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

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Uppsala University

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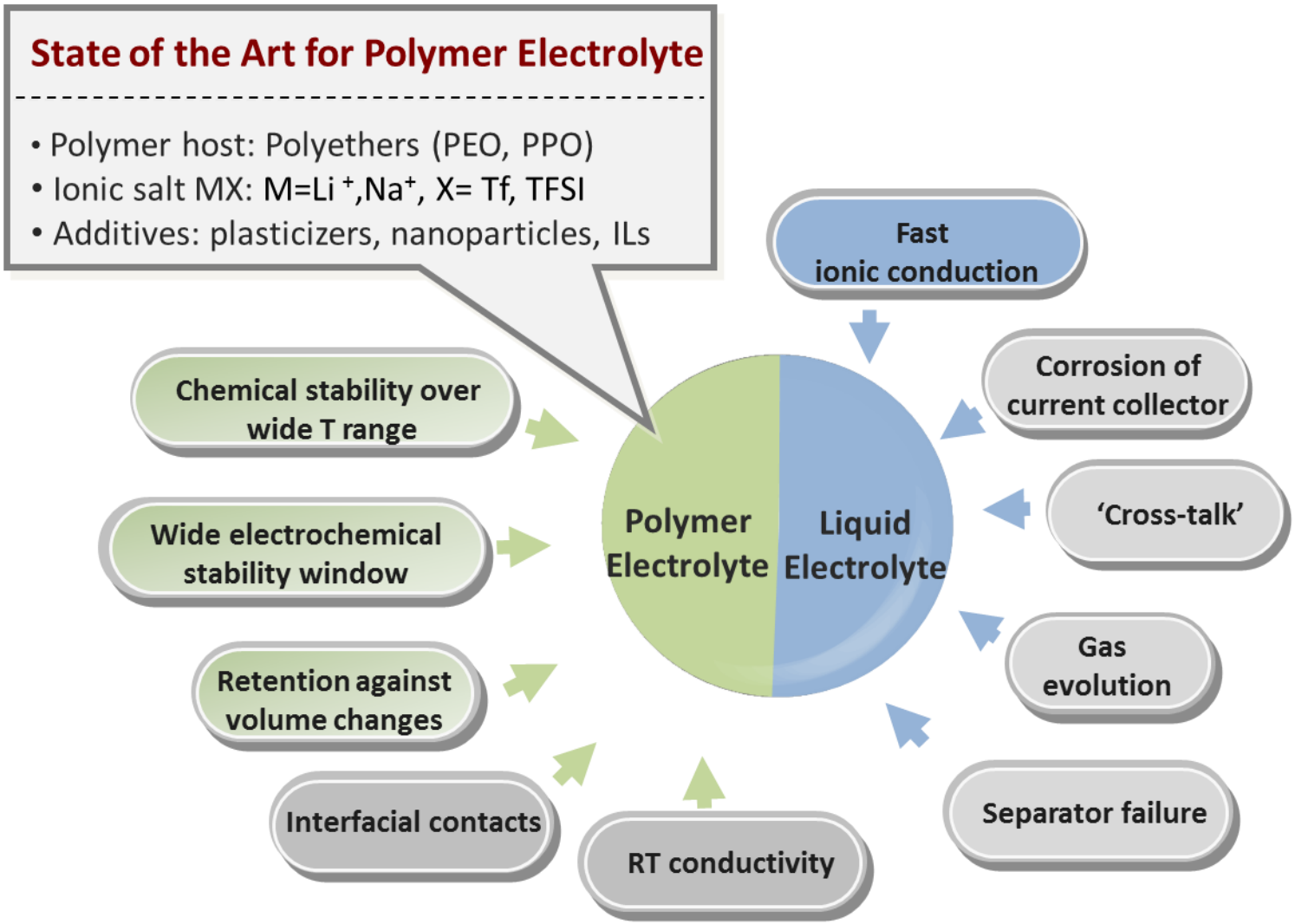
Designing Safe Electrolytes



John B. Goodenough, Y. Kim, *Chem. Mater.*, 22 (2010) 587.

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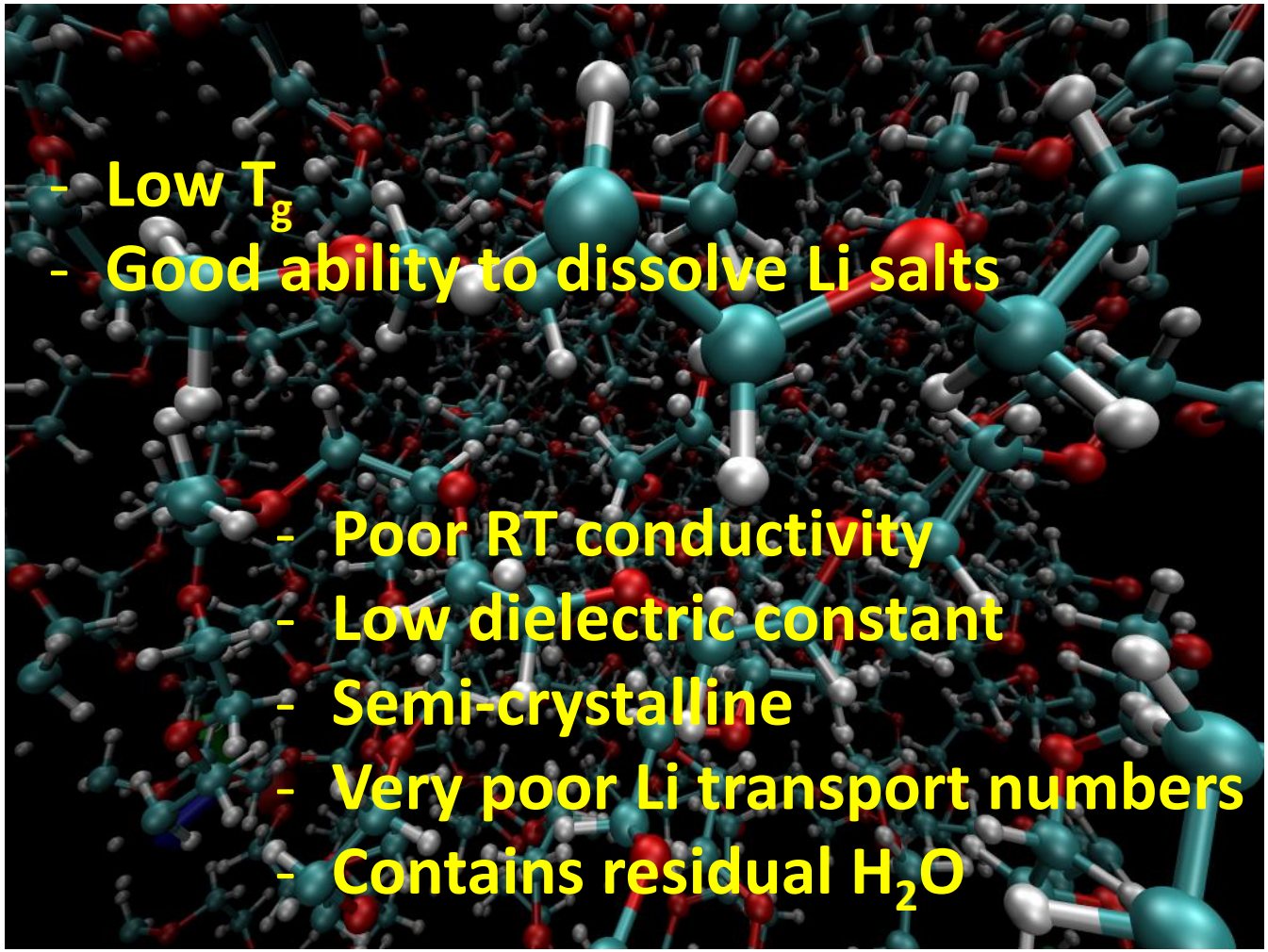
The archetype polymer host: PEO - polyethylene oxide $-(CH_2CH_2O)_n-$



Insufficient, yet dominating scientific literature!

