 V vs. Li$^+$/Li in both liquid and polymer electrolytes containing imide-salts like LiTFSI and LiBETI.$^{98–100}$ Although such reactions would be less pronounced in SPEs due to the slower dynamics as compared to liquid electrolytes, concerns may arise for high-voltage and high-temperature battery applications. Salts which are more stable under abusive conditions, such as LiBOB and LiBF$_2$(C$_2$O$_4$),$^{16,101–103}$ have been introduced as additives to promote SPE stability.

Other concerns in the practical use of Li-poly batteries also involve the challenge to enhance the electrode/solid electrolyte interfacial contacts. Previous work has demonstrated several approaches through the optimization of fabrication methods (e.g., in-situ radical polymerization, thermal polymerization).$^{104,105}$ Attempts to promote selective adsorption and/or strong adhesion through functionalization of electrolytes or electrode surfaces have been demonstrated.$^{106–108}$ Strategies for implementation of functional monomers and polymers in Li-batteries are addressed in Section 3.

2.3 From 2D to 3D battery designs

For conventional Li-ion batteries, the current battery design is organized in a planar configuration, which uses either thick or thin layers of electrodes (energy or power optimized, respectively). As illustrated in Fig. 7, thin-electrode configurations are ideal to realize fast ion conduction due to short diffusion paths, and can thus deliver a high power density (W/g). On the other hand, thick electrodes contain more active material and have higher energy densities (Wh/g) than thin film electrodes, but have to compensate in power density due to longer diffusion paths, and are also associated with risks of losing mechanical integrity. Using a 2D configuration, a compromise must be made between high energy and power densities for the battery performance.

An effective strategy to improve the overall performance in a battery can be realized by a transition from 2D to 3D battery architectures, as is shown in Fig. 7. This idea to configure thin-film electrodes along a 3D geometry was initiated by the need to power microelectromechanical (MEMS) devices with small dimensional volumes (1–10 mm$^3$).$^{41}$ The major benefit to construct a 3D battery is the significant increase in power density on a small footprint area through a higher surface area of the electrodes. 3D electrodes,
utilizing a ‘skyscraper’ configuration, intrinsically possess more active material than their planar counterparts on a fixed bottom surface area, and also provide at least 10 times higher areal capacities (capacity per footprint area), reaching up to 10 mAh cm$^{-2}$.\textsuperscript{40,109}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7.png}
\caption{Battery designs based on 2D planar (thin-film and thick-film) electrodes and 3D electrodes.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig8.png}
\caption{Schematic illustration of various 3D electrodes for 3DMBs: (a) 3D-interdigitated or interlaced, (b) 3D-trench, (c) 3D-concentric and (d) aperiodic architectures. Reprinted with permission from the authors.\textsuperscript{110}}
\end{figure}

\textbf{Fig. 8} shows some models of 3D electrode architectures which have been proposed.\textsuperscript{110} \textbf{Fig. 8a, 8b and 8c} illustrate periodic architectures with electrodes of ‘interdigitated’, ‘trenched’ and ‘concentric’ geometries, respectively. Micromachining of current collectors using micro-etching, photolithography and 3D printing methods (e.g., selective laser melting) are commonly used to shape micro-channel plates or pillar arrays.\textsuperscript{40,111–114} Alternatively, electrochemical fabrication methods with obvious advantages in ease and low cost of processing large area electrodes have been developed,\textsuperscript{38,43,115} for example using pulsed galvanic deposition to form Al- and Cu-nanopillars as current collectors.\textsuperscript{38,44,116,117} These electrode configurations have also been used here in Papers I-V. Active electrode materials, such as Fe$_3$O$_4$\textsuperscript{118,119}, SnO$_2$\textsuperscript{119}, Cu$_2$Sb\textsuperscript{117} and Cu$_2$O,\textsuperscript{40,120,121} can be sequentially deposited. \textbf{Fig. 8d} illustrates an ‘aperiodic’ architecture, which is also commonly referred to as
a ‘foam’ or ‘sponge’ geometry. Foam-like current collectors (e.g., reticulated vitreous carbon; RVC) are utilized as substrates for electrodeposition of active materials, such as Cu$_2$O\textsuperscript{122}, MnO$_2$\textsuperscript{123}, polyaniline\textsuperscript{124} and LiFePO$_4$\textsuperscript{125}. Such electrodes have been investigated in Papers III-IV. Successful microfabrication of 3D electrodes generally demonstrates a significant improvement in battery performance. For example, polyaniline (PANI) deposited onto 3D RVC foam or carbon felt showed high power capability and good capacity-retention at high C-rates\textsuperscript{1}, e.g. from C/10 to 10 C, due to the area gain and the great reduction of Li-ion diffusion paths in the 3D geometry.\textsuperscript{44} Comparing with the cycling performance of PANI deposited on 2D stainless steel, about 10–20 times enhancement in areal capacity (from 0.01 mAh cm$^{-2}$ up to 0.27 mAh cm$^{-2}$) was shown.

Optimization of 3D electrodes via tailoring the length, the inter-space distances in the electrodes as well as the distribution of active materials was studied using Finite Element Analysis (FEA) by V. Zadin et al.\textsuperscript{110,126–128} It was shown that the electrochemical activity for the interdigitated cell design could be optimized via increasing the pillar length (not more than 100 µm) to reduce polarization.\textsuperscript{127} When comparing systems using liquid electrolytes and polymer electrolytes, the latter can display better capability to ensure uniform electrochemical activity at moderate current rates, for a range of different electrode pillar lengths and interdistances in 3D nanopillar architectures.

The complete assembly of a 3DMB requires an optimization of each battery component and their interfaces. However, this has been proven technically challenging to achieve for 3D battery configurations. Table 2 demonstrates some examples of cell designs used to assemble a whole-cell\textsuperscript{ii} 3DMB, which has been the major goal for the research field. Almost all of these systems have utilized liquid or gel electrolytes with great contents of organic solvents by infiltration.\textsuperscript{40,112,113} Moreover, examples using a combination of the different 3D electrode configurations – both Al nanopillars and LiFePO$_4$ coated RVC foam – have also been tested in a prototype whole-cell.\textsuperscript{129} The first route (Fig. 9a) is to separately produce two 3D interdigitated electrodes, then position them symmetrically to achieve minimum volume occupation. The electrolyte can be filled up to the rest of the cell volume. Most of the cells of interdigitated and trenched electrodes are based on this route using a GPE. Another route, illustrated in Fig. 9b, could be realized using a thin

\textsuperscript{1} The cycling C-rate of a battery is a measure of the theoretical time within which the battery should be fully discharged or charged. 1C corresponds to 1 hour, 2C corresponds to half an hour, C/2 to two hours, etc.

\textsuperscript{ii} A whole-cell or ‘full-cell’ refers to a cell composed of a cathode, an electrolyte/separator and an anode which is not the metallic Li anode. A cell design which uses metallic Li as anode is called a half-cell.
solid electrolyte coating separating the two electrodes – i.e., one electrode or the current collector of 3D design is used as the substrate and the counter electrode is then backfilled onto the electrolyte. Sufficient active material is demanded in order to deliver as much energy as possible within a limited volume, which as a consequence requires the electrolyte to occupy as little volume as possible. A stable electrolyte separating the greatly enlarged electrode surfaces is critical to suppress potential side-reactions at the interfaces.

Figure 9. Sketches illustrating two examples of whole-cell assembly from 3D-interdigitated electrodes: (a) cathode and anode embedded within the electrolyte matrix; (b) subsequent deposition of each battery component.

Table 2. Examples of 3DMBs cells employing different cell designs.

<table>
<thead>
<tr>
<th>Architecture type</th>
<th>Components (electrode, electrolyte)</th>
<th>Cell type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 8a 3D-interdigitated</td>
<td>Interdigitated carbon arrays with and without electrodeposited polypyrrole, 1M LiClO₄ in EC:DMC 1:1</td>
<td>Whole cell</td>
<td>H.-S. Min et al.¹³⁰</td>
</tr>
<tr>
<td>Fig. 8b 3D-trench</td>
<td>LiMn₂O₄ and Li₄/₃Ti₅/₃O₄ microarray PMMA soaked with 1M LiClO₄ in EC:DMC 1:1; Bicontinuous Ni₃Sn and LiMnO₂ on porous Ni scaffold, 1M LiClO₄ in EC:DMC 1:1</td>
<td>Whole cell</td>
<td>K. Dokko, et al.¹³¹ and J. H. Pikul et al.¹¹³</td>
</tr>
<tr>
<td>Fig. 8c 3D-concentric</td>
<td>Prototype: Multilayers of interdigitated Li₄Ti₅O₁₂ and LiFePO₄, PMMA soaked with 1M LiClO₄ in EC:DMC 1:1</td>
<td>Whole cell</td>
<td>K. Sun et al.¹¹⁴</td>
</tr>
<tr>
<td>Fig. 8d Sponge</td>
<td>V₂O₅ xerogel and 3D ordered carbon, Poly(phenylene oxide) soaked with 1M LiClO₄/PC electrolyte</td>
<td>Whole cell</td>
<td>N. S. Ergang, et al.¹³²</td>
</tr>
</tbody>
</table>

Only a limited number of research studies on alternative electrolyte materials have so far been carried out for 3DMBs. For example, a solid ceramic electrolyte of lithium phosphorus oxynitride (LiPON) deposited on interdigitated Si electrodes via low pressure chemical vapor deposition was suggested for microbatteries.¹³³,¹³⁴ Alternatively, gel polymer electrolytes have been considered.¹³²,¹³⁵–¹³⁷ A gel network of polyacrylonitrile (PAN) and liquid electrolytes was employed in half-cells of MnO₂ deposited on conductive 3D substrates (e.g., tin-doped indium oxide, glassy carbon, Ni).¹³⁸,¹³⁹ Poly(methylmethacrylate) (PMMA),¹¹⁴,¹³¹ poly (phenylene oxide)¹³⁸,¹⁴⁰,¹⁴¹
and poly(vinylidene fluoride) (PVdF) were also used as polymer matrices to soak liquid electrolytes for 3DMBs. Nevertheless, a robust polymer electrolyte in the solid state could be better suited to minimize the electrolyte leakage and volume occupation. Such materials have been targeted in Papers I-IV.

The downscaling of volume in microdevices poses some specific requirements on a solid polymer electrolyte:

- **Thickness**: a conformal and uniform electrolyte coating with thickness downscaled to microns or submicrons is desired.
- **Conductivity**: solid-state ionic conduction is less of a problem when downscaling the electrolyte thickness, considering that the ionic diffusion path is greatly decreased. An ionic conductivity in the range of \( >10^{-6} \text{ S cm}^{-1} \) could be considered acceptable. More importantly, the electrolyte should maintain electronic insulating to avoid self-discharge (e.g., \( \sigma_{\text{electronic}} < 10^{-10} \text{ S cm}^{-1} \)).
- **Electrochemical stability**: A wide electrochemical window (\( > 4 \text{ V} \)) in the polymer electrolytes is preferable.
- **Mechanical stability**: As a separator, the electrolyte needs to be mechanically robust to ensure physical separation of the electrodes.
- **Pinhole-free**: pinholes of nano-scale dimensions formed at electrolyte surfaces could easily short-circuit a cell. The electrolyte layer should be pinhole-free to accommodate further deposition of the second electrode material.
- **Chemical inertness and thermal stability**: the electrolyte should be chemically and thermally inert during the processing and cell assembly.
- **Ease of up-scaling and safety**.

