A Renaissance for Li-Battery Solid Polymer Electrolytes: Polycarbonate-based SPEs

Bing Sun, Jonas Mindemark, Daniel Brandell

Department of Chemistry-Ångström Laboratory
Uppsala University
Designing Safe Electrolytes

**State of the Art for Polymer Electrolyte**

- Polymer host: Polyethers (PEO, PPO)
- Ionic salt MX: M=Li⁺,Na⁺, X= Tf, TFSI
- Additives: plasticizers, nanoparticles, ILs

The archetype polymer host: PEO - polyethylene oxide - (CH₂CH₂O)ₙ -

- Low $T_g$
- Good ability to dissolve Li salts
- Poor RT conductivity
- Low dielectric constant
- Semi-crystalline
- Very poor Li transport numbers
- Contains residual H₂O

Insufficient, yet dominating scientific literature!
Alternative Polymer Hosts: Polycarbonates

Macromolecule Solvents for SPEs

- **PEO**
- **PPO**

Polyethers

Organic Solvents for Liquid Electrolytes

- **Cyclic carbonates**
- **Linear carbonates**
- **Cyclic ethers**

- Amorphous
- High dielectric constant
- Thermally stable
- Biodegradable

Possibilities for functionalization – for low-Tg, for surfactant properties, for x-linking, etc,...
The first PTMC half-cell

This cell cycled at near full capacity for close to a year!

Interface Mediator: Oligomer PTMC

- LiFePO$_4$/PTMC-LiTFSI/Li, 60°C
- LiFePO$_4$/PTMC-LiX + oligomer/Li, 60°C

- LiTFSI displayed better stability than LiBF$_4$.
- High initial capacity achieved by applying oPTMC.
- Oligomer PTMC showed superior compatibility in cell studies.

Functionalized polycarbonates

Functional units for:
- Plastization
- Cross-linking

Record-low Tg achieved

Improved conductivity as compared to PTMC at low temperatures
PTMC-SPES: Surface Adhesion Enhancement

- Surface adhesion: side group modification

![Chemical structure of PTMC](image)

Scatch Testing

- PTMC-OH on TiO$_2$
- PTMC on TiO$_2$
- Enhanced surface adhesion for SPEs containing –OH groups

B. Sun, J. Mindemark, D. Brandell
*Polymer Chemistry, 6* (2015) 4766.
PTMC-SPES: Conductivity Enhancement

- Co-polymerization: TMC and ε-caprolactone (CL)

Poly(trimethylene carbonate-co-ε-caprolactone)

\[ \text{P(TMC/CL)}_n \text{LiTFSI (n=4.6)} \]

\[ \text{P(TMC/CL)} = 20:80 \text{LiTFSI} \]

RT Functionality of P(TMC/CL) Copolymer

Comparatively good cell performance in P(TMC/CL)-SPEs was realized at ambient temperatures.
**Functionalized Polycarbonates for 3DMBs**

RT-performance in all-solid-state Li-polymer 3DMBs was demonstrated.

\[
\text{Cu}_2\text{O} + 2\text{Li}^+ + 2\text{e}^- \Leftrightarrow 2\text{Cu} + \text{Li}_2\text{O}
\]
Insights on Ion Transport in SPEs

• Transport of Li\textsuperscript{+} is assisted by Li\textsuperscript{+}-ether oxygen coordination along the polymer chains;
• Anion diffusion via dissociation from the ion pairs with Li\textsuperscript{+}.

Polyether-LiX

Polyether-LiX

X= PF\textsubscript{6}, BF\textsubscript{4}, ClO\textsubscript{4}, TFSI

Polyester-LiX

PTMC

LiTFSI

P(TMC/CL)

Ion Transport in PTMC-LiTFSI

- Dominating Li\(^+\)-carbonyl oxygen coordination.
- \(^1\)H and \(^7\)Li NMR showed direct correlation in spin-spin relaxation \(T_1\), likely due to coupling of the two motions.
Ion Transport in P(TMC/CL)-LiTFSI

* [O\(\text{C}=\text{O}\)] P(TMC/CL) [O\(\text{C}=\text{O}\)]

**Preferential Li\(^+\)-carbonyl oxygen (CL) coordination as compared with Li\(^+\)-carbonyl oxygen (TMC)**

P(TMC/CL=20:80)\(_x\)LiTFSI (\(x=\infty\); 6.6; 4.6 from left to right)

![FTIR spectra](image)
The Role of the interphase layers:

- Safety
- Coulombic efficiency
- Capacity retention
- Rate performance

Solid polymer electrolyte/electrode interfaces

PEO-LiTFSI: SEI Formation on Graphite

**Graphite/PEO\(_{25}\)LiTFSI/Li, C/50 at 50°C**

- **Liquid electrolyte cell**
- **Polymer electrolyte cell a (2300 ppm)**
- **Polymer electrolyte cell b (675 ppm)**

**Water Content from Karl-Fischer Titration [ppm]**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>PEO (Aldrich)</th>
<th>PEO (BDH)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50 °C</td>
<td>120 °C</td>
</tr>
<tr>
<td>5</td>
<td>690</td>
<td>142</td>
</tr>
</tbody>
</table>

**PEO\(_{25}\)LiTFSI (dried with different setups)**

<table>
<thead>
<tr>
<th>Designed container</th>
<th>Soft-bag</th>
</tr>
</thead>
<tbody>
<tr>
<td>675</td>
<td>2300</td>
</tr>
</tbody>
</table>
XPS Analysis on Graphite/PEO Interface

Salt decomposition dominated on cycled G/PEO interface; Water residues in PEO-LiTFSI might contribute to LiOH formation.

C. Xu, B. Sun, T. Gustafsson, K. Edström, D. Brandell, M. Hahlin
SEI Formation: PTMC-Based SPE

Graphite/PTMC_{8}LiTFSI

Proposed salt decomposition in LiTFSI-containing SPEs:

PTMC host may undergo electrochemical/chemical reactions to form PTMC-Li carbonate (PTMC-Li-C) or PTMC-Li alkoxide (PTMC-Li-A).
No obvious degradation products observed on the cathode/SPE interfaces; complex degradation reactions dominantly occurred at interfaces close to the anode (i.e., Li or graphite).
Alternative SPEs using **functionalized poly(trimethylene carbonate)** showed promising cycling performance and RT functionality;

Experimental and simulation studies on PTMC-based SPEs displayed **coupling between Li ions and polymer chains**, with preferential Li$^+$-ester carbonyl group coordination observed.

Compositional studies of SEI formation for **hygroscopic PEO-LiTFSI** displayed LiTFSI degradation and LiOH as a product due to water contamination;

XPS studies on interphase layers for **PTMC-LiTFSI** suggested salt and polymer degradation primarily on the anode.
Acknowledgement

Co-workers:
Bing Sun
Jonas Mindermark
Matthew Lacey
Tim Bowden
Kristina Edström
Torbjörn Gustafsson
Maria Hahlin

Chao Xu
David Rehnlund
Habtom Desta Asfaw
Laura Imholt
Erik Törmä

External collaborators:
Luciano Costa, Brazil
Prof. István Furó, KTH
Prof. Patrik Johansson, Chalmers

Thank you for listening!
ISPE-XV
International Symposium on Polymer Electrolytes
Fundamentals and Applications

Uppsala, Sweden
15-19th August 2016

- Solid polymer electrolytes
- Ionic liquids
- Hybrids and gels
- Etc...

- Li- and Na-ion batteries
- Fuel cell membranes
- Photoelectrochemical applications
- Etc...

www.delegia.com/ispe2016