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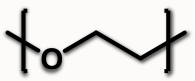
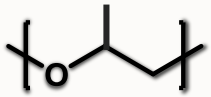
Alternative Polymer Hosts: Polycarbonates

Macromolecule Solvents for SPEs

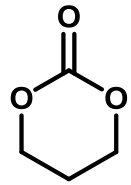
PEO



PPO

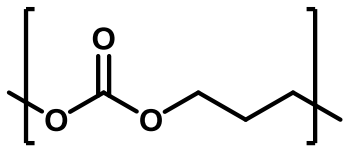


Polyethers



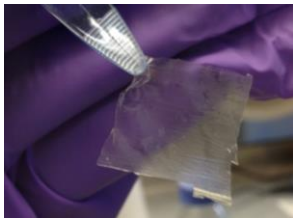
TMC

$Sn(Oct)_2$

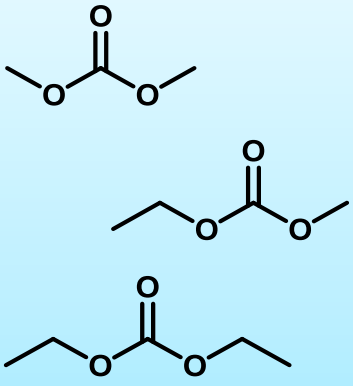


PTMC

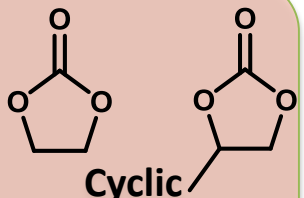
- ✓ Amorphous
- ✓ High dielectric constant
- ✓ Thermally stable
- ✓ Biodegradable



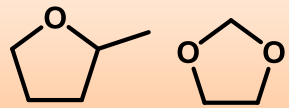
Organic Solvents for Liquid Electrolytes



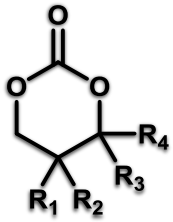
Linear carbonates

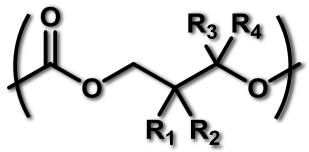


Cyclic carbonates



Cyclic ethers





Possibilities for functionalization – for low-Tg, for surfactant properties, for for x-linking, etc,…

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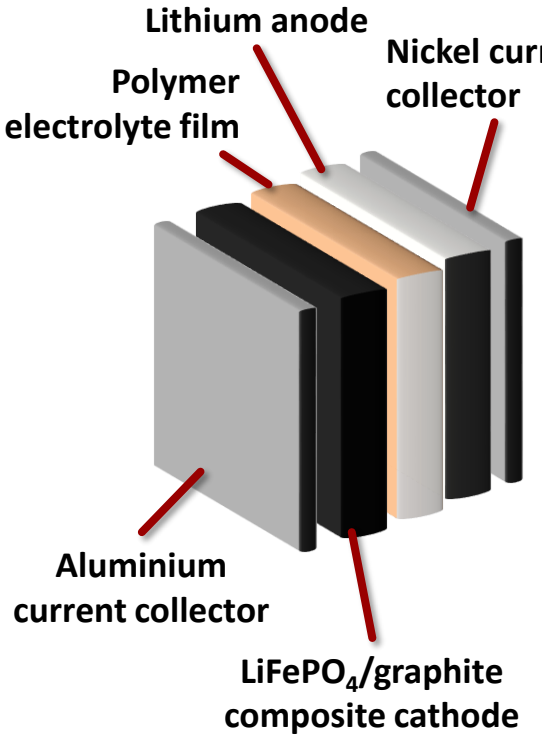
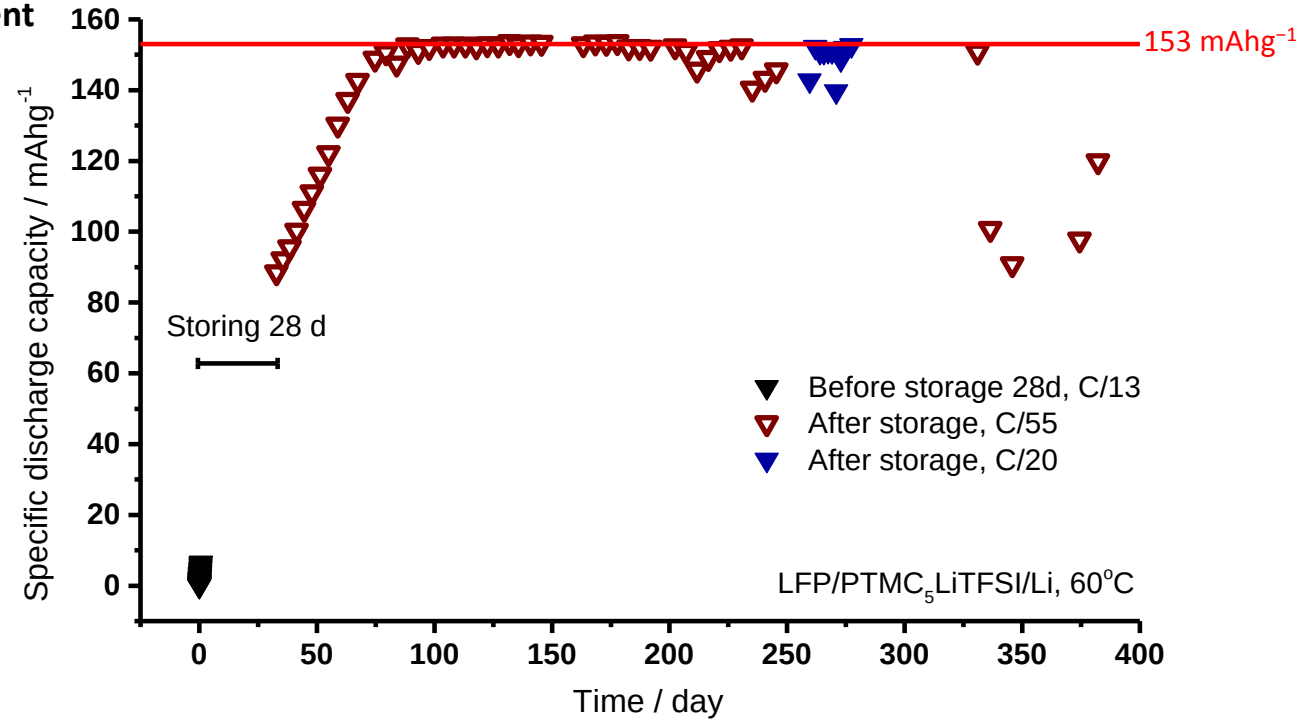
The first PTMC half-cell



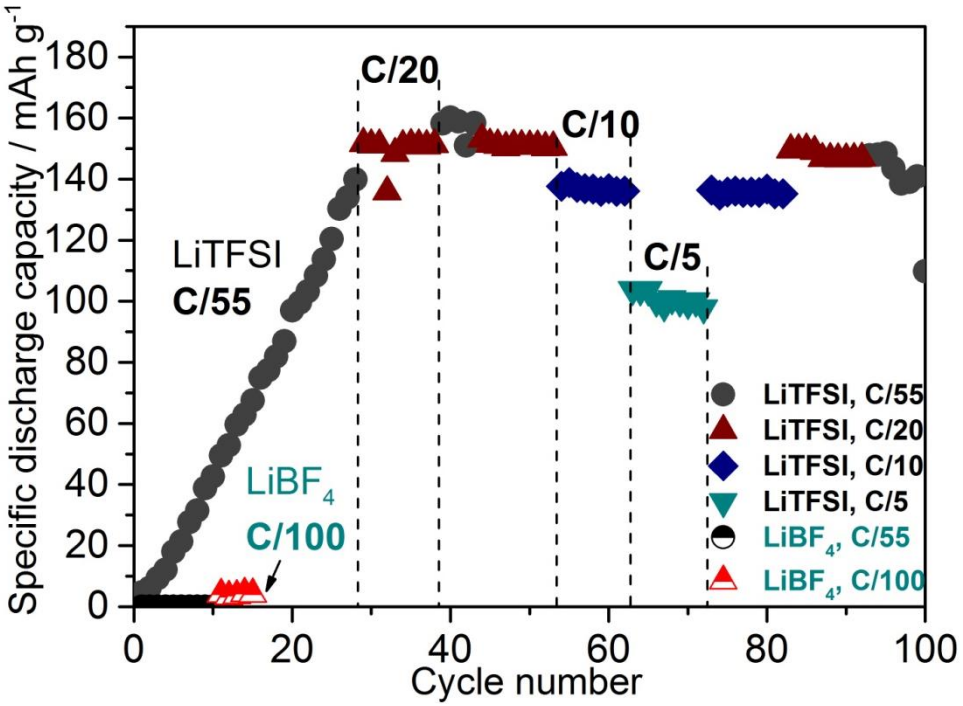


This cell cycled at near full capacity for close to a year!

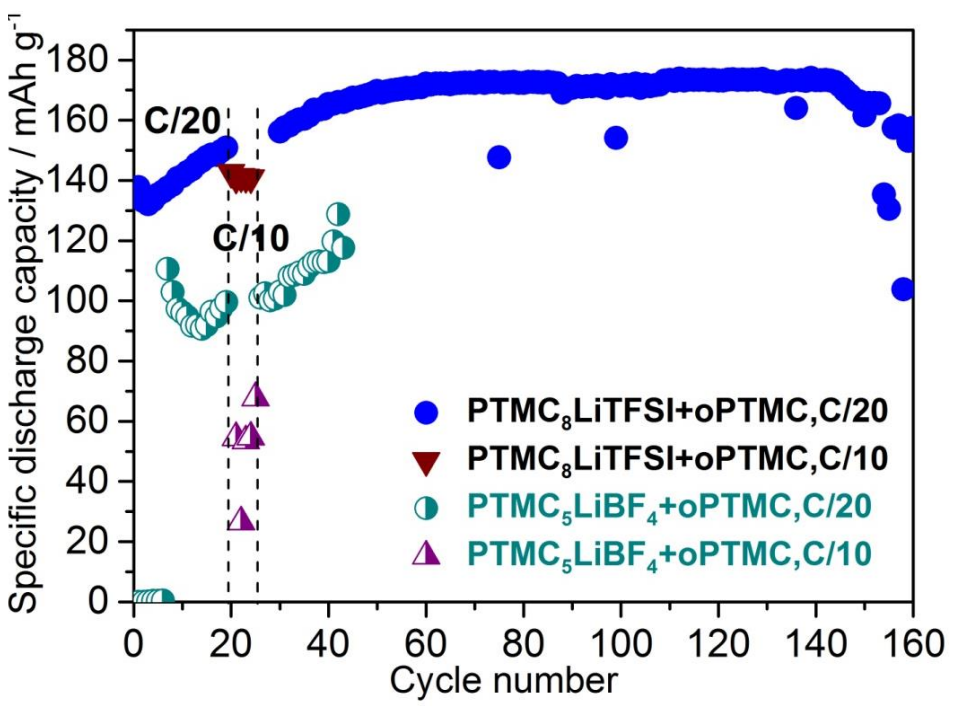
Sun, B.; Mindemark, J.; Edström, K.; Brandell, D. *Solid State Ionics* **2014,** *262,* 738–742