It is, however, a great challenge to realize all these criteria. One key task for 3DMB development is to optimize the thickness and the uniformity of the electrolyte layer, not least considering the complex structure of the electrodes. One-dimensional ionic conduction may occur evenly on a uniformly coated electrolyte with optimized thickness. On rather rough (semi-3D) and 3D surfaces, as illustrated in Fig. 10a, non-uniform and poor coatings of polymers on non-planar substrates can be expected using conventional deposition methods, such as chemical deposition (e.g., plasma deposition) and physical deposition (e.g., solution-casting, doctor-blading or spin-coating), unless favorable surface adsorption properties (e.g., selective and strong physisorption and/or chemisorptions) can be included in the polymer structure. In comparison, as depicted in Fig. 10b, conformal and uniform polymer electrolytes deposited on non-planar surfaces may be achieved using in-situ polymerization techniques, such as electropolymerization or self-assembly approaches, which have been explored in Papers I-III. Good coverage and strong adhesion to different surfaces – e.g., metals and
metal oxides, silicon and organic conducting substrates – may be realized via chemisorption or physisorption of functional polymers using these methods.\textsuperscript{146}

\textit{Figure 10.} Comparison of a solid electrolyte layer deposited onto rough surfaces using (a) conventional deposition and (b) well-controlled polymerization routes. Redrawn from ref.\textsuperscript{35}.

A ‘conformal’ profile of the pinhole-free solid electrolyte is a critical step in the whole-cell assembly, especially for the 3D-concentric (Fig. 8c) and aperiodic architectures (Fig. 8d). In the work discussed in this thesis, the overall aim of the electrolyte development for 3DMBs is to develop solvent-free polymer electrolytes with favorable functionality and simple fabrication procedures. Tailoring of the monomer or polymer properties via synthetic modification to integrate the electrolyte onto various 3D electrodes (i.e., nanopillars and ultraporous foam) has in this context been the major focus.

2.4 Polycarbonate as an alternative polymer host

As mentioned in Section 2.1, polyethers with ethylene oxide (EO) or propylene oxide (PO) repeating units were the first and are still the most investigated polymers for solid Li ion conductors. Appropriate design of their polymer architectures to constrain crystalline domains and enhance their flexibility has to some extent generated improvements in conductivity. There are, however, some major concerns with polyethers for SPEs. For example, the semicrystallinity in high molecular weight PEO/salt systems restrict fast ionic conduction. There are commonly distinct conductivity changes close to \( T_g \) and \( T_m \) of the salt-polymer complexes, caused by the recrystallization or melting of polymer crystallites, respectively.\textsuperscript{49} In this context, PPO constitutes an amorphous alternative to PEO, though it has generally displayed lower conductivity than PEO-based counterparts at high temperatures (over 60 °C).\textsuperscript{51} For practical use in conventional batteries, realization of appreciable ionic conductivities (e.g., \( >10^{-3} \text{ S cm}^{-1} \)) and cationic transference number (e.g., \( t_+>0.5 \)) at ambient temperatures remain the greatest obstacles for PEO-based SPEs. Additionally, the hydrophilicity of PEO may lead to side-reactions due to the evolution of water clusters in moist environments.
Several non-polyether host materials have been explored for SPEs. Table 3 lists some examples of non-polyether hosts and their comparisons with polyethers in terms of \( T_g \) and \( T_m \). Flexible materials like polysiloxanes have been applied for battery applications, but the inferior mechanical strength in low \( T_g \) homopolymers often demands further synthetic modifications. A few rigid polymers featured by high \( T_g \), such as poly(phenylene oxide), exhibit good mechanically integrity but at the expense of low conductivity. PVdF and the associated copolymer PVdF-HFP, which both are capable to trap large amounts of liquid electrolytes, are commonly used as electrode binder and host materials of GPEs.

### Table 3. Examples of homopolymer host materials, their chemical structures and \( T_g/T_m \) values (adapted from ref. 152).

<table>
<thead>
<tr>
<th>Polymer host</th>
<th>Repeat unit</th>
<th>Glass-transition temperature, ( T_g ) (°C)</th>
<th>Melting temperature, ( T_m ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (ethylene oxide)</td>
<td>([-\text{CH}_2\text{CH}_2\text{O}]_n)</td>
<td>-64</td>
<td>65</td>
</tr>
<tr>
<td>Poly (propylene oxide)</td>
<td>([-\text{C}(-\text{CH}_3)\text{CH}_2\text{O}]_n)</td>
<td>-60</td>
<td>---</td>
</tr>
<tr>
<td>Poly(trimethylene carbonate) a)</td>
<td>([-\text{OC(O)O-} \text{(CH}_2)_3\text{]}_n)</td>
<td>-15</td>
<td>---</td>
</tr>
<tr>
<td>Poly ((\varepsilon)-caprolactone) b)</td>
<td>([-\text{OC(O)}(-\text{CH}_2)_3\text{]}_n)</td>
<td>-65</td>
<td>56</td>
</tr>
<tr>
<td>Poly(dimethylsiloxane)</td>
<td>([-\text{SiO-} \text{(CH}_3)_2\text{]}_n)</td>
<td>-127</td>
<td>-40</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride-hexafluoropropylene)</td>
<td>([-\text{CH}_2\text{CF}_2\text{]}_n)</td>
<td>-65</td>
<td>135</td>
</tr>
<tr>
<td>Poly(acrylonitrile)</td>
<td>([-\text{CH}_2\text{C(-CN)}]_n)</td>
<td>125</td>
<td>317</td>
</tr>
<tr>
<td>Poly(phenylene oxide)</td>
<td>([-\text{C}_6\text{H}_5\text{O}]_n)</td>
<td>215</td>
<td>---</td>
</tr>
</tbody>
</table>

* a) Paper V; b) Ref 166; c) Amorphous.

As the solid analogue to liquid carbonates and lactones, high-molecular-weight polycarbonates and polyesters, exemplified by poly(trimethylene carbonate) (PTMC) and poly(\(\varepsilon\)-caprolactone) (PCL), have here been considered as promising alternative polymer hosts (Papers V-VIII). These hydrophobic polymers are widely used as nontoxic and biodegradable materials in biomedical applications. Through well-controlled organocatalytic ring-opening polymerization of five or six-membered cyclic carbonates or esters, tailorable properties can be realized in the derived monomers and polymers, as shown in Fig. 11. M. J. Smith and M. M. Silva et al. first considered the use of PTMC for battery electrolytes and studied a series of PTMC/LiX (X = BF\(_4\), ClO\(_4\), Tf, PF\(_6\)) complexes. PCL, a polyester, has also been applied for polymer electrolytes. The ion transport behavior in either PTMC or PCL was never clearly explained, but it was suggested that the carbonyl oxygen may play a similar role as the ether oxygen in polyethers regarding cation coordination. The incorporation of polar carbonate units in the polymer host was found to effectively increase the dielectric constant and facilitate the separation of ion pairs. Recent studies by Y. Tominaga et al. reported a high salt solvation – up to 188
mol% of LiFSI – and an ionic conductivity of $10^{-4}$ S cm$^{-1}$ at 60 °C in poly(ethylene carbonate) (PEC), with a cationic transference number around 0.54 in PEC$_{0.53}$LiFSI.$^{76}$ In such a polymer-in-salt system, increasing Li-doping led to a continuous decrease in $T_g$, which might be as result of a decoupling between ion conduction with segmental motions, similar to those observed for a few other rigid polymers with high salt contents.$^{52,64,75}$

Figure 11. Ring-opening polymerization of substituted cyclic carbonates.

Despite the interesting properties of polycarbonate-based SPEs, their performance in Li-batteries has barely been reported before this thesis work. Therefore, one major motivation has been to explore the functionality of PTMC as an alternative host material for high-performance batteries. Synthetic modifications of the polymer properties have been targeted to enhance chain flexibility and/or to incorporate functional side-groups, as is discussed in Section 3.1.

2.5 At the electrode/polymer electrolyte interfaces

Achieving optimal properties in the electrolyte itself does not necessarily ensure a well performing cell. In practical Li-ion battery applications, the critical role of the surface chemistry at the electrode/electrolyte interfaces should not be overlooked. Early studies on Li-batteries using both liquid and polymer electrolytes confirmed spontaneous formation of a protective layer on Li metal surface.$^{171,172}$ The term Solid Electrolyte Interphase (SEI) was introduced to describe the passivation layer formed on the anode surface, which can act as an electronic insulating interphase between the anode and the electrolyte. Later, a Solid Permeable Interphase (SPI) formed on the cathode side has also been explored.$^{173}$ On the one hand, these interphase layers constitute a beneficial protecting layer that reduces the rate of further electrolyte (or electrode) decomposition; on the other hand, it limits the power capabilities of the cell due to slow ion transfer and it can be a security hazard where secondary reactions may lead to thermal runaway and gas evolution causing detrimental battery failures. The importance of these thin interphase layers has been proven in context of safety, capacity retention, rate compatibility and cycle life of batteries.$^{84,173–177}$

The origin of SEI and SPI formation can be illustrated by Fig. 12. The electrolyte’s electrochemical stability window (ESW) defines its operational
potential limits. Beyond this range, destructive electrolyte consumption through chemical and electrochemical reactions will occur at the electrode/electrolyte interfaces. Conventional non-aqueous liquid electrolytes typically have reduction limits of around 1.0–1.4 V vs. Li⁺/Li, below which reduction of salt anions and solvents can proceed simultaneously to form the SEI layer. For example, LiTFSI in EC/DEC can undergo hydrogen abstraction and ring-opening polymerization reactions to form organic/inorganic composites and ethylene oxide based oligomers or polymers. In the presence of moisture, further reactions may lead to the formation of LiOH.

![Figure 12. Schematic illustration of the electrochemical stability window of the electrolyte with respect to the electrode potentials. Adapted from ref. 21.](image)

Similar to the general requirements on any solid electrolyte, a suitable SEI for high performance batteries would be an electronic insulator and a good ionic conductor, flexible and mechanically stable against electrode volume changes, and uniform in morphology and composition. A rapid formation or recovery of the SEI is also favorable to effectively stabilize the interfaces during the initial cycles to enable long term cell stability. In reality, the morphological structure of the SEI layer is very complicated. Its thickness is often suggested to range from a few nanometers to a few hundred nanometers. Mosaic or multilayered structures, or mixtures of these models, have been proposed to describe the morphological characteristics of the SEI. The composition has been found to vary to a great extent depending on the properties of electrolyte system, the nature of electrodes, and the operation conditions, such as contaminations, depth of charge/discharge, or temperature. A general picture for the interphase layers formed at the liquid electrolyte/electrode interfaces is that inorganic compounds (e.g., Li₂CO₃, LiF, and Li₂O) are formed closest to the active electrode surface in the lower thickness regime, followed by a much thicker outer organic layer (e.g., containing ROCO₂Li and ROLi; R depends on the solvent) which renders flexibility to the SEI layer.
The work in this field has dominantly been focused on the liquid electrolyte/electrode interfaces, especially the anode side, to reveal the SEI composition and its evolution during electrochemical cycling. Much less effort has been devoted to the electrode/polymer electrolyte interfaces, and Papers IX and X are so far the only ones to investigate these with X-ray photoelectron spectroscopy. A few studies have been carried out on PEO-based SPEs using electrochemical impedance analysis to probe the evolution of interfacial resistances, indicating a major contribution to the overall cell resistance from the interfacial resistance at the electrode/SPE interface. Complementary studies using impedance and in-situ NMR imaging techniques on LiFePO₄/PEO₂₀LiTFSI/Li half cells indicated that the significant increase in the interfacial resistance at the cathode/SPE interface could be attributed not only to anion decomposition, but also a change of morphology and/or contacts between pulverized cathode particles and the SPE during cycling. Other impedance results also suggested that a portion of this resistance might be attributed to large salt concentration gradients in the SPE at the vicinity of the electrode surface. The influence of electrode composition and salt could alter this process significantly.

Moreover, dendrite formation has also been observed at the interface between Li metal and SPEs. From in-situ observations of the cross-section of symmetrical Li/PEOₓLiTFSI/Li cells, a dynamic growth of lithium dendrites with a diameter of around 20 µm was shown. The growth rate of dendrites was shown to be dependent on the anion mobility and the electric field. The mechanical stability of the Li/SPE interfaces will be of critical importance for ultrathin electrolytes with thicknesses in the micro- or nano-regimes. Design of SPEs with high mechanical strength (e.g., a shear modulus greater than 6 GPa) to restrain dendrite formation has also been explored.

