Recent Developments in Block Copolymer Electrolytes for Lithium Metal Battery Applications

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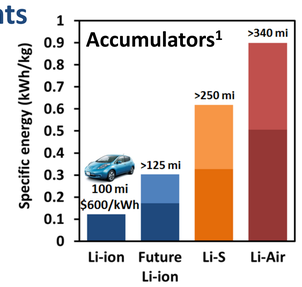
Context

- **High demand of energy storage devices**

Windmill *Photovoltaic* *Transportation* *Electronic*

- **Battery requirements**

- Low cost ($150/kWh)
- Long life (>10 years)
- Safe
- High energy density



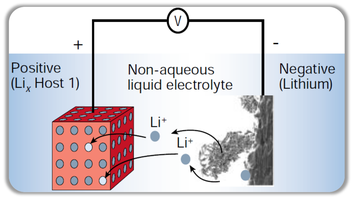
→ Today's solution: Li-ion
→ **Beyond: Li metal**

- **Conventional liquid electrolyte[2]**

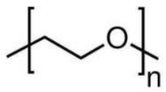
- Composition: Li salt in polar organic solvents (alkyl carbonates family)

- Liquid electrolytes are flammable
→ Li-ion battery hazards: short-circuit, thermal runaway

- Liquid electrolyte with Li metal electrode
→ Dendrite growth on Li electrode upon charging

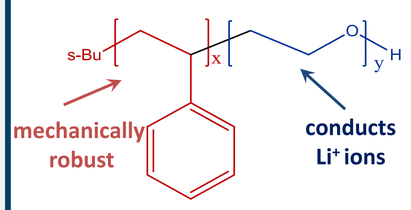


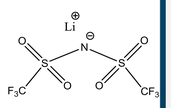
- **Solid polymer electrolyte[3]**
Poly(ethylene oxide) (PEO)



- Pros: **Li metal stability**
flame resistant, flexible, non-toxic
- Cons: Too soft to suppress Li dendrite growth

NITASH BALSARA GROUP'S SOLUTION
Nanostructured Block Copolymer Electrolyte[4,5]



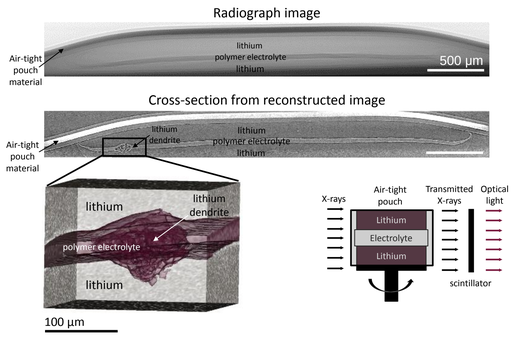


polystyrene-*b*-poly(ethylene oxide)
SEO

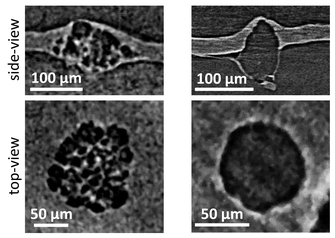
Li salt (LiTFSI)
r = [Li+]/[EO]

Lithium Dendrite Growth

- **X-ray microtomography imaging[6]**

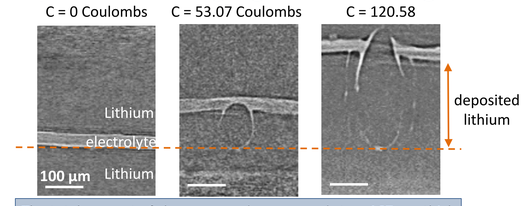


- **Dendrite morphology is dependent on cycling routine**

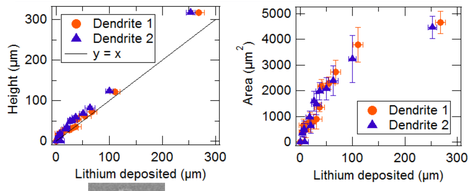


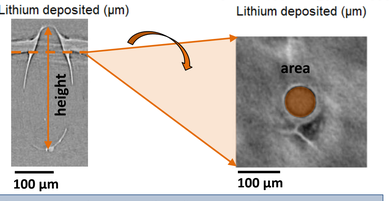
Dendrite morphology
When lithium ions are passed in one direction, simulating one long charge, the resulting dendrite consists of one large, lithium-filled globule instead of many small globules

- **Stop-motion imaging of dendrite growth**

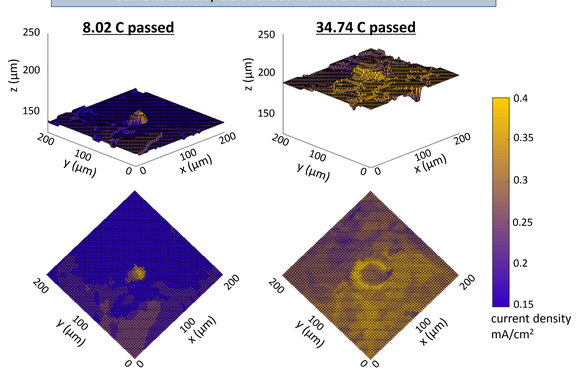


The total amount of charge passed corresponds to a **167 µm** thick layer of lithium moved from the top to the bottom electrode