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.**

B. Sun, J. Mindemark, K. Edström, D. Brandell, *Electrochemistry Communications,* **52** (2015) 71.

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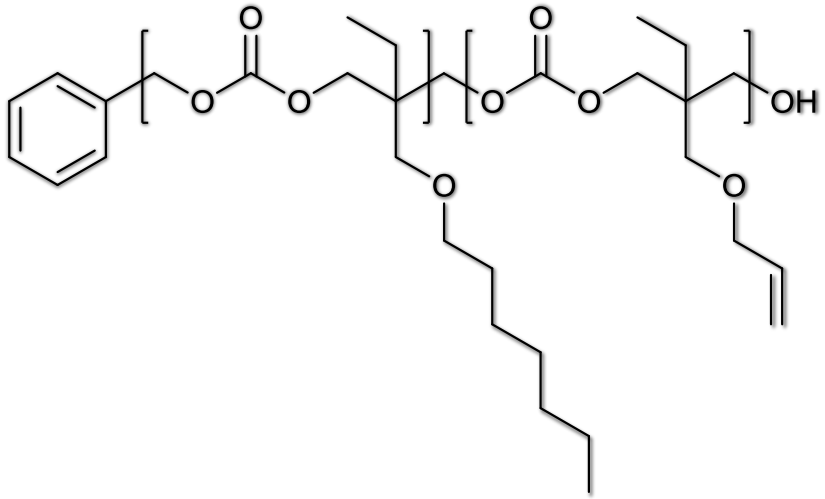
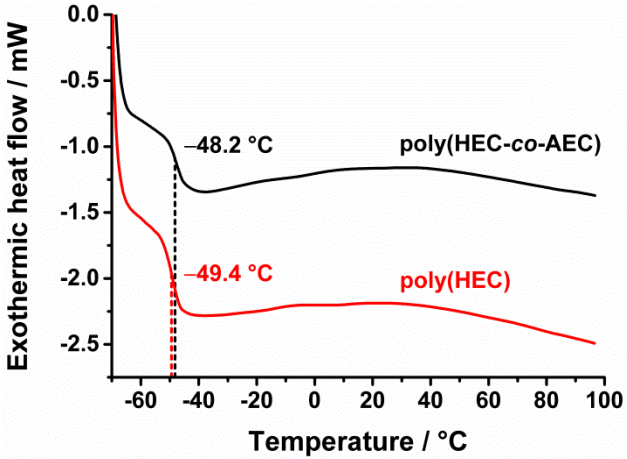
Functionalized polycarbonates

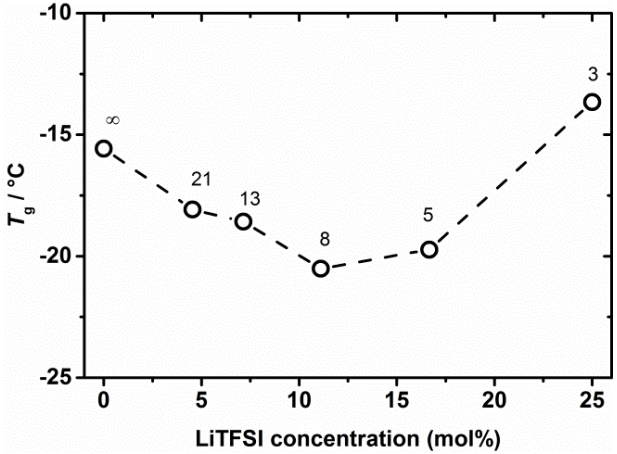


Functional units for:

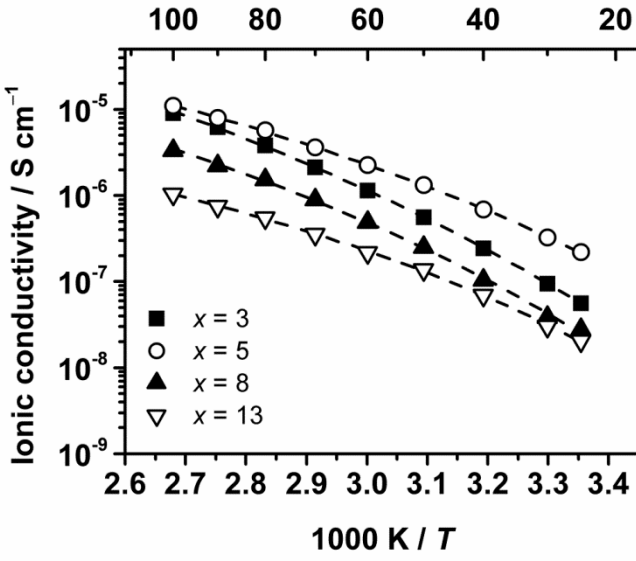
- **Plastization**
- **Cross-linking**

Record-low Tg achieved



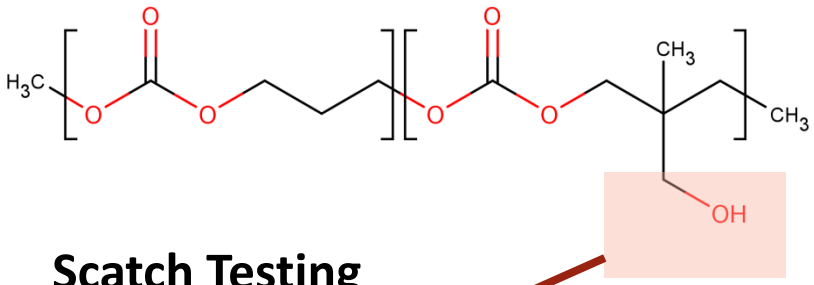


Improved conductivty as compared to PTMC at low temperatures

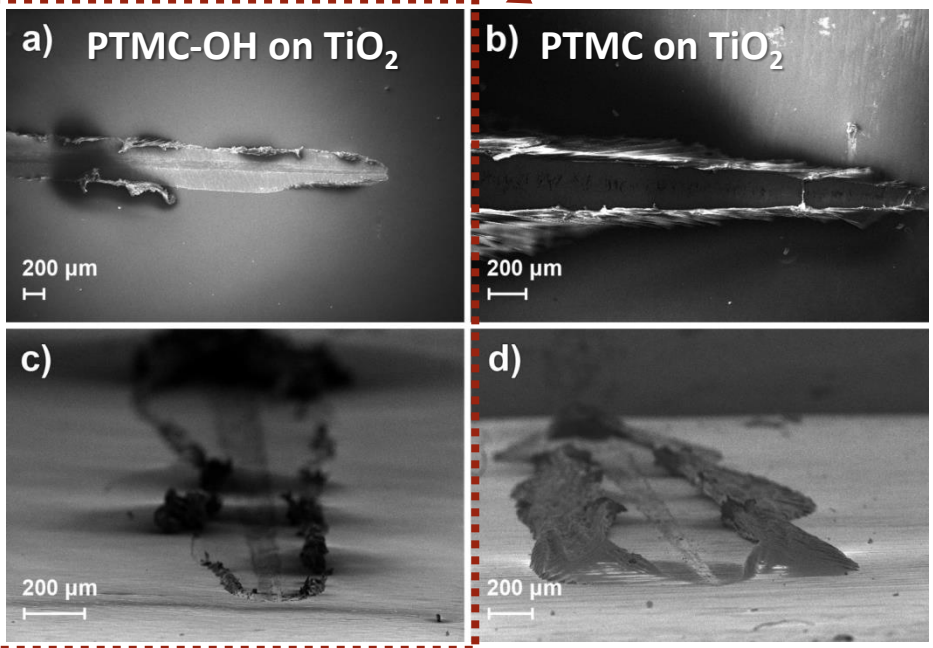


PTMC-SPEs: Surface Adhesion Enhancement

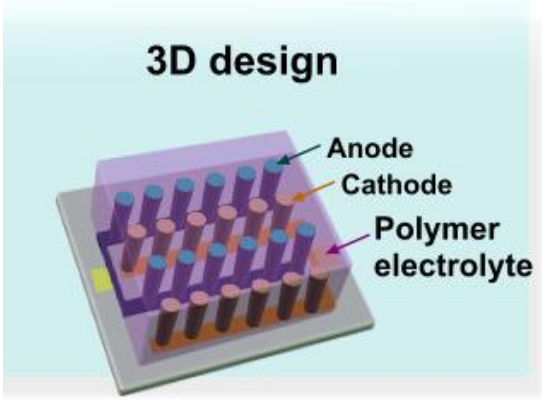
- Surface adhesion: side group modification