The work presented in this thesis initiates studies to reveal the composition of the interphase layers formed at the electrode/SPE interfaces. Particular interest has been focused on commercial electrode materials, such as LiFePO₄ and graphite, in half-cells containing either PEO- or PTMC-based SPEs.
3. Methodology

*Life is a dream. Realize it.*
-Mother Teresa

The methodology presented in this thesis focuses on the following major themes: development of functional monomers and polymer electrolytes through synthetic routes; fabrication methods of polymer electrolytes for multidimensional Li-batteries; characterization techniques employed to investigate polymer electrolyte properties.

3.1 Polymer functionalization

The incorporation of multifunctionality in monomers and polymers via synthesis is an important strategy to tailor polymer properties. Functionalization of the polymer by tailoring the backbone and/or side-chains could be achieved by controlling the monomer architecture before polymerization. By definition, a multifunctional monomer refers to a monomer incorporating more than one functional group in the resulting polymer chains. The interactions and the amount of active groups can result in different polymer structures with a variety of functions. Generally, the backbone of a polymer has great influence on its bulk properties, while the side-groups can influence the chemical properties at the interface to foreign substances or substrates. In the work described in **Paper I** and **III**, the functionalization of side-groups was considered to enhance the surface adsorption of SPEs to electrode surfaces. In **Paper VII**, the polymer backbone was tailored by incorporating flexible co-polymer units for favorable ionic transport properties.

3.1.1 Functional side-groups

A key consideration for the practical application of polymer coatings is the adhesive properties of the material with respective to different substrates. The incorporation of beneficial functional side-groups, e.g., for obtaining self-assembling features to promote the formation of strong interface linkages, has been considered in this work. Take polyether acrylates as an example. The length of the polyether chain and the number of acrylic functional side-groups in the monomer can considerably influence the thickness and the physical properties (e.g., mechanical strength) in the obtained polymer films. Fig. 13 illustrates possible architectures of polyethers with mono-
and di-acrylate end-groups. Brush-like and linear structures (shown in Fig. 13a) could propagate from mono-acrylates. In comparison, diacrylates, *i.e.*, with two acrylic end-groups in the monomer, tend to form additional branching, crosslinking, loops and/or networks due to interchain bonding (see Fig. 13b). Cross-linked and/or 3D-network structures can give rise to a robust polymer, but also lead to high rigidity in the polymer network, which is unfavorable for fast ion transport.

![Figure 13](image)

*Figure 13.* Expected molecular structures of polyether acrylates and their conformations: (a) monoacrylate, (b) diacrylate. The polymerized acrylate backbone is colored in dark gray and the polyether chains are in bright gray.

Previous studies by Sisbandini *et al.* have demonstrated a favorable modification of electrode surfaces by a polyether amine oligomer (PEA) for Li-ion battery applications. It was shown that the oligomer with amine end-groups could be self-assembled on the electrodes by hydrogen bond formation, leading to a capacity enhancement of about 13% in LiFePO$_4$ half-cells. This material was further developed by Tan *et al.* for potential use in 3DMBs. It was reported that a polymer electrolyte system consisting of PPO as the main chain and with amine end-groups could both solvate lithium salts and promote surface contacts on non-planar electrode surfaces, such as LiFePO$_4$ composite cathodes and 3D Cu$_2$Sb. Moreover, incorporation of several other functional groups (*e.g.*, –OH, –COOH and carboxyl groups) to polyether backbones could be realized by synthetic modifications and also proved to form secondary bonds to metal oxide surfaces.

In *Paper I*, additional functionality in the form of polymerizable acrylate groups has been introduced within the PEA monomer. The molecular structure of the novel monomer containing both acrylic and amine groups is shown in Fig. 14a. This monomer is supposed to possess multifunctionality, comprising a polymerizable unit, surfactant groups and main chains which can dissolve Li salts.

The synthesis of high-molecular-weight PTMC was achieved via ring-opening polymerization of six-membered TMC using Sn(Oct)$_2$ as the catalyst (the synthetic details are described in *Paper V*). Through functionalization of the TMC monomers, polymer hosts of TMC could be tailored to incorporate side-groups to the polymer backbones via ring-opening polymerization. Fig. 14b illustrates the chemical structure of the functionalized PTMC. In the work described in *Paper III*, monomers containing –OH side-groups intended to promote surface adhesion through the formation of hy-
drogen bonding to the oxygen-sites of electrode surfaces were added to the TMC backbone.

Figure 14. Molecular modification of (a) multifunctional PEA-based monomers with both –NH₂ and acrylate side groups; (b) PTMC with –OH functional side-groups.

3.1.2 Copolymerization

Another common strategy to achieve multifunctionality in polymers is via copolymerization to form a polymer backbone comprising several different basic units. This provides opportunities to tailor properties such as flexibility and mechanical stability via facile synthetic approaches. According to the sequencing of these units in the macromolecules, copolymers can be classified as alternating, random, graft and block copolymers (shown in Table 4).

Table 4. The structures of different types of copolymers.

<table>
<thead>
<tr>
<th>Class of polymer</th>
<th>Graft copolymer</th>
<th>Random copolymer</th>
<th>Block copolymer</th>
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</table>

After copolymerization, the T_g of the random copolymer will depend on the fractions of both monomers in the copolymer, which can be estimated from Eq. 7, in which w_{1/2} and T_{g,1/2} are the weight fractions and the glass-transition temperatures of homopolymers 1 and 2, respectively. In contrast to random copolymers, block and graft copolymers can display two glass-transitions of the homopolymers of each repeating units. Considering the contribution from the ordering of co-repeating units in the formation of crys-
talline domains, random copolymers often effectively disrupt such patterns and form amorphous polymer matrices.

\[
\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \tag{7}
\]

The study presented in Paper VII focuses on the optimization of the ionic conductivity in PTMC-based SPEs. Copolymerization of TMC with a flexible co-monomer unit was applied to suppress the rigidity of the polymer backbones (i.e., increasing chain flexibility and reducing \(T_g\)). Poly(\(\epsilon\)-caprolactone) has previously been studied as a polymer host for polymer electrolytes,\textsuperscript{149,164–166} and recent work includes systematic investigations of copolymers consisting of \(\epsilon\)-caprolactone (CL) and TMC monomer units with varied TMC:CL ratios.\textsuperscript{211} The synthetic route of the poly(TMC/CL) copolymers via ring-opening polymerization is shown in Fig. 15. The as-formed rubbery SPE films showed an obvious reduction in \(T_g\) from -15 °C to -41 °C when varying the TMC:CL ratio from 100:0 to 60:40. At the optimal salt concentration (28 wt\% of LiTFSI), a significant enhancement in the magnitude of the conductivities from \(10^{-8}\) S cm\(^{-1}\) to \(10^{-5}\) S cm\(^{-1}\) at 60 °C and from \(10^{-10}\) S cm\(^{-1}\) to \(10^{-7}\) cm\(^{-2}\) at 25 °C was obtained. Cell studies in LiFePO\(_4\) half cells displayed stable performance with useful capacity of around 160 mAh g\(^{-1}\) and 140 mAh g\(^{-1}\) at C/50 and C/5 at 60 °C, respectively. Continuing from this approach, Paper VII explores the functionality of P(TMC/CL) in Li-batteries operating at ambient temperatures.

**Figure 15.** Synthetic route of trimethylene carbonate (TMC) and \(\epsilon\)-caprolactone (CL) monomer units to form random copolymers.

### 3.2 Fabrication of solid polymer electrolytes

Depending on the demands of the specific cell designs, SPEs can be fabricated using different approaches. Two conventional ways are solution-casting and hot-pressing methods and primarily the former method was used in this thesis. Moreover, since non-planar electrodes demand thin and conformal coatings, *in-situ* polymerization methods (e.g., UV-initiated and electro-initiated polymerization) were considered for 3DMB applications.
3.2.1 Solution-casting

Solution-casting is a straightforward method for polymer electrolyte preparation which involves dissolving the electrolyte components in solution and casting it in a well-shaped mold or directly onto the electrode substrates. A solvent removal step is required. The solvent should be selected to facilitate the dissolution of high-molecular-weight polymers and also for convenient solvent removal. In laboratory scale experiments, acetonitrile and tetrahydrofuran (THF) – with boiling points in the range of 60 to 100 °C – are frequently used. Water is one of the most common contaminants, which should be carefully avoided to eliminate its influence on the conductivity data and unwanted side-reactions. It is also worth to note that solution-casting of electrolyte solutions directly onto composite electrodes can enhance contacts between the SPE and the electrode surfaces (this is discussed in Paper VI), which may promote the battery performance.

3.2.2 UV-initiated polymerization

In-situ UV-initiated polymerization is known as a rapid and simple polymer fabrication technique which is suitable for up-scaling. It commonly requires an unsaturated monomer (e.g., acrylate, styrene), a photo-initiator and often a suitable solvent. Controlled amounts of salt can be added to increase the ionic conductivity of the synthesized material.

![Free-radical initiation of photoinitiators:](image)

**Figure 17.** Initiation reactions of free-radicals formed from IRGACURE 2022.

The principle of UV-initiated polymerization is the free-radical polymerization mechanism. A photoinitiator, typically consisting of ketones which contain both aromatic and carbonyl groups, is introduced to supply free-radicals by chemical cleavage of the initiator. It dissociates to form radicals
at wavelengths near UV (300–400 cm⁻¹). An example of the initiation process of a photoinitiator, IRGACURE 2022, is demonstrated in Fig. 17.²¹² After initiation, the reactive radicals attack the vinyl double bond in the acrylates to initiate the formation of monomer radicals for further propagation reactions. It should be noted that the presence of atmospheric oxygen is commonly destructive for free-radical polymerization since oxygen may function as a quencher of the initiated species, and thus inhibits the preferred polymerization reaction.

In Paper I, in-situ UV-curing of bifunctional PEA monomers was investigated. Optimization of the mechanical properties and the ionic conductivity via variation of the degree of crosslinking could be achieved by controlling the power and light source exposure time, as well as the monomer-solvent composition.

3.2.3 Electro-initiated polymerization

When comparing UV-initiated and electro-initiated polymerizations, the major difference is the origin of the active species (i.e., free radicals) during the initiation process. In electro-initiated polymerization, the monomer itself functions as the initiator to form radical anions. Electro-initiated polymerization and/or electrografting (a sub-route during electropolymerization) can be self-limiting processes. The self-limiting nature of electropolymerization is particularly beneficial when forming pinhole-free organic deposits onto conductive substrates. Since the polymer produced during polymerization is electronically insulating, it inhibits further propagation of electroactive radicals, which can result in ultrathin polymer layers with thicknesses down to 10 nm under certain conditions.⁴¹

Surface modifications using electropolymerization have been well investigated for a broad variety of substrates, such as metals,²¹³ metal oxides,¹³⁹ carbons¹⁴³,²¹⁴ and electroactive polymers.²¹⁵ A group of vinyl monomers, such as acrylonitrile and various (meth)acrylate derivatives has been applied for corrosion protection and in biochemical applications.²⁰⁴,²¹⁶–²¹⁸ However, only a few electropolymerized polymer electrolyte systems have so far been developed and reported for microbattery applications.¹³⁸–¹⁴⁰,¹⁴³

In principle, electrografting of ultrathin polymer layers (commonly less than a few hundred nanometers) onto battery electrodes could be achieved depending on some key parameters, such as the competition between the adsorption of the solvent and the monomer on the substrates as well as the solvation of polymers.¹⁴⁶,²¹⁹ Strong covalent linkages between chemisorbed acrylate-based polymers grafted to the substrate have been found,²²⁰ which also demonstrated to be able to withstand repeated rinsing in Paper II.

Competitive polymerization reactions can also occur during electro-initiated polymerization. Fig. 18 shows some possible electroinitiated radical polymerization reactions involving acrylic monomers. Desorption and
polymerization in solution may lead to non-grafted films or non-attached free radicals being trapped in the grafted layers. This may influence the homogeneity and other properties of the polymer electrolytes when the thickness is downscaled to a few nanometers. More often, multilayers of grafted polymers with non-grafted components trapped are expected, but can still result in useful SPEs as long as the grafted polymer is stable enough.