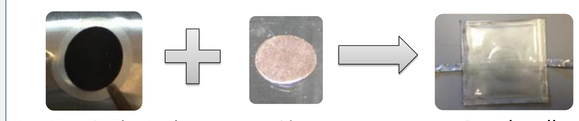
Current density delocalizes from dendrite center



Solid State Battery

- **Battery assembly**

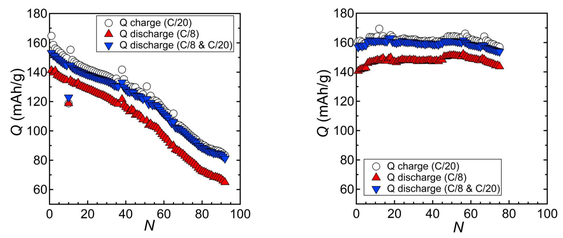
Positive	$LiFePO_4$ 70 wt.%	SEO-LiTFSI 25 wt.%	Carbon 5 wt.%
Electrolyte	SEO-LiTFSI (r = 0.085)		
Negative	Li		



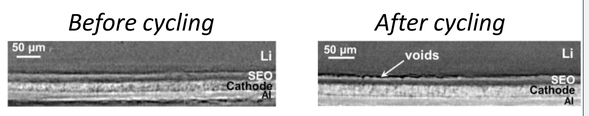
Positive & Electrolyte Li Pouch cell

- **Battery cycle life**

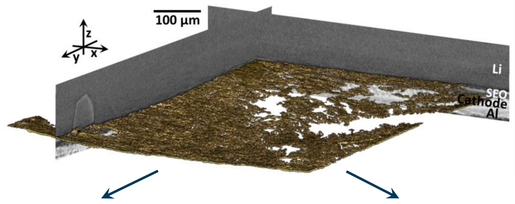
- Battery cycling between 2.0 & 3.8 V
- Charge: C/20 → Discharge: C/8 then C/20
- Two characteristic profiles:



- ***Ex*-situ X-ray microtomography & model[7]**

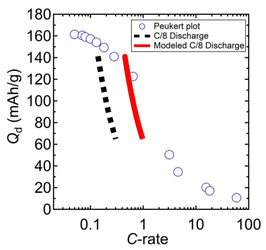


→ **Void volume**



Effective Surface: S_{eff}

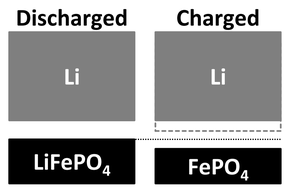
$S_{eff} = \alpha . S$
α: contact area fraction
Average: α = 0.37 ± 0.05



Effective *C*-rate = 1/(α.*t*)

Volume: V_{void}

ΔV: difference in electrode volumes in the charged and discharged battery



V_{void} / ΔV = 2.3 ± 1.2

→ **Delamination is due to the finite volume change during cycling**
→ **X-ray tomography is a powerful tool to study Li metal polymer battery interfaces**

Single-Ion Conducting Electrolyte

- **Typical polymer electrolyte**

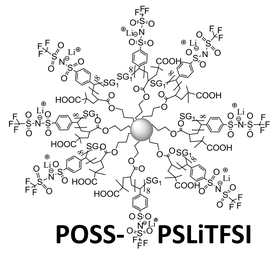
Main disadvantage: Ambipolar conductivity
- Li^+ transference number $t^+ < 1$
- Concentration polarization effect
- Reduced performance

Possible Solution:

Single-ion-conducting electrolyte

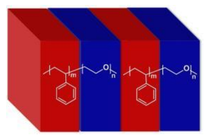
- **Single-ion-conducting electrolyte design**

- Anchor the anion ($PSTFSI^-$) to silsesquioxane nanoparticles[8] (POSS) by covalent bonds
- These nanoparticles can be used as a lithium source in SEO polymers



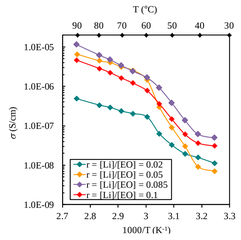
POSS-PSLiTFSI

+



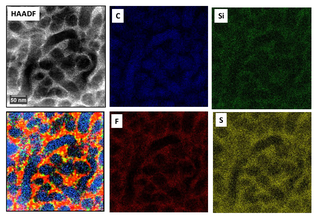
PS-*b*-PEO (SEO)
PS: 70 kg/mol
PEO: 74 kg/mol

- **Physico-chemical characterization**

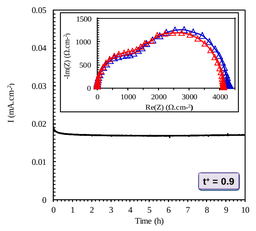


The highest ionic conductivity (σ) is for the SEO/POSS-PSLiTFSI electrolyte with r = 0.085

STEM/EDS images of the SEO/POSS-PSLiTFSI (r = 0.085) Images confirm a cylinder morphology and the location of the nanoparticles in PEO phase



Cation transference number (t^+):



$$t^+ = \frac{I^\infty(\Delta V - I^0 R_{int}^0)}{I^0(\Delta V - I^\infty R_{int}^\infty)}$$

The inset shows the ac impedance of the cell (red) before and (blue) after polarization

→ **Single-ion-conducting nanoparticles in block copolymers lead to cylinder morphologies at high *r* values with a t^+ close to the unity**

References

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