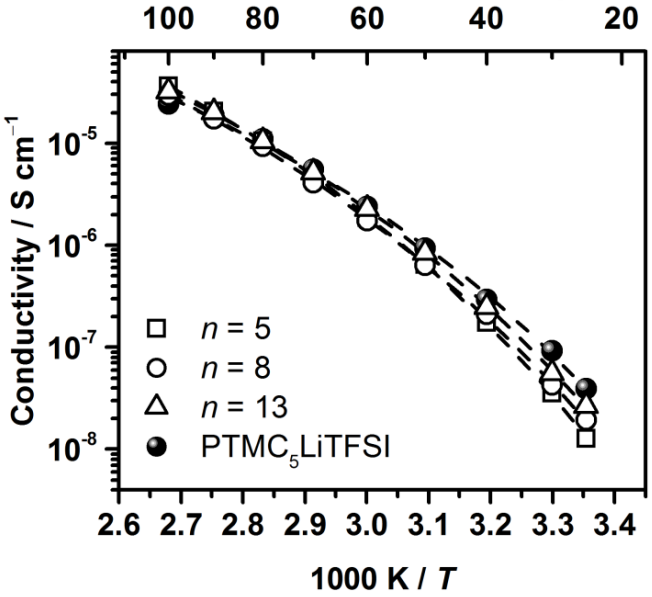


Scatch Testing



Enhanced surface adhesion for SPEs containing –OH groups

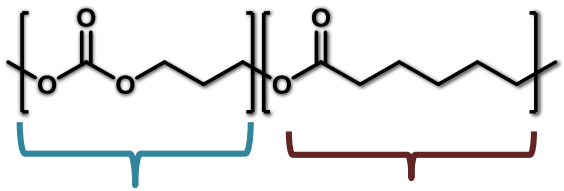




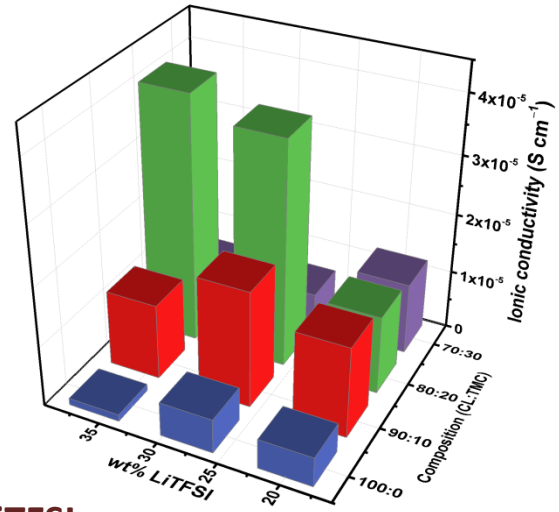
B. Sun, J. Mindemark, D. Brandell
Polymer Chemistry, **6** (2015) 4766.

PTMC-SPEs: Conductivity Enhancement

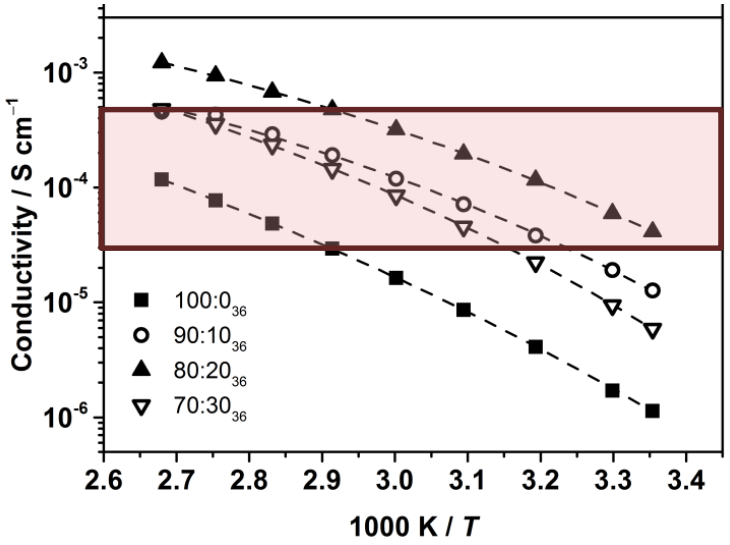
- **Co-polymerization: TMC and ε-caprolactone (CL)**



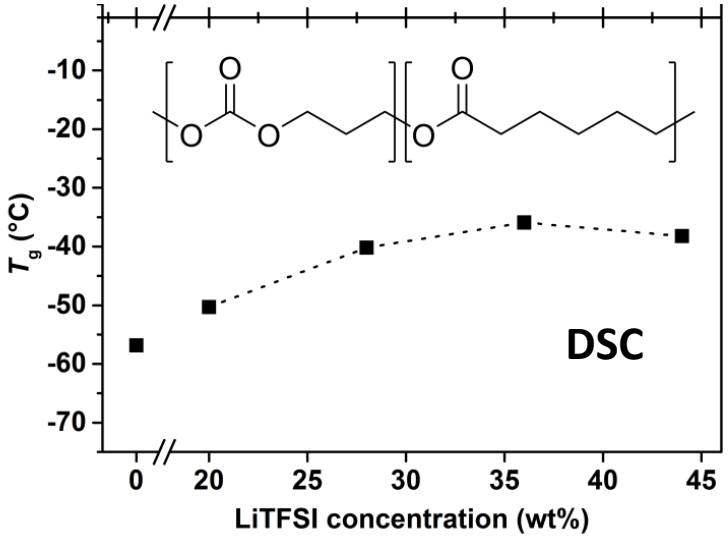
Poly(trimethylene carbonate-*co*-ε-caprolactone)



P(TMC/CL)$_n$LiTFSI (n=4.6)

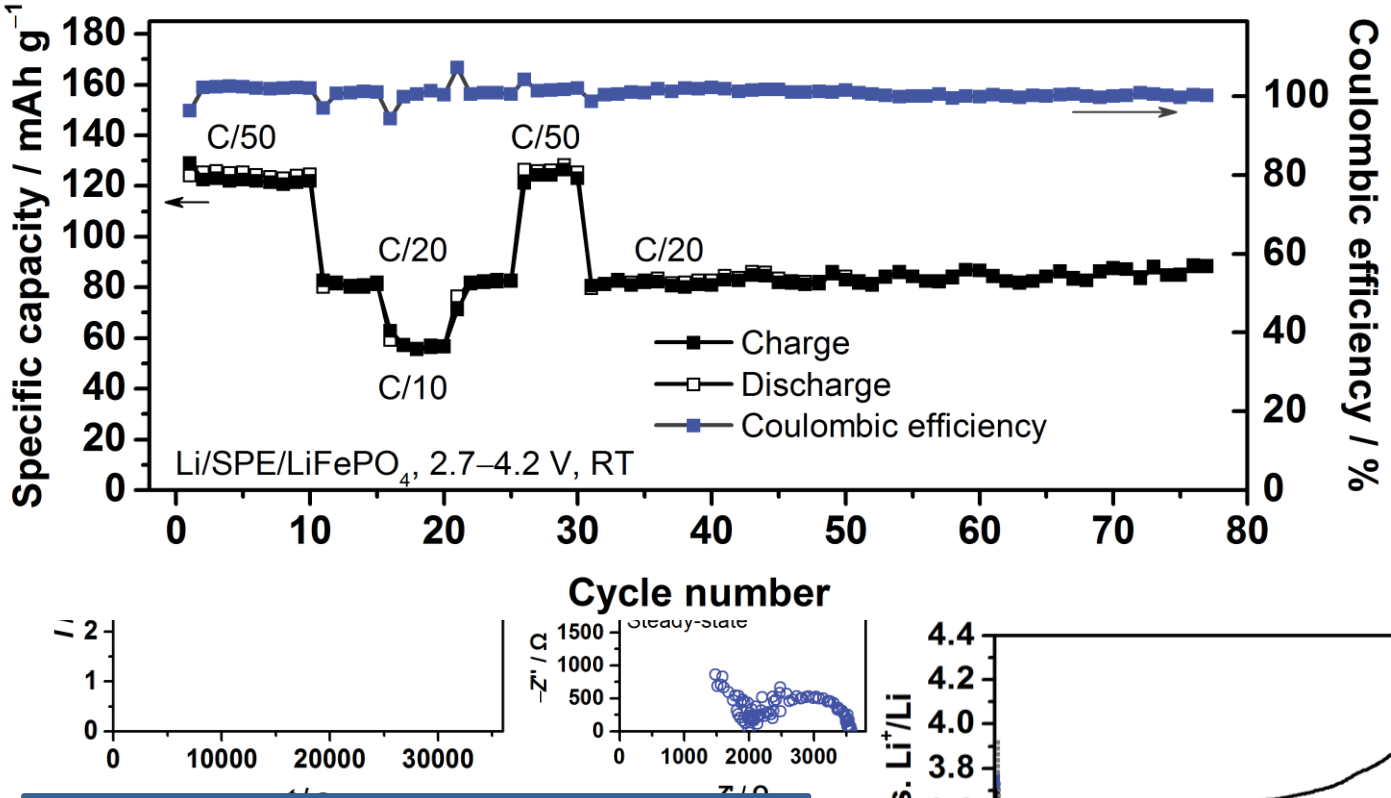


P(TMC/CL)=20:80$_x$LiTFSI

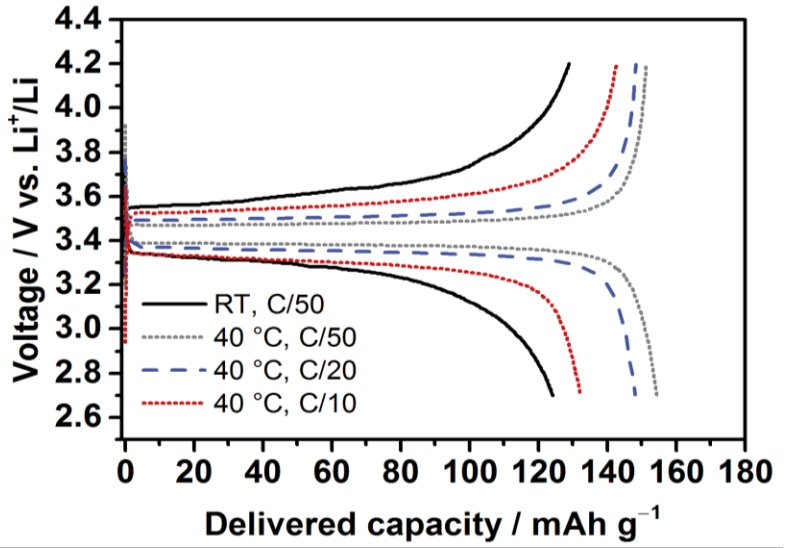


J. Mindemark, B. Sun, E. Törmä, D. Brandell, *Journal of Power Sources,* **298** (2015) 166

RT Functionality of P(TMC/CL) Copolymer



Comparatively good cell performance in P(TMC/CL)-SPEs was realized at ambient temperatures.