Acrylic monomers, both functionalized PEA and a poly(propylene glycol) diacrylate (PPGDA), can be electropolymerized (Paper II). The acrylate end-groups in the monomers are expected to be electrografted onto the metal oxide substrate surface through the formation of carboxylate-metal oxide bonds, propagating to form a cross-linked polymer network. Lithium salt can be integrated by soaking a salt-free electropolymerized polymer in a salt-rich solution for an extended time. Alternatively, as demonstrated in Paper II, LiTFSI salt can be directly co-deposited in the polymer matrix during electropolymerization. Also, controlled current chronopotentiometry using either constant-current or pulsed current was compared for polymerization on 3D Cu-nanopillar substrates.

Figure 18. Schematic illustration of possible routes during electro-initiated polymerization: electrografting and bulk polymerization.
3.3 Materials Characterization

This section briefly describes the major experimental techniques applied for materials analysis in the thesis. Conventional methods to characterize polymer bulk properties include vibrational spectroscopy, nuclear reasonable spectroscopy (NMR), thermal analysis and mechanical characterization. The electrochemical properties of polymer electrolytes are usually studied by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). Diffusion NMR experiments are also commonly applied to probe the ionic diffusion and transport properties in polymer electrolytes. Surface and interface characterization of polymer materials can be carried out either ex-situ or in-situ. X-ray photoelectron spectroscopy (XPS) is a surface sensitive method used to identify and quantify the interphase composition. In-situ studies to trace the evolution of interphase layers can be performed with EIS during electrochemical cycling. The morphology of surfaces and interfaces could be directly observed by scanning electron microscopy (SEM).

3.3.1 Vibrational spectroscopy

Qualitative characterizations of chemical modifications in organic materials can normally be carried out using vibrational spectroscopy. Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy are both versatile methods yielding chemical and physical structural information of polymers.

*Figure 17.* Illustration of the working principle of attenuated total reflection (ATR-IR) (upper left); SPEs of PEO-LiTFSI and PTMC-LiTFSI (upper right) and their IR spectra (bottom).
FTIR with an attenuated total reflectance accessory (ATR/FTIR) is frequently used for surface and thin film characterization of materials which are not transparent or difficult to study in the transmission mode. It allows qualitative and quantitative determination of polymer materials by distinguishing between the vibration modes of different functional groups and their binding status. The ion-ion and ion-polymer interactions can also be traced. As demonstrated in Fig. 17, a source of IR light with a certain incident angle penetrates and interacts with the sample. This causes transitions between the vibrational levels, corresponding to stretching and bending movements in the specimen. A probing depth of several micrometers is usually expected.

Table 4. Proposed peak assignments for LiTFSI-doped PEO and PTMC.

<table>
<thead>
<tr>
<th>Spectral region (cm⁻¹)</th>
<th>PEO/LiTFSI</th>
<th>Spectral region (cm⁻¹)</th>
<th>PTMC/LiTFSI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1380-1300</td>
<td>νₐ (SO₂) + δ(C-H)</td>
<td>1735-1740</td>
<td>νₐ (C=O)</td>
</tr>
<tr>
<td>~1240</td>
<td>νₛ (CF₃)</td>
<td>1360-1330</td>
<td>νₛ (SO₂) + δ(C-H)</td>
</tr>
<tr>
<td>1230-1190</td>
<td>νₛ (CF₃)</td>
<td>1240-1180</td>
<td>νₛ (CF₃) + ν(C=O)</td>
</tr>
<tr>
<td>1120-1140</td>
<td>νₛ (SO₂) + ρ₁(C-H)</td>
<td>1120-1140</td>
<td>νₛ (SO₂) + ρ₁(C-H)</td>
</tr>
<tr>
<td>~1060</td>
<td>νₛ (SNS) + δ(C-H)+ ρ₁(C-H)</td>
<td>~1060</td>
<td>νₛ (SNS) + δ(C-H)+ ρ₁(C-H)</td>
</tr>
<tr>
<td>~740</td>
<td>ν(SNS)</td>
<td>~740</td>
<td>ν(SNS)</td>
</tr>
<tr>
<td>~654</td>
<td>δ(SNS)</td>
<td>~654</td>
<td>δ(SNS)</td>
</tr>
</tbody>
</table>

a-asymmetric, ν-stretching, δ-bending, ρ₁-wagging, ρ₁-twisting.

Examples of IR spectra for PEO₇LiTFSI and PTMC₈LiTFSI are shown in Fig. 17. The vibrational bands of interests are listed in Table 5. The band at around 740 cm⁻¹ is usually assigned to free imide ions, and the splitting of the TFSI anion peaks around 1353 cm⁻¹ in PTMC₈LiTFSI suggests the presence of contact ion-pairs. Polymerization reactions can also be monitored by tracing the transition from C=C to C-C bond, which can be seen in the reduction of vinyl stretching bands at around 1600-1700 cm⁻¹. The twisting bands at 810 cm⁻¹ accompanying with the increase of C-C and aliphatic C-H stretching bands can also be observed.

3.3.2 Nuclear Magnetic Resonance spectroscopy

NMR is a power technique in organic chemistry providing insights on the molecular structures and the characteristics of molecular diffusion in solutions. In the field of polymer electrolytes, NMR has been utilized to probe the ion-polymer coordination and ionic dynamics (e.g., relaxation and diffusion) via the relevant nuclei, for example ⁷Li and ¹⁹F for F-containing salts or ¹H and ¹³C for the polymers.

In principle, NMR is based on the response of NMR-active nuclei, i.e., nuclei with an intrinsic angular and magnetic moment, in the presence of radiofrequency (rf) pulses (considered as the oscillating magnetic fields).
and $^{13}$C which have an angular momentum (I) of 1/2 can split into two states under an applied magnetic field ($B_0$). In an NMR relaxation measurement, after the excitation of a rf pulse, the spin-lattice relaxation time ($T_1$, a time-constant for longitudinal relaxation) and the spin-spin relaxation time ($T_2$, a time constant for transverse relaxation) are recorded as the nuclear magnetization approaches equilibrium. The correlation times and activation energies of the molecular motions of the active species (e.g., polymer segmental motion, cation hopping) can then be studied. Long-range ion-ion and ion-polymer interactions in polymer electrolytes may also be estimated via NMR relaxation experiments.

Figure 18. Illustration of a pulsed-gradient spin-echo (PGSE) pulse-sequence.

Diffusion NMR using spin-echo pulse-sequencing is based on magnetic field gradients. Pulse-flips of $90^\circ_x$ and $180^\circ_y$ are performed with certain duration ($\tau$). The diffusion occurring during the time (from $t_i$ to $t_i+\Delta$) is recorded. Fig. 18 illustrates the PGSE pulse-sequence. The Stokes-Einstein’s equation (see Eq. 8) can be used to determine the diffusion coefficient $D$ (in the unit of $m^2 \text{s}^{-1}$ or $cm^2 \text{s}^{-1}$).

$$D = \frac{k_B T}{6\pi \eta r} \quad (8)$$

Here, $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature, $\eta$ is the viscosity, and $r$ is the hydrodynamic radius of a spherical particle.

According to the Nernst-Einstein equation, the transference number of the cation or anion can then be calculated from Eq. 5 and 6 (Section 2.1). Long-lived associated species, e.g., ion pairs and clusters, are however not easily detected using NMR.\textsuperscript{228} Combinational studies involving NMR and electrochemical measurements of the diffusion properties of polymer electrolytes are therefore preferred (see Paper VIII).
3.3.3 Electrochemical impedance spectroscopy

Some highly important parameters for polymer electrolytes, such as the ionic conductivity and transference number, are conventionally measured by electrochemical impedance spectroscopy (EIS). This is a non-destructive and rapid technique which can be used to obtain information about both bulk and interfacial properties at solid/solid or solid/liquid interfaces of solid electrolytes. However, the interpretation of the data is often complex and challenging.

Figure 19. Nyquist plots showing (a) a vector illustration of the impedance $Z$ and (b) the impedance of a blocking interface from an ideal smooth interface (dotted line) and a rough interface (solid line), in which a Randle circuit model provides a simplified fitting.

In principle, conventional EIS is commonly performed by applying a small magnitude of ac voltage (e.g., 10 mV) in a sinusoidal manner between two electrodes while recording the current response. The complex impedance $(Z)$ can be described by Eq. 9:

$$Z(\omega) = Z' + jZ''$$

(9)

in which $j$ is the imaginary number ($j \equiv \sqrt{-1}$) and $Z'$ and $Z''$ refer to the imaginary ($Z_{\text{Im}}$) and real impedance ($Z_{\text{Re}}$), respectively. $Z$ may be plotted as a planar vector by the vector sum of the real and imaginary components (see Fig. 19a). This constitutes the Nyquist plot, and typically displays contribution from both the interface and the bulk phase(s). Alternatively, a Bode plot which plots $\log(-Z_{\text{Im}})$ and $\log Z_{\text{Re}}$ against the logarithm of frequency can be used. Depending on the choice of electrodes (e.g., blocking electrode \text{iii} or non-blocking electrode) as well as the electrode surface conditions (e.g., surface roughness and adhesion), the characteristics of current response will be altered. Fig. 19b shows the Nyquist plot when measuring at blocking

\text{iii} Blocking electrodes refer to those which allow equilibration of charge species across the interfaces. In comparison, non-blocking electrodes have faradic reactions in the potential range and no immediate equilibration of charge species.
interfaces. Two characteristic regions can be observed: a semicircle at high frequencies related to the bulk response of the electrolyte and a spur at low frequencies. In practice, rough electrodes typically give a certain angle to the low-frequency response against the real axis. An equivalent Randle circuit (RC) model is illustrated as a simplified model of the electrical behavior. C represents the high-frequency dielectric capacitance in relatively resistive solid ion conductors and R is the bulk resistance and C is the capacitance of double layers. The conductivity is then estimated from Eq. 10:

\[
\sigma = \frac{l}{RA}
\]  

(10)

where l is the thickness of the electrolyte, A is the electrode area, and R is the electrolyte bulk resistance.

The fundamental difference of electrochemistry in liquid and solid electrolytes can give rise to different capacitive behavior and therefore different interpretation of the EIS data. As a non-ideal electrolyte, the effect of non-uniform electrical fields and low conductivity of an SPE (e.g., \(10^3\) or \(10^4\) lower than for liquid electrolytes) is typically pronounced. According to Eq. 11, a specific RC time constant (\(\tau\)) determined at the maximum of the semicircle can be related to an associated frequency (\(f^*\)) (Fig. 19b).

\[
\tau = RC = \frac{1}{2\pi f^*}
\]  

(11)

Compared to liquid systems, \(\tau\) would be much larger (i.e., \(f^*\) being much lower) in magnitude for the more resistive SPEs. The high frequency semicircle may not be in the measurable range for liquid electrolytes, but may well be for SPEs. For stable blocking electrodes, the total resistance in an SPE is therefore commonly determined from the low-frequency intercept in the Nyquist plot.

EIS is also commonly employed to study the transport properties of polymer electrolytes (see Paper VII and VIII). In combination with potentiostatic polarization (also termed steady-state) techniques, the self-diffusion coefficients and transference numbers can be determined. The steady-state method uses a symmetric Li/SPE/Li cell and applies a small dc polarization current to yield a concentration gradient through the SPE. The cationic transference number can be estimated as a function of temperature, concentration and type of salt using Eq. 12:

\[
t^+ = \frac{I_{ss} (\Delta V - I_o R_0)}{I_o (\Delta V - I_{ss} R_{ss})}
\]  

(12)
in which $I_0$ and $I_{ss}$ refer to the initial and steady-state currents, respectively, and $R_0$ and $R_{ss}$ are the electrode resistance before and after polarization, respectively.

Several other methods have been developed to measure the diffusion properties in polymer electrolytes, such as PGSE-NMR and galvanostatic polarization (GP). Each method has advantages and disadvantages; the GP method can give accurate analysis for concentrated solutions but the steady-state method is more conveniently used, and NMR is suitable for characterizing multicomponent systems. For reasonable estimations, a combination of several methods should be employed.

### 3.3.4 Cyclic voltammetry

Cyclic voltammetry (CV) is a versatile tool to study redox processes in solid electrolytes for obtaining information regarding material stability and reaction intermediates. It can also be used for deposition of active electrode materials or to initiate polymerization of functional monomers on conductive substrates under controlled conditions.

