Composite Electrolyte to Stabilize Metallic Lithium Anodes

Project ID: BAT273

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Chemical Science Division

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Overview – Composite Electrolytes to Stabilize Li Metal Anode

- Timeline
  - Start: October 2014
- Budget
  - $400k FY18
  - $400k FY19
- Technical barriers
  - Energy density (500-700 Wh/kg)
  - Cycle life, 3000 to 5000 deep discharge cycles
  - Safety

- Partners and collaborators
  - Oak Ridge National Laboratory (lead)
  - Collaborators:
    - ORNL collaborators – A. Westover, R. Sacci, F. Delnick
    - Ohara Corporation, CA
    - J. Schaefer, Univ Notre Dame
    - K. Hatzell, Vanderbilt Univ.
    - MERF for LLZO powders

Relevance and impact to VTO mission:

- Multi-year program plan identifies the Li metal anode and its poor cycling as the fundamental problem for very high energy Li batteries.
- Li metal confined and protected a solid electrolyte is the best route to safety & efficiency.
- Success of our composite electrolyte will enable:
  Li-NMC and Li-S and Li-Air to meet the technical cost objectives.

Objective for Li batteries → optimize energy density

also, cycle life, processing cost and safety

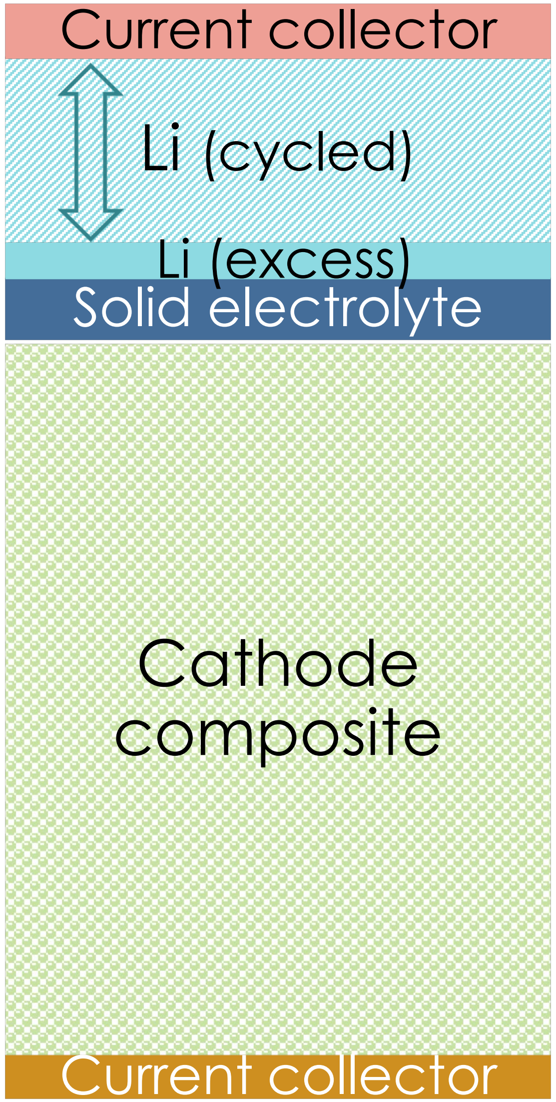
Thin or zero

Equal capacity, no excess

Thick for high energy

- Self supported
- Composites of active + SE

Thin film, not foil



Current collector - <10 μm

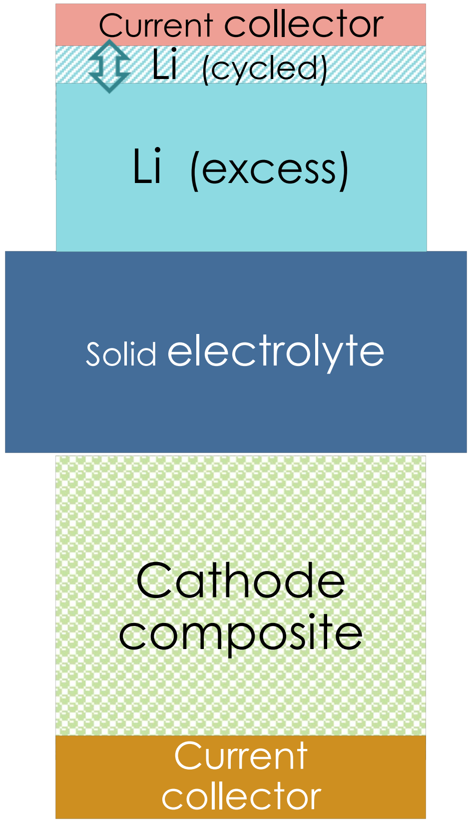
Li anode – 1-5 μm seed + 15-40 μm from cathode