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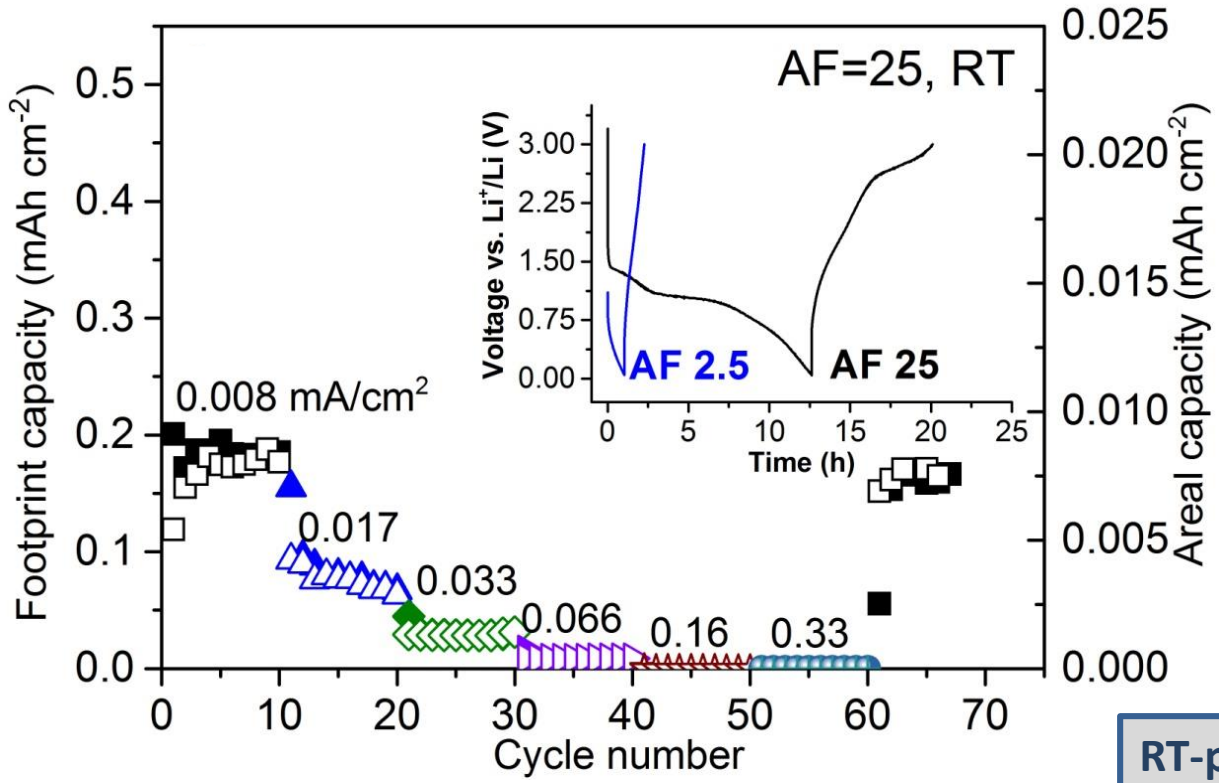
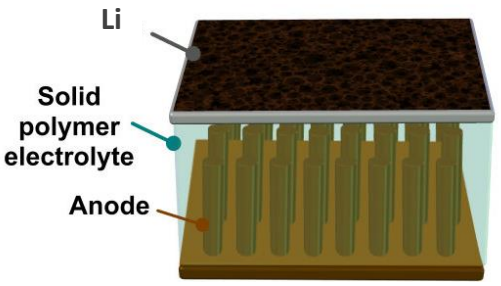
Functionalized Polycarbonates for 3DMBs

3D-Cu_2O/ P(TMC/CL) 20:80$_{4.6}$LiTFSI/Li, RT

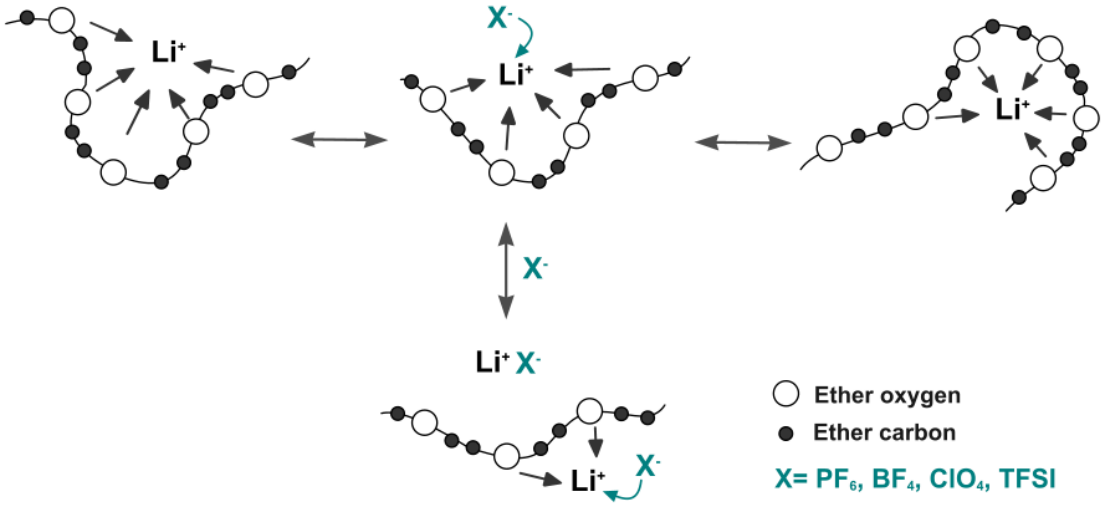




$$Cu_2O + 2Li^+ + 2e^- \Leftrightarrow 2Cu + Li_2O$$

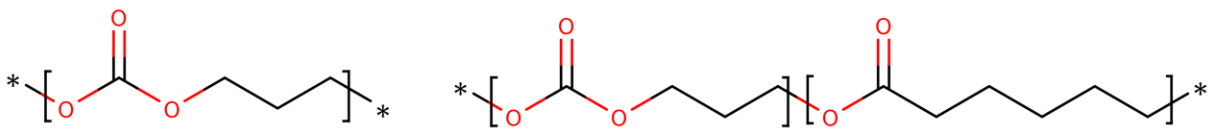
RT-performance in all-solid-state Li-polymer 3DMBs was demonstrated.

Insights on Ion Transport in SPEs

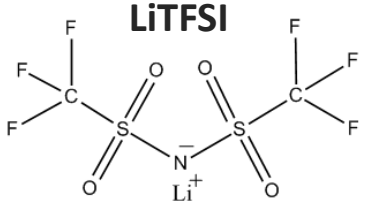


Polyether-LiX

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



LiTFSI



Polycarbonate-LiX
Polyester-LiX

Fiona M. Gray, Polymer Electrolytes, RSC Mater., Canterbury, UK, 1997, p18.