CV is based on sweeping the potential of a working electrode (WE) reversely at a constant rate while the current response is recorded. Three-electrode cyclic voltammetry is performed using a WE, an auxiliary counter electrode (CE) and a reference electrode (RE). A typical example of a CV measurement is carried out in a solution containing a redox active species, such as $\text{K}_3\text{Fe(CN)}_6$. Here, the cyanide complex can undergo redox reactions involving Fe(II) and Fe(III), as shown below:

$$\text{Fe(CN)}_6^{4-} \leftrightarrow \text{Fe(CN)}_6^{3-} + e^-$$

An important test for polymer electrolytes intended for 3DMB applications is the investigation of presence of pinholes in micro- and nano-dimensions. CV has been used to examine the redox activity of a redox probe (e.g., cyanide and hydroquinone) before and after applying a polymer electrolyte layer onto selected electrodes (see Papers I and II). Polymer electrolyte coatings are electronic-insulating, which should result in an obvious reduction (even absence) of the redox reactions observed in solutions.

The electrochemical stability window of an SPE is also commonly measured by CV or linear sweep voltammetry (LSV). A two-electrode configuration using a blocking working electrode against a Li metal counter electrode is typically used for SPE samples to probe the reactivity of the solvent, salt and contaminants (e.g., water and oxygen).
3.3.5 Thermal analysis

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are popular thermoanalytical techniques used to determine for example glass transition temperatures and the thermal stability of the obtained polymer electrolytes. In DSC, the amount of heat consumed to maintain an identical temperature of both the sample and a reference is detected as a function of temperature. TGA measures the mass variation as a function of the temperature under a controlled atmosphere. Mass loss may reflect vapor formation during heating while mass gain could be due to oxidation or corrosion reaction.

As the sample experiences a physical transformation (e.g., phase transition, phase separation) or a chemical degradation, the change of heat flow in DSC will indicate an exothermic (heat gain) or endothermic (heat loss) reaction. For example, the glass transition of amorphous polymers is an endothermic process which typically corresponds to one or more endothermic peaks (shown in Fig. 20a). The temperatures corresponding to energy transfer processes from the glass-transition ($T_g$), crystallization ($T_c$), melting ($T_m$) and degradation/decomposition ($T_D$) can be recorded. The relative percentage of crystallinity can also be estimated by DSC through an estimation of the heat of fusion from a crystalline phase ($\Delta H_m$). TGA, on the other hand, can be used to evaluate the polymer flammability and provide an overview of decomposition in the form of weight loss or gain as a function of the temperature and/or time. Fig. 20b illustrates the procedural and the final temperatures ($T_i$ and $T_f$) as well as the reaction interval ($T_i-T_f$), which refer to the onset of a mass change and the completion of the change, respectively.

![Figure 20.](image)

Figure 20. (a) DSC scan showing the key features of energy transfer processes in a polymer material; (b) thermogravimetric response illustrating the mass loss as a function of the temperature.

3.3.6 Morphological analysis

Morphology analysis can be carried out by scanning electron microscopy (SEM). SEM provides images of a surface with a lateral resolution in the
nano-regime. It functions by applying a high-energy electron beam to the sample and scanning the emitted signals (e.g., backscattered electrons, BSEs). Secondary electrons are more sensitive to the conditions of the sample surface (i.e., local slope) and tilt angle. Elements with different atomic numbers can be differentiated with backscattered electrons since heavy elements can produce more BSE than light ones and thereby appear brighter in the image. Cross-sectional views of a multilayered specimen also allow a quick estimation of the thickness of each layer.

An SEM instrument is often equipped with an energy-dispersive X-ray spectroscopy (EDS) detector, which can identify the relative amounts of each element at a point or an area of the sample. The characteristic X-rays emitted from the sample are recorded and may be further converted into elemental or atomic weight concentrations.

3.3.7 X-ray photoelectron spectroscopy

One of the most successful techniques to study the SEI/SPI composition both qualitatively and quantitatively is X-ray photoelectron spectroscopy (XPS), also called Electron Spectroscopy for Chemical Analysis (ESCA). It allows the identification of chemical elements and their binding environment on a solid surface. The principle of XPS is the so-called photoelectric effect, which involves the emission of core or valance electrons when X-rays with enough photon energy are irradiated on the sample surface (see Fig. 21). According to Eq. 13, the measured kinetic energy \( E_k \) of the emitted photoelectrons can be correlated to the binding energy \( E_b \) for the specific elements:

\[
E_b = h\nu - (E_k + \Phi)
\]

where \( \Phi \) is the work function of a solid (by definition, the energy difference between the vacuum level and the Fermi level). The penetration depth is typically around 10 nm given a monochromatized AlK\( \alpha \) radiation with an energy of 1486.6 eV.

Special sample preparations for XPS analysis on non-conducting polymers are required. Most polymers are very stable under ultra-high vacuum conditions. Considering the fact that polymer electrolytes are commonly insulating, the charging effect, i.e., a broadening of peaks due to accumulation of electrons, needs to be compensated for. This may be achieved either through the use of a neutralizer (a low energy electron gun) during the measurement or through corrections based on a known reference peak during peak fitting. The C1s peak at 285 eV corresponding to hydrocarbon is conventionally used as the reference peak for polymers. Moreover, technical challenges for studies of SPEs can arise from the disassembly of sticky inter-
faces. The adhesion of polymers to electrode surfaces may be greatly increased during storage and/or cycling at elevated temperatures. A compromise is therefore needed to balance between useful electrochemical performance and ease of disassembly.

**Figure 21.** XPS instrument and illustration of the principle of photoelectron emission.

**Figure 22.** (a) XPS survey spectrum for LiTFSI-doped poly(propylene glycol) diacrylate (PPGDA) after electropolymerization; (b) chemical structure of the PPGDA monomer; (c,d) XPS spectra for O1s and C1s, respectively, in which PO refers to the propylene glycol repeating unit and the peaks with the blue peak corresponding to salt signals.

**Fig. 22** displays the XPS survey spectrum for an electropolymerized PPGDA/LiTFSI coated on RVC foam. The element peaks show the presence of the expected elements, *i.e.*, F1s, N1s, S2p and Li1s from the LiTFSI salt and C1s and O1s from the polymer. Information about the oxidation state and chemical environment of an element, *e.g.*, C-O and C=O bondings in PPGDA (**Fig. 22b**), can be obtained from the electron density distribution in the respective cases. Deconvoluted peaks are commonly observed; exemplified by the high-resolution spectrum of C1s, a stronger bonding between F⁻...
C$^{δ+}$ than O$^{δ-}$-C$^{δ+}$ results in a loss of kinetic energy of photoelectrons escaping from carbon and thus a higher binding energy. By identifying and assigning the corresponding signals, electrografting of polymer coatings with doped salt can be confirmed. Moreover, systematic studies of the electrode/SPE interfaces after electrochemical cycling allow the evolution of SEI or SPI layer formation to be followed under given conditions, which can provide valuable information, regarding e.g., degradation mechanisms and factors controlling the interfacial stability.
4. Results and Discussion

*If passion drives you, let reason hold the reins.*
-Benjamin Franklin

The following section includes the key results covering the three major research themes of this thesis: functionalized monomers and polymers for 3DMBs (Papers I-IV); high performance polycarbonate-based thin film Li batteries for ambient- to high-temperature applications (Papers V-VIII); and the surface chemistry at electrode/SPE interfaces (Papers IX-X).

4.1 Solid polymer electrolytes for 3DMBs (Papers I-IV)

The focus for the development of SPEs for all-solid-state 3DMBs in this thesis has been polymer design and electrolyte fabrication to produce conformal and thin coatings on 3D architectures. Targeted for small-volume microbatteries, a thin solid polymer coating with thickness of few microns or sub-microns is desired. Here, both LiFePO₄ porous composites (considered ’semi-3D’) and 3D electrodes (i.e., Cu₂O-nanopillar, RVC foam loaded with polyaniline and LiFePO₄) have been implemented as non-planar substrates.

4.1.1 In-situ polymerized electrolytes on 3D substrates

Functionalized polyether amine (PEA) with both amine and acrylate side-groups was synthesized and studied in *Paper I*. *In-situ* UV-initiated polymerization was applied to composite LiFePO₄ electrodes, which yielded thin and conformal electrolyte coatings (*Fig. 4* in *Paper I*). The ionic conductivity of the cross-linked electrolyte was found to depend on the monomer-to-salt ratio and the degree of cross-linking. Preparation conditions (i.e., [PO]:[Li⁺] = 20:1 and 2 min UV exposure time) were applied in accordance with previous studies on unmodified PEA-based electrolyte systems.¹⁰⁴,¹⁴⁴,¹⁴⁵

Differences between a blend electrolyte (PPGDA/unmodified PEA-LiTFSI) and functionalized PEA-LiTFSI could be seen from the ionic conductivity and their physical properties (e.g., T_g). As illustrated in *Table 3*, the blend of PPGDA/unmodified PEA had a higher T_g than functionalized PEA before polymerization.¹⁰⁴ This could be due to that substitution of amine group(s) with a more bulky acrylic group introduces chain flexibility.
After polymerization, the intermolecular bonding in the blend electrolyte should be weaker than the covalent bonding in functionalized PEA, and thus a higher $T_g$ was obtained in the crosslinked system. Crosslinks are likely to generate a more rigid polymer matrix and as a consequence lower ionic conductivities should be obtained after UV-curing.

### Table 3. Comparison of the ionic conductivity and the glass-transition temperature in different electrolyte systems at a concentration of $[\text{PO}]:[\text{Li}^+] = 20:1$.

<table>
<thead>
<tr>
<th>Electrolyte system</th>
<th>Ionic conductivity $\sigma_{\text{ion}}, \text{S cm}^{-1}$</th>
<th>$T_g, {}^\circ\text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Funct. PEA before polymerization</td>
<td>$9.97 \times 10^{-6}$</td>
<td>$1.00 \times 10^{-4}$</td>
</tr>
<tr>
<td>Funct. PEA after UV irradiation, 2min</td>
<td>$5.28 \times 10^{-7}$</td>
<td>$8.05 \times 10^{-6}$</td>
</tr>
<tr>
<td>PEA:PPGDA=2:1 before polymerization</td>
<td>$5.10 \times 10^{-6}$</td>
<td>$1.10 \times 10^{-4}$</td>
</tr>
<tr>
<td>PEA:PPGDA=2:1 after UV irradiation, 2min</td>
<td>$3.50 \times 10^{-6}$</td>
<td>$5.80 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Redox-probe analysis on UV-curved electrolytes with thicknesses of a few microns on a planar substrate of FTO was applied to characterize the presence of pinholes. Fe($\text{CN}$)$_6^{3-}$ was used as a redox probe in aqueous solution. **Fig. 23** compares the cyclic voltammograms from the functionalized PEA-LiTFSI and the blended PPGDA/unmodified PEA-LiTFSI for pinhole analysis. A clear absence of the voltammetric response for the functionalized system was seen. The blended system, however, displayed a small redox response which could be an indication of pinholes. There could also be influences from the size of the redox probes and the wettability of the solvent. For a different redox probe (ferrocene) in the non-aqueous solvent acetonitrile, the redox peaks was not observable for a coated sample.

![Figure 23. Cyclic voltammograms of bifunctional PEA-LiTFSI and a blend of unmodified PEA/PPGDA-LiTFSI recorded in 1 mM Fe(CN)$_6^{3-}$ in 0.1 M KCl before and after coating on FTO substrates.](image)

The cycling performance of the ultrathin electrolyte (~1 µm) on LiFePO$_4$ initially displayed reasonable specific discharge capacities (ca. 140 mAh g$^{-1}$...
at C/50) at 60 °C (Fig. 8 and 9 in Paper I). The cells were, however, not stable after ca. 10 cycles. This may indicate mechanical instability which could be a result of accumulated Li plating at the Li/electrolyte interface. This is also implied by the gradual increase in the capacity seen during initial cycles (from about 100 to 140 mAh g⁻¹) as the Li surface became roughened during the dissolution/deposition processes. As described in earlier studies which recorded the morphological changes at the Li/SPE interface, enhanced Li surface roughness accompanied with bulky dendrite formation (with cross-sections of up to 20 µm and lengths of up to 100 µm within 100 h in a Li/PEO₂₀LiTFSI/Li cell) can be expected.¹⁹⁹ This will considerably influence the mechanical integrity at the Li/SPE interfaces for ultrathin layers. As observed from comparative experiments, it was less of a problem to achieve longer cycling using thicker SPEs (i.e., >50 µm).