Electrolyte separator– 1-20 μm

Cathode– 45-200 μm

Current collector – <10 μm

Starting point for most Li metal batteries



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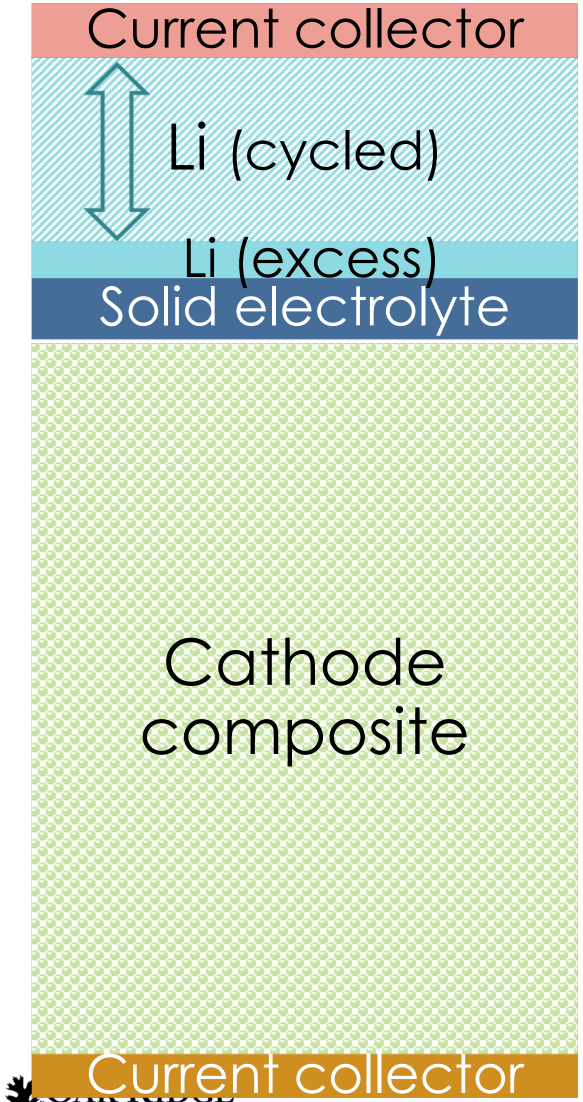
Our approach: composite electrolytes → new materials → practical processing → interfaces → cells