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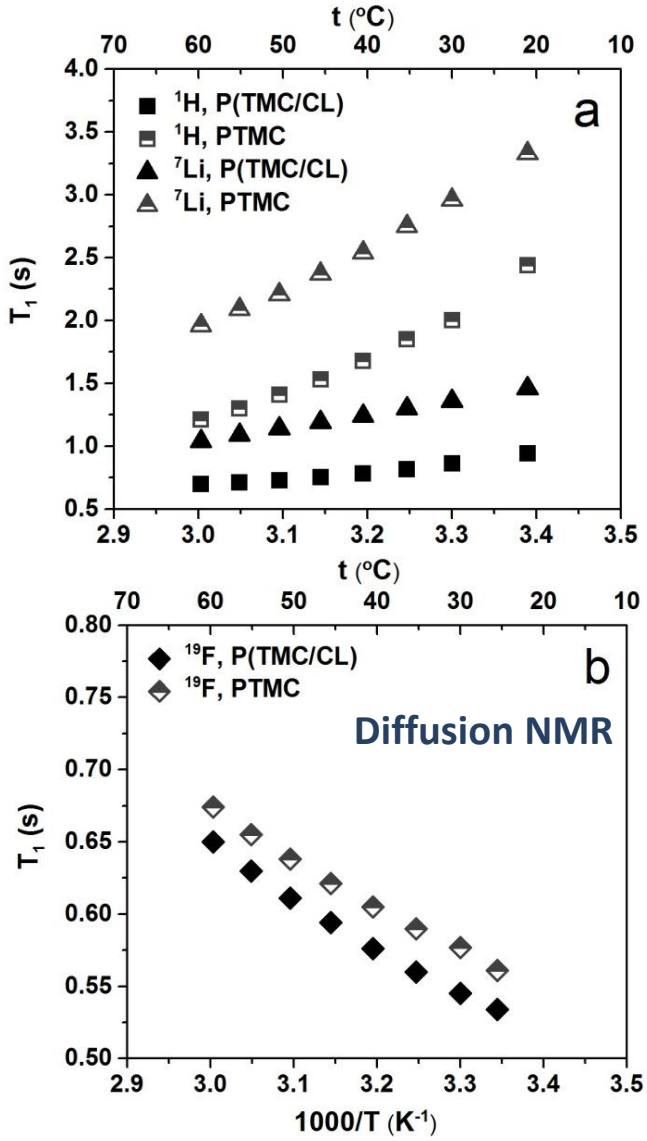
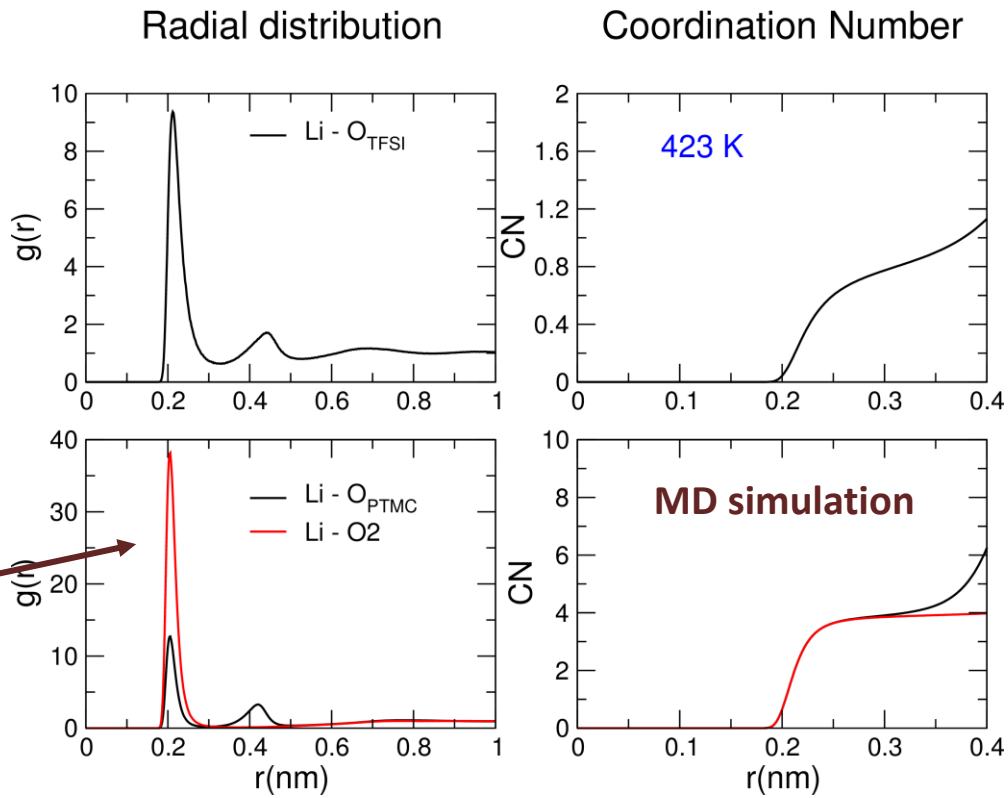
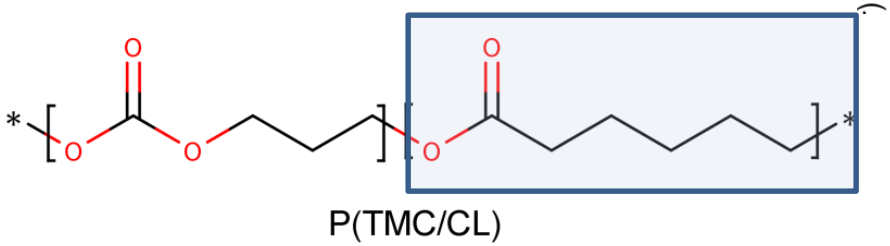
Ion Transport in PTMC-LiTFSI



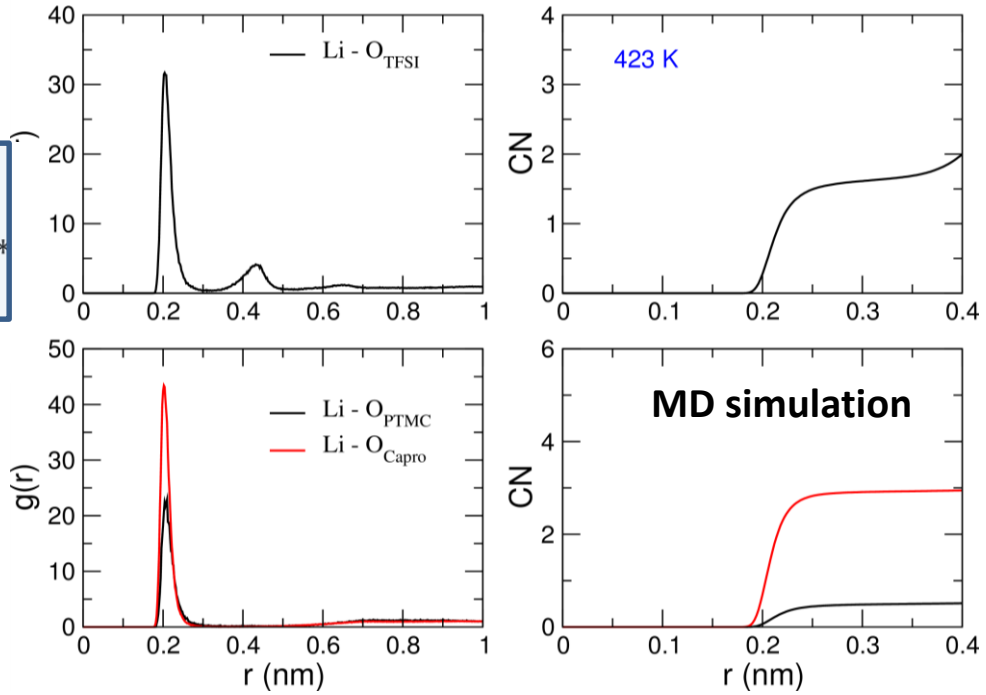


- Dominating Li$^+$-carbonyl oxygen coordination.
- ^{1}H and ^{7}Li NMR showed direct correlation in spin-spin relaxation T$_1$, likely due to coupling of the two motions.