**Figure 24.** SEM micrographs of (a) LiFePO₄ composite; (b) Cu₂O-nanopillar; (c) RVC foam.

In Paper II, another in-situ polymerization approach was explored. Uniform and conformal polymer coatings with thicknesses down to nanodimensions were realized via electro-initiated polymerization of PPGDA-LiTFSI. In addition to LiFePO₄ composite electrodes, two 3D configurations – 3D Cu₂O-nanopillars and a RVC foam – were used as substrates (Fig. 24). Details on the 3D electrode preparations are provided elsewhere.⁴⁴,¹²⁴,¹²⁵,²³⁷

**Figure 25.** SEM micrographs of (a) EP-PPGDA/LiTFSI on Cu₂O-nanopillars; (b,c) EP-PPGDA/LiTFSI on PANI-deposited RVC foam (different magnifications); (d) cross-sectional view of the EP-PPGDA on PANI/RVC foam.
As shown in Fig. 25, conformal coatings can be seen on the complex surfaces. The thickness of the deposited coatings on the Cu$_2$O-nanopillars was generally kept in sub-microns. 3D sponge architectures were also investigated using the same approach. A cross-sectional view of both the polyaniline (PANI) layer and the electrolyte coating can be seen in Fig. 25d, which indicates a total thickness of around 1µm.

The role of pinholes may be more pronounced as the down-scaling of the polymer coatings reaches nano-dimensions. To examine this, pinhole analysis was again performed. Considering the Pourbaix diagram (i.e., potential-pH equilibrium diagram) of Cu in aqueous solutions, hydroquinone (HQ) was chosen as a suitable redox probe for Cu$_2$O. Fig. 26 compares the voltammetric response for EP-PPGDA/LiTFSI coated onto both 2D (Fig. 26a) and 3D (Fig. 26b) Cu$_2$O-substrates. A redox response was observed in both cases when measuring on the fresh samples directly after electropolymerization. A post-synthesis heating treatment (50 °C for 15 h) on the EP-PPGDA/LiTFSI coated 2D and 3D samples obviously helped to reduce the redox signals. Post-synthesis heating might soften the polymer coatings to some extent which facilitates pore-filling of some pinholes. Moreover, it is likely that a further polymerization of the fraction of non-crosslinked monomer and/or not fully crosslinked oligomers was achieved thermally. This was confirmed by FTIR analysis, in which a reduction of peaks from acrylic groups was seen with increasing heating time (Figs. 7 and 8 in Paper II).

4.1.2 Polymerization conditions and cell assembly

In Paper II, the influence of constant-current and pulsed-current EP on electrodes with complex 3D geometries was particularly studied. Fig. 27 compares the EP-PPGDA/LiTFSI coatings produced under different electropolymerization conditions. Through conventional constant-current
chronoamperometry, an incomplete polymer coating was obtained, leaving uncovered surfaces at the pillar tips (Fig. 27a). This effect is usually present when long pillars are used (e.g., >2 µm). Unlike planar substrates, the concentration gradient along the height of 3D pillars is considered to be critical for the electrochemical behaviour. As demonstrated in FEA simulations of 3D interdigitated electrodes, non-uniform electrochemical activities in 3D substrates can be expected. In comparison, pulsed-current enables the formation of radicals in the vicinity of the electrode surface in the 3D geometry and mediate the uneven concentration gradient. This obviously helped to enhance the homogeneity and improved the coverage of the polymer coatings, especially on the long pillars (Fig. 27b).

Figure 27. SEM micrographs of EP-PPGDA/LiTFSI coated on nanopillars using (a) constant current; (b) pulsed current.

Another practical issue for electropolymerized SPEs is related to doping salt into the polymer coatings. This has typically been achieved via a post-synthesis treatment by soaking the coated substrates in a liquid electrolyte for an extended time, as described previously. Certain swelling of the polymer matrix to form a gel electrolyte is favorable in terms of conductivity, but is accompanied with risks of de-adsorption of polymers from the substrates and/or the dissolution of polymers into the liquid solutions. Paper II presents an alternative and facile approach of salt doping into the polymer matrix in parallel with the electropolymerization. XPS results on EP-PPGDA/LiTFSI-coated Cu₂O-nanopillar (Fig. 9 in Paper II) and PANI-RVC foam (Fig. 28) confirmed the presence of salt on the samples surfaces. For each sample, five different sampling regions were examined and consistent results were shown. A comparison of the spectra from rinsed and un-rinsed samples deposited on PANI-RVC foam showed that the salt remained on the surface also after thorough rinsing with ethanol. Further evidence of successful salt co-doping was demonstrated by EIS analysis. Using a delicate setup consisting of a glassy carbon electrode coated with polymer electrolytes and a GaIn eutectic liquid to provide gentle contact onto the thin electrolyte coatings, the ionic-conductivity of the EP-PPGDA/LiTFSI after rinsing was determined to be around 10⁻⁶ S cm⁻¹ at room temperature (Fig. 6 in Paper II).
Attempts to build 3DMB half-cells and whole-cells were performed using thin SPE layers of EP-PPGDA/LiTFSI with a Li anode, PANI-coated carbon foam and Cu$_2$O-nanopillars. Following the approach illustrated in Fig. 9b, an ideal whole-cell 3DMB would be a combination of a 3D electrode, a conformal and thin SPE coating, and a back-filled counter electrode. Starting from the Cu$_2$O-nanopillar configuration, a thin layer of EP-PPGDA/LiTFSI (around 200–300 nm) was applied, followed by a deposition of LiFePO$_4$. The back-filling was performed by solution-casting the composite slurry onto the as-coated thin electrolyte and the solvent was removed afterwards. Fig. 29 shows the morphology of respective components in the whole-cells after assembly. There is an indication of pore-filling of the second electrode along the 3D geometry of polymer coatings. Nevertheless, these cells appeared to be short-circuited.

Such failures might originate from the micromechanical properties of the thin polymer coatings in nano-scale dimension. It could be questioned if such a thin polymer layer is mechanically stable enough to act as a robust separator against the LiFePO$_4$ deposits. The ultrathin coating might have been incapable to withstand the mechanical strength posed from the bulky composite layer. Concerns regarding the chemical homogeneity of nano-scaled electrolyte coatings due to formation of salt and polymer aggregates or cracking of the polymers during solvent drying have also been brought up by other researchers.\textsuperscript{140,143} This might generate an uneven distribution of the current density during 3DMB operation. Moreover, matching the anode and cathode volumetric capacities remains a challenge. Suitable techniques and solvents for backfilling should be carefully chosen to achieve good penetration into the free volume of the nanoscaled interspaced architectures and without de-adsorbing the polymer coating from the substrate.
The issues mentioned above indicate that a rethinking is perhaps necessary for the optimization of SPE systems for 3DMBs. A natural consideration is to enhance the electrolyte intrinsic properties (i.e., ionic conductivity, mechanical strength) and increase the electrolyte thickness up to a few microns. A few specific systems have here been targeted for a self-assembled robust polymer electrolyte with good surface adhesion and/or improved ionic conductivity: OH-functionalized PTMC and P(TMC/CL) copolymers.

Figure 29. SEM micrographs of (a) EP-PPGDA/LiTFSI-coated Cu$_2$O nanopillars and (b) with backfilled LiFePO$_4$ deposited on the electrolyte; (c) EP-PPGDA/LiTFSI deposited on the PANI-RVC foam and (d) with backfilled Li$_4$Ti$_5$O$_{12}$ on the electrolyte.

4.1.3 Functionalized polycarbonates

Modifications of high-molecular-weight PTMC was targeted for promoting ionic conductivity via copolymerization of TMC and CL (Paper VII) and enhancing the surface adhesion via incorporating functional OH groups (Paper III), respectively. As seen in Fig. 30a, DSC results from the homopolymers showed that pure PTMC is amorphous with $T_g$ around -16 °C while pure PCL is a semicrystalline polymer with similar $T_g$ and $T_m$ as PEO.166 The copolymer P(TMC$_{20}$CL$_{80}$) is amorphous and display a significantly lower $T_g$ (-56 °C) than pure PTMC. After functionalization, PTMC-OH displays a slight increase in $T_g$ (around -7 °C) as compared to pure PTMC, which might be due to the formation of intra- and intermolecular hydrogen bonds and thus a loss of chain mobility in the polymer.

The ionic conductivities of three PTMC systems, PTMC$_5$LiTFSI, P(TMC$_{20}$CL$_{80}$)$_{4.6}$LiTFSI and PTMC-OH$_5$LiTFSI are compared in Fig. 30b. The obtained Arrhenius plots demonstrate VTF behavior for all systems, indicating the amorphous nature of the electrolytes. This was also confirmed by the absence of melting endotherms in DSC experiments. The ionic con-
ductivity of PTMC and PTMC-OH-based SPEs are generally in the order of \(10^{-8} - 10^{-10} \text{ S cm}^{-1}\) at RT and \(10^{-6} - 10^{-7} \text{ S cm}^{-1}\) at 60 °C, respectively. A slight gain in ionic conductivity in the PTMC-OH system as compared to PTMC might be contributed to the ion-polymer interactions involving the –OH side-groups. The best system in terms of conductivity is clearly the copolymer SPE of P(TMC_{20}CL_{80})/LiTFSI, showing useful RT conductivity in the range of \(10^{-4} \text{ and } 10^{-3} \text{ S cm}^{-1}\) for different salt concentrations (see supporting information Fig. S2 in Paper VII). The molecular-level origin to the enhanced ion dynamics was further investigated in Paper VIII and is also addressed in Section 4.2.2.

![Figure 30](image)

**Figure 30.** Arrhenius plots of the total ionic conductivity for three PTMC-based SPE systems.

![Figure 31](image)

**Figure 31.** SEM micrographs of PTMC with hydroxyl side groups cast on ultra-porous carbon foam coated with LiFePO_4; (a) and (b) show images with different magnifications.

In Paper IV, half-cell studies using solution-cast PTMC-based SPEs, P(TMC_{20}CL_{80})_{4.6}LiTFSI and PTMC-OH_{8}LiTFSI, were performed using two different 3D electrodes: LiFePO_4-coated C-foam and Cu_2O nanopillars, respectively. For the copolymer system, a polymer electrolyte layer was applied to pore-fill the Cu_2O-nanopillars (with thickness of 4–8 \(\mu\)m), following an approach similar to Fig. 9a and a Li foil was applied on top to form an all-solid-state cell. In the latter system, hydroxyl groups were found to favor the formation of conformal coatings along the 3D electrode surfaces. Scratch testing on thin polymer layers coated on 2D metal oxide substrates (e.g., TiO_2 and Cu_2O) confirmed the strong adhesion of PTMC-OH to the sub-
strates as compared with neat PTMC (Fig. 5 and 6 in Paper III). SEM micrographs shown in Fig. 31 also illustrate the good coverage of PTMC-OH$_8$LiTFSI electrolytes coated on 3D electrodes, e.g., LiFePO$$_4$$ deposited on C-foam.

**Figure 32.** Half-cells results from Li/P(TMC$_{20}$CL$_{80}$)$_{4.6}$LiTFSI/Cu$_2$O-nanopillars (area gain factor = 2.5) at (a) 22±1 °C and (b) 60 °C. Filled symbols refer to discharge capacities and unfilled represent charge capacities. The footprint area was considered to determine the current density and the capacity.