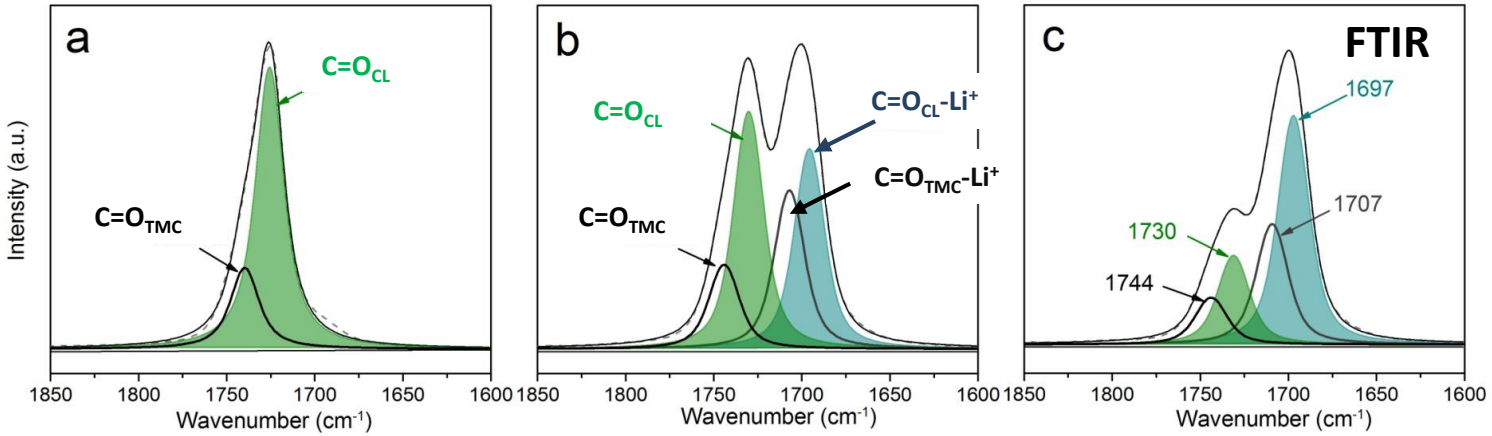
Ion Transport in P(TMC/CL)-LiTFSI



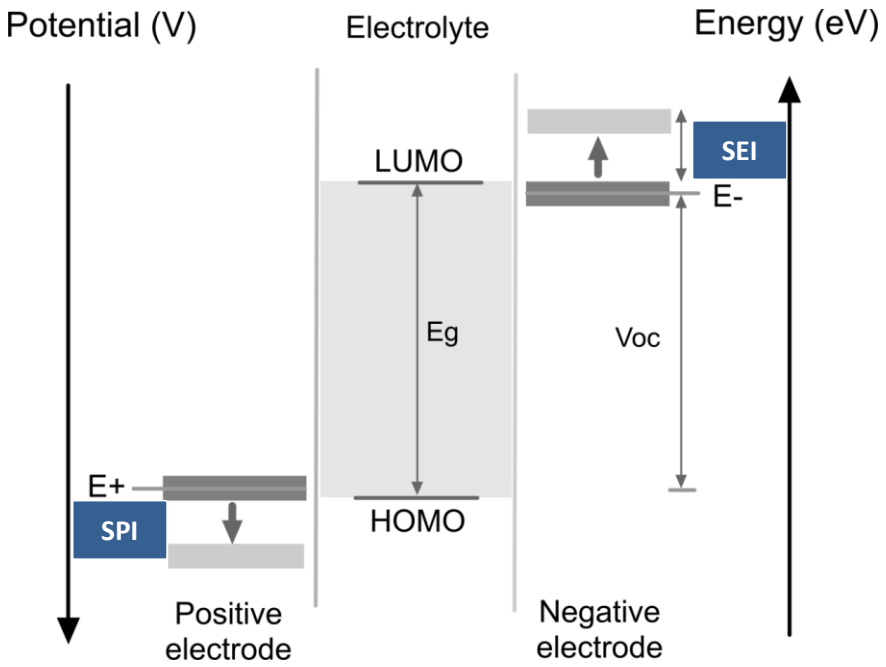
Preferential Li^+-carbonyl oxygen (CL) coordination as compared with Li^+-carbonyl oxygen (TMC)



$P(TMC/CL=20:80)_xLiTFSI$ (x= ∞; 6.6; 4.6 from left to right)



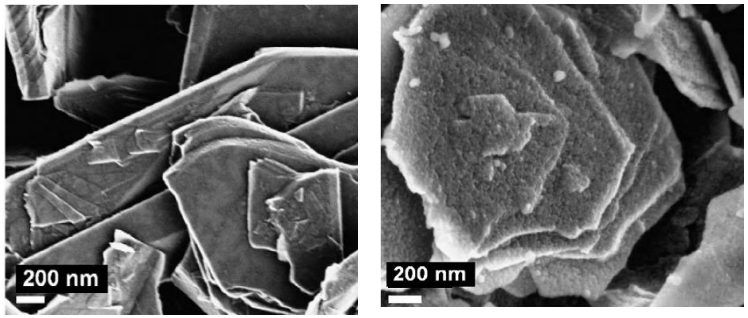
Interphase Layers: Cell Stability and Safety



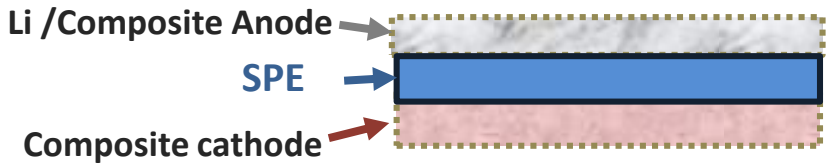
The Role of the interphase layers:

- ❑ Safety
- ❑ Coulombic efficiency
- ❑ Capacity retention
- ❑ Rate performance

Pristine Graphite **SEI on Intercalated Graphite**

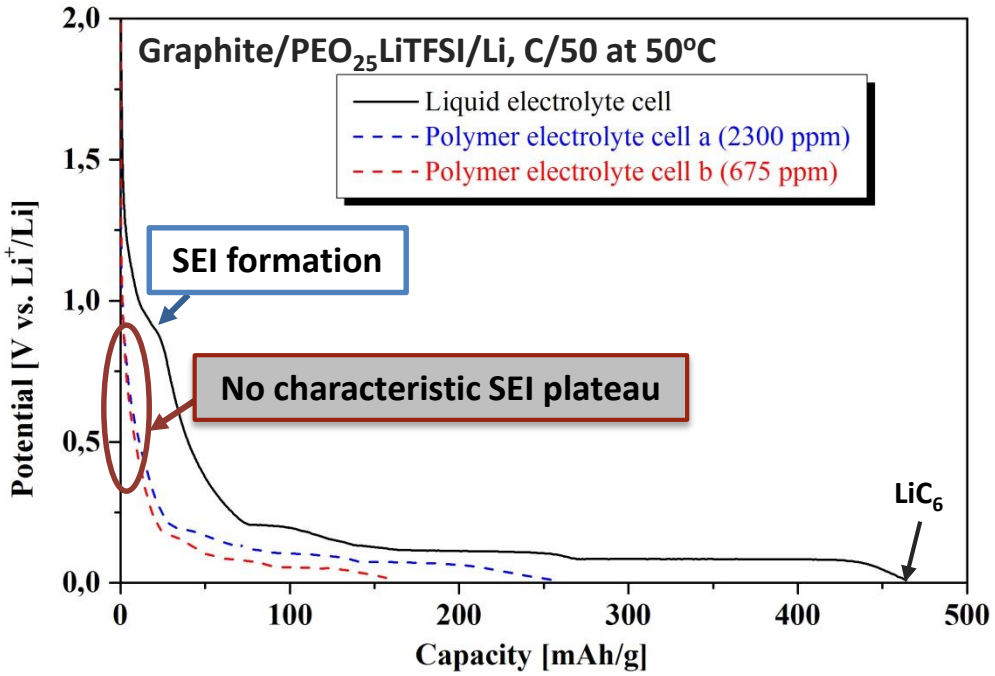


Solid polymer electrolyte/electrode interfaces



J. B. Goodenough, Y. Kim, *Chem. Mater.*, 22 (2010) 587.
J. Vetter, et al, *J. Power Sources*, 147 (2005) 269.
P. Verma, et al, *Electrochim. Acta*, 55 (2010) 6332.

PEO-LiTFSI: SEI Formation on Graphite



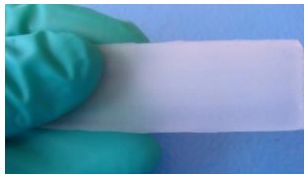
Water Content from Karl-Fischer Titration [ppm]

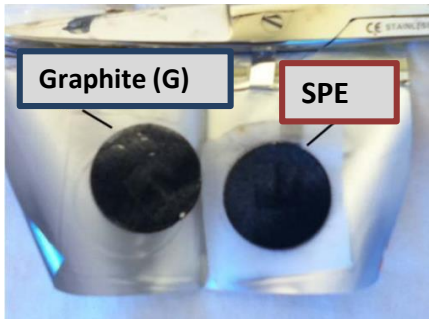
Solvent	PEO (Aldrich)		PEO(BDH)	
	50 °C	120 °C	50 °C	120 °C
5	690	142	150	86

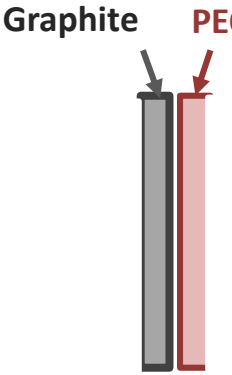
$PEO_{25}LiTFSI$ (dried with different setups)	
Designed container	Soft-bag
675	2300

XPS Analysis on Graphite/PEO Interface

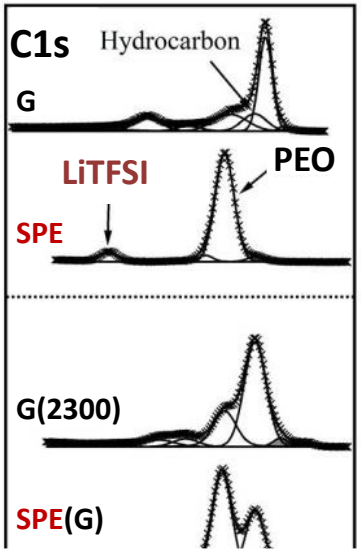
$PEO_{25}LiTFSI$

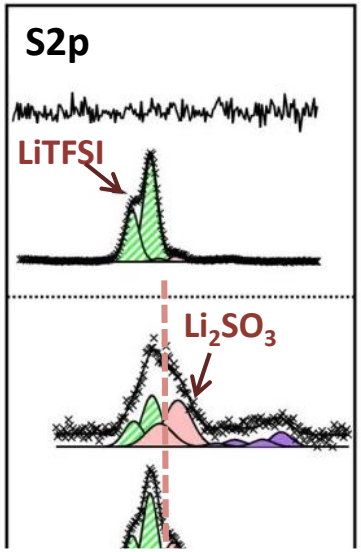


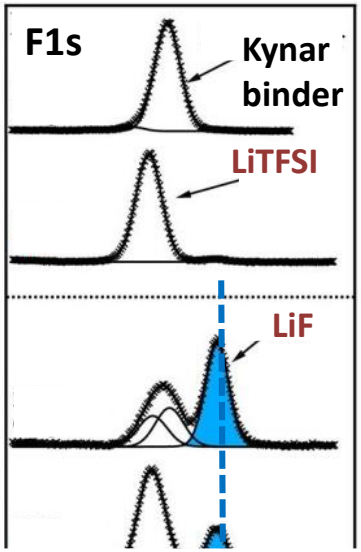


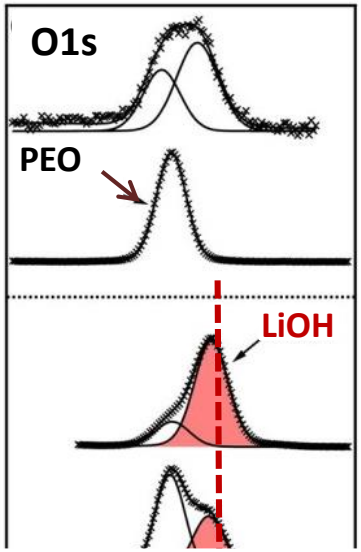


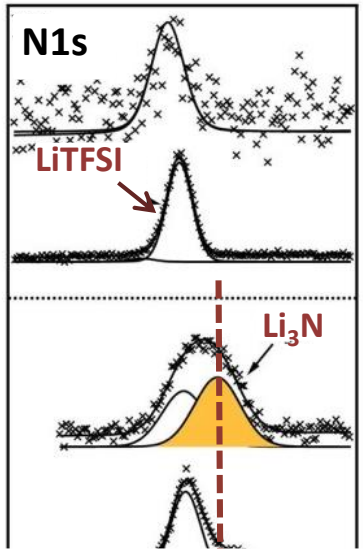
C. Xu, B. Sun, T. Gustafsson, K. Edström, D. Brandell, M. Hahlin
Journal of Materials Chemistry A, **2** (2014) 7256.









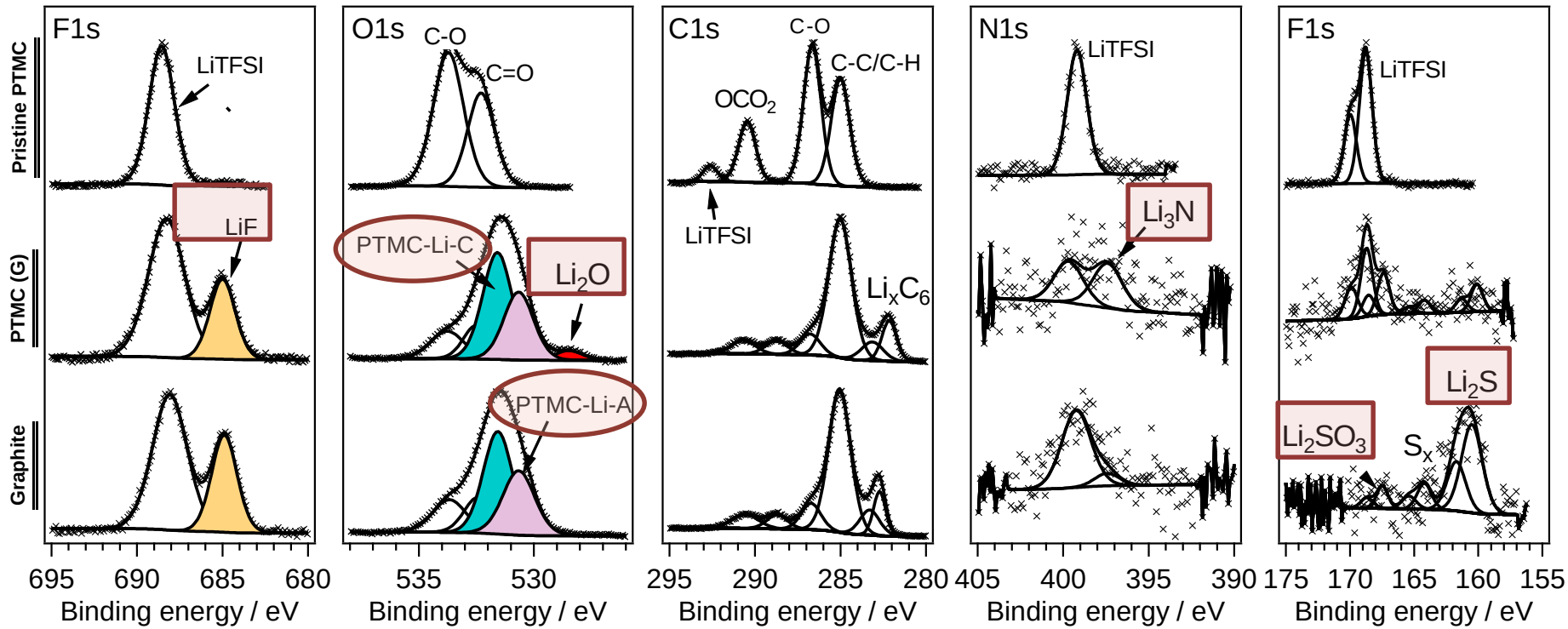


Salt decomposition dominated on cycled G/PEO interface;
Water residues in PEO-LiTFSI might contribute to LiOH formation.

SEI Formation: PTMC-Based SPE

Graphite/**PTMC$_8$LiTFSI**

B. Sun, C. Xu, J. Mindemark, T. Gustafsson, K. Edström, D. Brandell
Journal of Materials Chemistry A, **3** (2015) 13994.



➢**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).

$$LiN(SO_2CF_3)_2 + nLi^+ + ne^- \longrightarrow Li_3N + Li_xS_yO_z + LiF + C_2F_xLi_y$$

$$LiN(SO_2CF_3)_2 + 2e^- + 2Li^+ \longrightarrow Li_2NSO_2CF_3 + LiSO_2CF_3$$

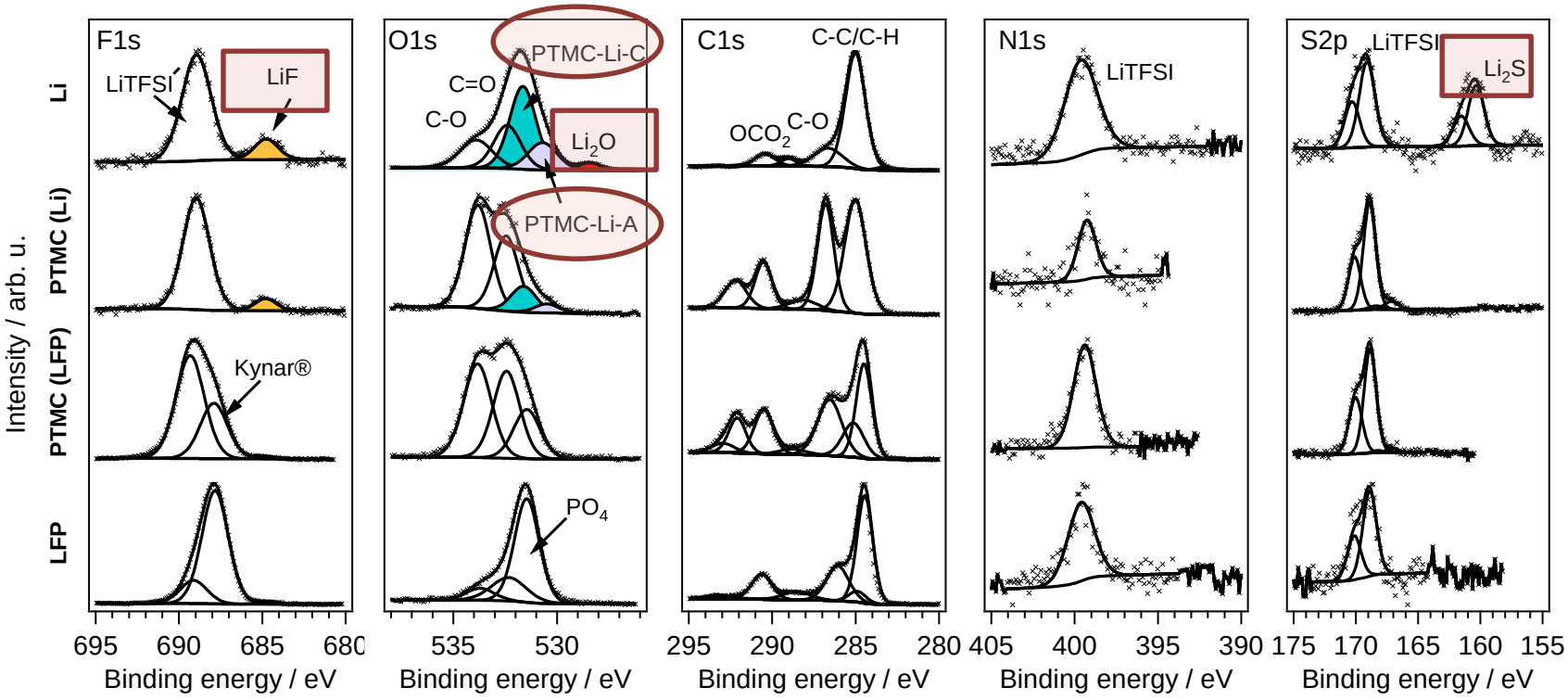
$$Li_2S_2O_4 + 6e^- + 6Li^+ \longrightarrow 2Li_2S + 4Li_2O$$

$$Li_2S_2O_4 + 4e^- + 4Li^+ \longrightarrow Li_2SO_3 + Li_2S + Li_2O$$

PTMC-Li-C PTMC-Li-A

SPE/Cathode Interfaces

Li/**PTMC$_8$LiTFSI**/LiFePO$_4$, 1st cycle



No obvious degradation products observed on the cathode/SPE interfaces; complex degradation reactions dominately occured at interfaces close to the anode (*i.e.*, Li or graphite).

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Summary

❑ 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.

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Thank you for listening!


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