The cycling behavior of Li/P(TMC$_{20}$CL$_{80}$)$_{4.6}$LiTFSI/Cu$_2$O-nanopillar all-solid-state cells was tested at RT and 60 °C, respectively (Fig. 32). The conversion mechanism of Cu$_2$O in Li-batteries involves the reversible reduction reactions of Cu$_2$O and oxidation of Cu (embedded within a matrix of Li$_2$O):

$$\text{Cu}_2\text{O} + 2\text{Li}^+ + 2e^- \leftrightarrow 2\text{Cu} + \text{Li}_2\text{O}$$

The theoretical capacity of Cu$_2$O is around 375 mAh g$^{-1}$. The forward reaction during discharge and the backward reaction during charge are expected to show plateaus at 1.4−1.0 V and >2.5 V, respectively. The all-solid-state cells display consistent cycling behavior (Fig. 9b inset in Paper IV). It was also found that when increasing the amount of pillars deposited (e.g., pillars with an area gain factor of 2.5 as compared with 25), an increase of the footprint area capacity from around 0.02 to 0.20 mAh cm$^{-2}$ was obtained at room temperature with a current density of 0.008 mA cm$^{-2}$ (Fig. 9 in Paper IV). As suggested from studies on Cu$_2$O-nanopillar half-cells using liquid electrolytes, pulverization of Cu$_2$O as a result of electrochemical milling can enlarge the active surface of the particles during continuous cycling. For a binder-free electrode, the interfacial contacts between a solid electrolyte and newly formed particles might not be as good as those using liquid electrolytes. This could explain why no similar trend of capacity increase was seen for the all-solid-state cells. It can be seen that a larger discharge capacity than the corresponding charge capacity was achieved at lower C-rates or higher temperatures. At higher operational temperatures, an
improved capacity was generally achieved, which likely was due to improved electrolyte conductivity and better interfacial contacts.

4.2 Polycarbonate-based thin-film Li-batteries (Papers V-VIII)

The development of PTMC-based SPEs for all-solid-state batteries with conventional thin-film design was targeted in Paper V-VIII. A robust SPE with the thickness in the range of 50–200 µm is generally suitable for such applications. Self-standing films of SPEs prepared from solution-casting have primarily been fabricated. To evaluate the functionality for practical battery applications, the cell performance for PTMC-based SPEs was investigated from ambient to elevated temperatures.

4.2.1 Poly(trimethylene carbonate) homopolymers

High-molecular-weight PTMC doped with LiTFSI was investigated in terms of conductivity and applied for the first time in prototype thin-film Li batteries in Paper V. The cycling performance in LiFePO₄/PTMCₓLiTFSI/Li half cells, shown in Fig. 33a, demonstrated a low initial capacity followed by a clear capacity increase during two months, until a capacity plateau stabilized at 153 mAh g⁻¹. Similar capacity increases during initial cycles were observed also in other SPEs system, such as the cell studies using a thin UV-crosslinked functionalized PEA (Fig. 9 in Paper II). This suggests a potential influence from the surface contacts at the interfaces since a thick solid polymer material experiences difficulties to properly contact and penetrate the composite electrode. It was also found that the magnitude of the capacity increase correlates well with the time the cells were being stored (Fig. 6 in Paper V).

Figure 33. Cycling performance of (a) Li/PTMCₓLiTFSI/LiFePO₄ and (b) Li/PTMCₓLiX+oPTMC/LiFePO₄ (X=BF₄ or TFSI) at different C-rates at 60 °C.
The origin of such a cycling profile was further examined using SEM/EDS by comparing a fresh cell and a cycled cell. Obvious differences were noticed in the coverage of the electrolyte on the composite particles (Fig. 2 in Paper VI). This observation stimulated the development of cells using a PTMC oligomer (oPTMC) to mediate the composite electrode/SPE interfaces. Fig. 33b compares both the influence of varying the SPE salt type and introducing oPTMC between the composite electrode and the SPE. A rapid capacity increase can be seen when oPTMC is used as an interfacial mediator (i.e., accommodating the surface contacts), regardless the type of the salt. The contribution of the salt to interfacial stability is different, and SPEs containing LiBF₄ display poor cycling performance. As indicated by earlier studies on liquid electrolytes, LiBF₄ functions better than LiTFSI against Al corrosion. On the other hand, it shows inferior thermal stability when compared to LiTFSI. EIS studies of the Li/SPE interface also suggested a rapid increase in the interfacial resistance in the presence of LiBF₄, which indicate a more resistive SEI layer. Moreover, oPTMC was compared with a polyether-based oligomer, poly(ethylene glycol) dimethylether (oPEGDME), and their role of interfacial mediation was studied in cells. As shown in Fig. 1c in Paper VI, the difference is obvious – oPEGDME displayed poorer cycling stability than oPTMC in cells, which might be due to inferior compatibility between the PTMC/LiTFSI bulk electrolyte and the PEGDME oligomer.

Figure 34. Radial distribution functions (RDFs) and coordination numbers (CN) of Li⁺-OTFSI, Li⁺-OPTMC and Li⁺-O₂ (carbonyl oxygen) in PTMC₈LiTFSI obtained from Molecular Dynamics simulations at 423 K.

There is a lack of fundamental knowledge regarding to the ion transport mechanisms in polycarbonate-based SPEs. Considering the discrepancy in the polymer structure between polycarbonates and polyethers, a natural
question would be how Li ions are coordinated and transported along the carbonate units. A first study on the ion transport mechanism in PTMC-based SPEs is presented in Paper VIII. As suggested by the radical distribution functions (RDFs) and the coordination number (CN) results from Molecular Dynamics (MD) simulation, the Li coordination sphere is dominated by carbonyl oxygens, with an average coordination number of around 4 for the shortest Li-O bond distances, and approximately 2 oxygens for the TFSI anions. The Li\(^+\)-TFSI\(^-\) coordination showed a stronger dependence on temperature than Li\(^+\)-polymer interactions (Fig. 8 in Paper VIII). A coupling of the cation with the segmental movements of the polymer chains was also observed from the NMR studies, while the anion motions were found less restricted by the polymer motions and contributed most to the total ionic diffusion.

### 4.2.2 Copolymers of poly(trimethylene carbonate)

Effective synthetic approaches to design copolymers of TMC and CL units with improved ion transport properties were implemented in Paper VII. Systematic studies on the properties of P(TMC/CL) copolymers with varied TMC/CL ratio were recently presented.\(^{211}\) It was observed that as the CL content increased (e.g., TMC:CL from 90:10 to 60:40), an enhancement of two orders of magnitude in the ionic conductivity could be achieved. By further increasing the monomer ratio towards a CL-dominated system (TMC:CL=20:80), an amorphous copolymer with useful RT ionic conductivity (i.e., \(4.1\times10^{-5}\) S cm\(^{-1}\) at 25 °C) was realized.

![Figure 35. Temperature-dependence of the spin-lattice relaxation times for (a) \(^1\)H and (b) \(^7\)Li and \(^{19}\)F in P(TMC\(_{20}\)CL\(_{80}\))\(_{4.6}\)LiTFSI and PTMC\(_{8}\)LiTFSI.](image-url)

Within the temperature range 22-60°C, a comparison of the temperature-dependence of spin-lattice relaxation (\(T_1\)) was made between the two systems (Fig. 35). A general increase of proton and lithium relaxation times can be seen when the temperature decreases. An opposite trend was observed in the \(^{19}\)F relaxation results, also less pronounced than the \(^1\)H and \(^7\)Li relaxa-
tions when changing the polymer host. The estimated activation energy ($E_a$) for the reorientation motion of the polymer chains appears to be reduced when the CL units are introduced into the copolymer system. As a result of the faster polymer dynamics in the more flexible copolymer, the local movements of $Li^+$ can be assisted through the coordination of $Li^+$-carbonyl oxygens along polymer chains (Figs. 7 and 8 in Paper VIII). This observation suggests a similar coupling phenomenon between Li-ion conduction and polymer segmental motions as seen for polyether-based SPEs. As also confirmed in FTIR studies (Fig. 5 in Paper VIII), a preferential Li coordination with the ester oxygens of CL units was observed in the LiTFSI-doped copolymer system.

Figure 36. Cycling performance of a LiFePO$_4$/P(TMC$_{20}$CL$_{80}$)$_{4.6}$LiTFSI/Li cell at (a) room temperature and (b) 40 °C within different voltage cut-offs.

The half-cell cycling performance presented in Fig. 36a shows the effect of different voltage cut-offs and C-rates at RT. Capacities over 100 mAh g$^{-1}$ could be achieved within a larger voltage range at C/20. On the other hand, at the higher C-rate of C/5 or within a smaller voltage range, an abrupt loss of capacity was observed (Fig. 36b). This was likely due to the suppressed conduction dynamics when decreasing the temperature towards RT. Capacities of up to 120 mAh g$^{-1}$ could however be reached when increasing the temperature to 40 °C, also for higher C-rates.

4.3 Interfacial chemistry of polymer electrolytes (Papers IX-X)

Paper IX comprises a first XPS study of the composition of interphase layers formed at the electrode/SPE interfaces, exemplified by graphite/PEO$_{35}$LiTFSI/Li cells. The influence of water contaminations in the system was noticeable as a consequence of different electrolyte preparation conditions. A follow-up study on polycarbonate-based SPEs is summarized in Paper X, demonstrating the composition of interphase layers formed in

66
PTMC₈LiTFSI-based LiFePO₄ and graphite half-cells. The following section provides an overview of the suggested schemes for SEI formation at the anode/SPE interface (i.e., Li and graphite) and SPI formation at the cathode/SPE interface (i.e., LiFePO₄).

Due to softening and/or melting of polymeric materials at elevated temperatures, it has been a technical challenge to obtain neat surfaces when disassembling the SPE thin-films from the electrode surfaces. Characterization on four surfaces per half-cell was routinely performed to get a complete picture of the surface characteristics.

4.3.1 SEI formation at anode/polymer electrolyte interfaces

As compared to liquid solvents, solid polymers are expected to be less reactive during chemical and electrochemical reactions due to their intrinsic chemical and thermal inertness. Nevertheless, as observed from EIS analysis, an increase of SEI resistance during time periods of up to days suggests a gradual formation or relaxation of passivation layers on the anode surface even without cycling. On the other hand, the lower cationic diffusion (usually 10 times lower than the anion) commonly observed in SPEs may result in slower reaction dynamics for the involved Li species.⁷⁶,²⁴¹

A key issue addressed in Paper IX is the comparison of SEI compositions at the graphite/SPE and graphite/liquid electrolyte interfaces. It should be noted that the water content in the SPEs was found to be significantly higher than that in liquid electrolytes. PEO is known to be hygroscopic, and so is LiTFSI. It was found that the amount of unremovable water being taken up during solution-casting correlates well with the formation of LiOH detected at the graphite surface. On the Li surface, ROLi was instead observed without any obvious trace of LiOH, suggesting that water might migrate with the Li ions towards the graphite surface during the first discharge. Furthermore, it was suggested that a catalytic effect of the active carbon atoms might initiate salt decomposition close to the graphite surface (see Fig. 2 in Paper IX).

PTMC, on the other hand, is more hydrophobic and there was also less amount of water (<40 ppm) detected in the as-formed SPEs using Karl-Fischer titration. Compared to the ‘hydrated’ PEO system, LiOH is unlikely to be present in the ‘dry’ PTMC system. The dominating peak located at 531.6 eV and 530.7 eV, respectively, in the O1s XPS spectrum from the interface of graphite/PTMC (Fig. 1 in Paper X) can rather be assigned to PTMC-derived Li alkyl carbonates and Li alkoxides. Polycarbonate species detected at both graphite and Li surfaces might be formed via the electrochemically-driven degradation reactions as seen for linear carbonates at low potentials.¹⁸¹,²⁴²,²⁴³

Obvious salt degradation was detected at the graphite/PTMC interface, showing pronounced peaks from sulfur-species (e.g., Li₂S, polysulfide and
Li$_2$SO$_3$) close to the graphite surface. These products are consistent with anion decomposition reactions proposed earlier$^{180}$ which contribute to the heterogeneous structure of the SEI. These observations indicate that the surface chemistry at the graphite/SPE interface, at least during short-term cycling, could obviously be affected by the presence of water as well as salt stability. Moreover, scheme 1 in Paper X provides explanations for the peaks for Li alkyl carbonates and Li alkoxides as detected at the PTMC/anode interface.

### 4.3.2 SPI formation at cathode/polymer electrolyte interfaces

Earlier work on commercial cathode materials and liquid electrolytes has shown that the SPI composition varies depending on the surface nature of the cathode materials.$^{173}$ Carbon-coated LiFePO$_4$ was found to be more stable, with an obvious absence of Li$_2$CO$_3$, than for example LiMn$_2$O$_4$ or LiCoO$_2$. The dominating species detected were rather salt-based products such as LiF, which increase in concentration at elevated temperatures.

As observed from the interfaces of Li/PTMC-LiTFSI and LiFePO$_4$/PTMC-LiTFSI, no obvious decomposition of salt was found (Fig. 2 in Paper X). Close to the Li metal surface, Li$_2$O as well as PTMC-derived Li alkyl carbonates and Li alkoxides were estimated as the main products. This suggests similar reactions of PTMC at the graphite surface also occurring at the Li metal surface at low potentials. Half-cells of Li/PTMC-LiTFSI+oPTMC/LiFePO$_4$ were also examined by XPS after long-term cycling, and further confirmed a stable SPI formation at the LiFeO$_4$ cathode surface (Fig. 4 in Paper X). Table 1 and Table S1 in Paper X lists a summary of the dominating species and the respective atomic concentration in both graphite and LiFePO$_4$ half cells containing SPEs.

In general, the SPI composition in LiFePO$_4$ half cells suggests that a stable interphase layer is formed in contact with both PEO and PTMC-based SPEs. For systems with relatively low levels of water, composites of LiF, Li$_2$O, Li$_2$S and Li alkoxide were formed at the Li/SPE interface. Only low concentrations of the decomposed salt were found close to the LiFePO$_4$ surface.
5. Conclusions

*Who knows where inspiration comes from? Perhaps it arises from desperation. Perhaps it comes from the flukes of the universe, the kindness of the muses.*
  - Amy Tan

This thesis explores the design and implementation of solid polymer electrolytes in all-solid-state Li-batteries, which are considered to be strong candidates for safe battery applications, ranging from small-scale to large-scale. To accommodate the transition from 2D to 3D battery designs, the research in this thesis work has covered the design of polymers for 3D electrodes, the fabrication of novel polymer electrolyte systems and insights into the interfacial chemistry of Li polymer batteries.

Functionalized monomers and polymers from both polyether- and ‘alternative’ polycarbonate host materials have been considered. Targeted for 3D electrode configurations, thin polymer coatings fabricated from multifunctional PPO-based monomers consisting of amine and/or acrylate groups were produced. *In-situ* polymerization methods using UV-initiated polymerization and electropolymerization showed the potential to deposit pinhole-free and conformal polymer layers with submicron thicknesses onto a variety of non-planar substrates (*e.g.*, LiFePO₄ composite, Cu₂O-nanopillars or porous carbon foam). Alternatively, improved surface adhesion and transport properties were realized via synthetic modifications of PTMC. These investigations have generally shown the potential to tailor polymer materials for specific needs in electrolyte systems, also for a delicate system such as an all-solid-state 3DMB. In addition to the successful design of the above-mentioned electrolyte properties, interfacial conditions when applying the second electrode and the surface mechanical strength of the electrolyte demand further development for realization of functioning 3DMB whole-cells. Not least should mechanical properties be highlighted in future synthetic development of SPEs for microbattery applications.

For the broader application area of all-solid-state Li-batteries with conventional thin-film design, it has been demonstrated that alternative polymer hosts to the conventional PEO-based systems might well provide a basis for future development of SPE materials. In this context, polycarbonate-based solid polymer electrolytes have been studied in particular, providing new insights and ideas regarding the development of lithium conductors. Hydro-
phobic and biodegradable PTMC and its derivatives (i.e., PTMC oligomer and copolymers) have been explored in this thesis. PTMC demonstrated good solvation of salt and promising performance in LiFePO$_4$ half-cells during long-term cycling, approximately 153 mAh g$^{-1}$ at 60°C with high coulombic efficiency was achieved after 150 cycles. To tackle the issue of poor surface contacts and to enable RT application of SPEs, PTMC oligomers were applied and a copolymer of TMC with CL units was developed. In the former case, the PTMC oligomers demonstrated to effectively mediate the surface contacts between the SPE and the composite electrode, rendering a distinct improvement in the initial cell performance and rate capability. For the latter system, enhanced cation diffusion was suggested when flexible chains of CL units were introduced. Li-ion conduction was found facilitated by the coordination of Li$^+$ to carbonyl oxygens from both experimental and computational studies. The best performing systems using P(TMC$_{20}$CL$_{80}$)$_{4.6}$LiTFSI and PTMC$_8$LiTFSI+oPTMC, respectively, demonstrate functionalities at close to ambient temperatures.

Initial research on the SEI and SPI formation at the electrode/SPE interfaces led to a better understanding of the interfacial stability and the effect of the water content in all-solid-state Li polymer batteries. As a result of water uptake (hundreds up to thousands of ppm) in PEO-based SPEs, noticeable amounts of LiOH were observed at the graphite/PEO-LiTFSI interface. Hydrocarbon species and salt decomposition products were consistently observed regardless of the amount of water. This generates a different image of the SEI as compared to those formed using conventional liquid electrolytes. When using more hydrophobic polycarbonate-based SPEs, the SEI was dominated by products from the decomposition of salt and polycarbonate residuals. High molecular weight PTMC may undergo similar degradation reactions as linear carbonate solvents at low potentials. The SPE systems appeared to be significantly more stable in LiFePO$_4$ half cells, with only small amounts of decomposed sulfur-species and LiF detected.
Perspectives

The emergence of novel battery concepts based on 3D electrode configurations provides new visions for the optimization of power and energy densities in energy storage devices. At the same time, demands regarding battery safety and stability pose new requirements on the electrolyte development. This not only requires materials which are cost-effective and easy to manufacture, but also stable for good practical performance in a long lifespan.

Suitable fabrication approaches will favor cost-effective methods which enable rapid coating on complex electrode configurations. UV-initiated polymerization is such a rapid and simple technique to form micron-sized and cross-linked polymer electrolyte films. Alternatively, electropolymerization provides a better option to yield ultrathin polymer coatings and enhance the adhesion at the organic electrolyte/inorganic substrate interfaces. Moreover, careful considerations in the molecular design of polymer materials are critical to achieve functioning polymer electrolytes with downscaled thickness. Enhanced mechanical strength in the polymer matrix appears to be critical in this context. Further studies may proceed by introducing block units with high mechanical strength through copolymerization strategies. Alternative polymerization methods may also be considered, such as surface-initiated polymerization, which employ polymerization reactions from functionalized electrodes. Related applications of ultrathin polymer electrolytes could perhaps be extended to the field of artificial interphase layers. Considering the chemical and morphological similarity between an ultrathin polymer electrolyte and a typical SEI, composites consisting of a suitable proportion of interfacially stable and sufficiently ion-conducting phases, which also allow the necessary electron transport, may be helpful to yield stable interphase layers and suppress electrolyte decomposition.

Future studies on the polycarbonate electrolyte systems could follow the polymer-in-salt approach. A decoupling of the cation dynamics from the polymer segmental motion could well be favorable for achieving fast ion conduction in such materials. Moreover, further synthetic modifications of the promising P(TMC/CL) copolymers could be developed for enhanced mechanical properties to suit high temperature applications. PTMC-based SPEs can also be applied for high-voltage cathodes considering its wide electrochemical stability window. It should then be noted that the incorpora-
tion of stable salts or additives would be necessary to suppress the salt decomposition at the interfaces as well as Al corrosion at high potentials.

In the context of the interfacial chemistry in Li polymer batteries, the preliminary studies here open up for acquiring knowledge on SEI and SPI formation. The roles of the respective components in the interphase layers still demand further investigations, particularly their evolution under varied cycling conditions (e.g., C-rate, depth of charge/discharge and electrode composition). Considering the difficulty associated with disassembling long-term cycled cells, extended work may be undertaken using complementary in-situ techniques, such as NMR-imaging.

As demonstrated in this thesis work, polymer electrolytes hold great potential for implementation in tomorrow’s Li-batteries. Via synthetic strategies for functionalization of monomers, different polymerization strategies and alternative fabrication methods, a tailoring of the electrolyte properties can be undertaken to generate materials which can fulfill a large number of requirements – for both large-scale and small-scale applications, operated at both low and high temperatures. The future for this field of materials research and development certainly looks bright.
Sammanfattning på svenska

Energilagring av elektricitet har under de senaste åren blivit en av de viktigaste potentiella lösningarna för att möta de långsiktiga ökningarna i oljepriset och de associerade miljöproblemen med fossila bränslen. I detta sammanhang sätts stort hopp till Li-jonbatteriet, vilket är ett laddningsbart batteri med lång batteritid och som är mer miljömässigt hållbart än engångsbatterier. Parallellt med den snabba utvecklingen för batterier inom olika miljötekniska tillämpningar (se Figur 1), finns också ett växande intresse för batterianvändning från allt från småskaliga tillämpningar (t.ex. mikrosensorer och mikromedicinska implantat) till storskaliga tillämpningar (t.ex. elfordon och elektriska kraftnät). Förbättrad säkerhet, låg kostnad och tillförlitlig prestanda är prioriterade krav för framtidens batterier.

Figur 1. Exempel på tillämpningar av Li-jon-polymer-batterier.

Ett Li-jon-polymer-batteri består av tunna filmer av två strömtilldelare, en polymerelektrolyt och två elektroder (katod och anod). I konventionella Li-jonbatterier används en brandfarlig vätska som lösningsmedel för elektrolyten, vilket ofta anses utgöra en stor säkerhetsrisk eftersom batterierna är benägna att fatta eld vid överladdning och överhettning. En stor förbättring av säkerheten skulle kunna fästa genom att dessa problematiska flytande komponenter elimineras. Li-jon-polymer-batterier, som använder polymerelektrolyter, är i detta sammanhang ett säkrare batterisystem då icke brandfarliga
polymerer i fast fas används som elektrolyter. Polymerelektrolyter är flexibla material, och finns därmed i olika former, och har dessutom låg vikt. Det gör elektrolytarna användbara i många nya tillämpningar, såsom flexibla batterier, tryckbara solceller och smarta fönster.

Figur 2. En jämförelse mellan batterier med 2D- och 3D-konfigurationer liknar den mellan ett plant hus och en skyskrapa.

Polymerelektrolyter med god stabilitet har också tagits i beaktande som en viktig komponent i vissa nya batterikonstruktioner. Ett nytt sorts batteri – ett tredimensionellt mikrobatteri (3DMB) – kommer att kunna avge högre effekt och innehålla mer energi än de tillgängliga Li-jonbatterier med plan (2D) konfiguration. Ett batteri med 3D-konstruktion utnyttjar de extra ytorna längs den tredje dimensionen av elektroderna. Detta går att likna vid en jämförelse mellan ett plant hus och en skyskrapa (se Figur 2) – genom att bygga på höjden kan mer få plats på en liten yta. Dessa mikrobatterier är viktiga komponenter för att driva elektronik i mikro- och nanostorlek, och är kapabla att lagra åtminstone tio gånger så mycket energi inom ett litet område som motsvarande 2D-konstruktion.

Figur 3. 3D-arkitekturer observerade från ett högupplösande elektronmikroskop: 3D-nanostavar av koppar belagda med en ultratunn polymerelektrolyt före (a) och efter (b) beläggning.

I den här doktorsavhandlingen beskrivs hur nya polymerelektrolyter syntetiserats och att de uppvisar gynnsamma egenskaper för användning i


Det anses generellt att under användning av batterier så styrs mycket av säkerheten och stabilitet av gränsytan mellan elektrod och elektrolyt. Här bildas tunna filmer som förhindrar ytterligare nedbrytning av elektrolyten, vilket är välstuderat för konventionella flytande elektrolyter i kontakt med anodmaterial (minuspol) som grafit. Föreliggande avhandling rymmer ett par pionjärstudier av hur den kemiska sammansättningen ser ut i sådana filmer när polymerelektrolyter används.
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