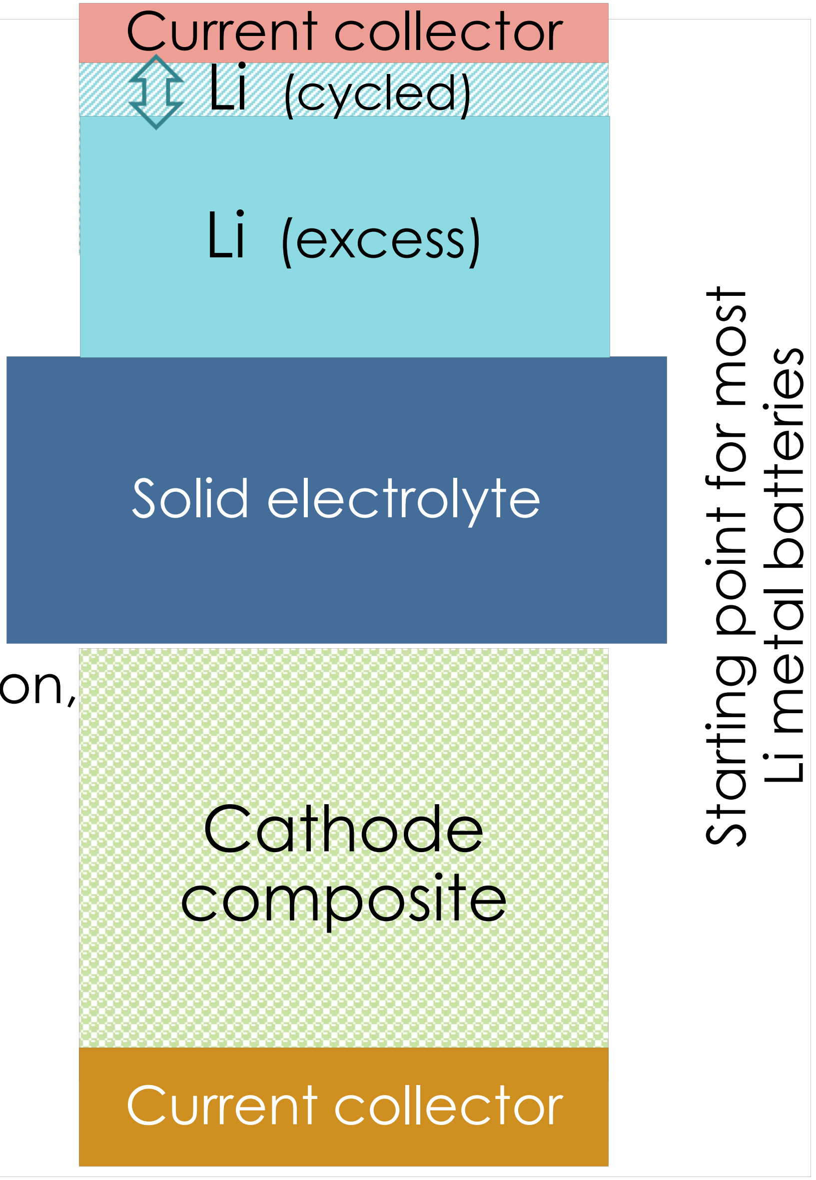


Objectives – Study, determine

Composite solid electrolytes – thin, robust, conductive
- Materials (polymer, ceramic)
- Structure
- Processing

Interfaces – stable, conductive
- Li – no reactions, no physical isolation, no dendrites
- HE/HV cathode

Full cells
- Cycle life
- Degradation processes



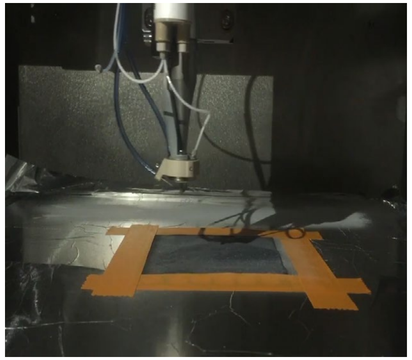
Milestones - FY19-20

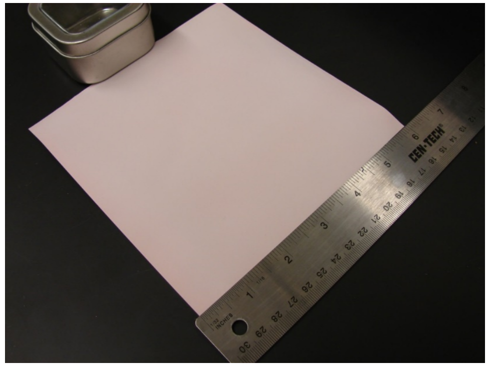
Milestones: FY19-FY20	**Target:**	**Status:**
Fabricate **gel composite electrolytes** with a target room temperature conductivity of **1×10^{-4} S/cm**. Thoroughly evaluate ion transport, thermal and structural properties.	Q3 FY19	✓
Expand composite materials portfolio to include **non-PEO polymer** electrolytes. Identify promising polymer ceramic systems with interfacial **ASR less than 10 ohm**.	Q4 FY19	✓ Lowest ~50 Ω ASR to date
Develop methods to minimize interconnected composite electrolytes' **interfacial resistance with lithium** by varying polymer chemistry.	Q1 FY20	✓
Fabricate **interconnected ceramic network** with different ceramic chemistry and particle size to increase strength of the composite.	Q2 FY20	On track, with MERF LLZO
Investigate the trade-off between **Li^+ transference number** and ionic conductivity of the gel composite electrolytes, and optimize it.	Q3 FY20	In progress
Fabricate **full batteries** using NMC cathode, composite electrolyte, and Li-metal anode. Identify cell **failure mode**.	Q4 FY20	In progress
Create chemical/physical bonding between polymer and interconnected ceramic network that leads to optimized interface to improve mechanical modulus and ionic conductivity.	Stretch FY20	

Milestones

Composite Electrolytes to Stabilize Metallic Lithium Anodes: challenges and approaches

- **Challenge 1**: fabricate composite with high ceramic loading → spray coating



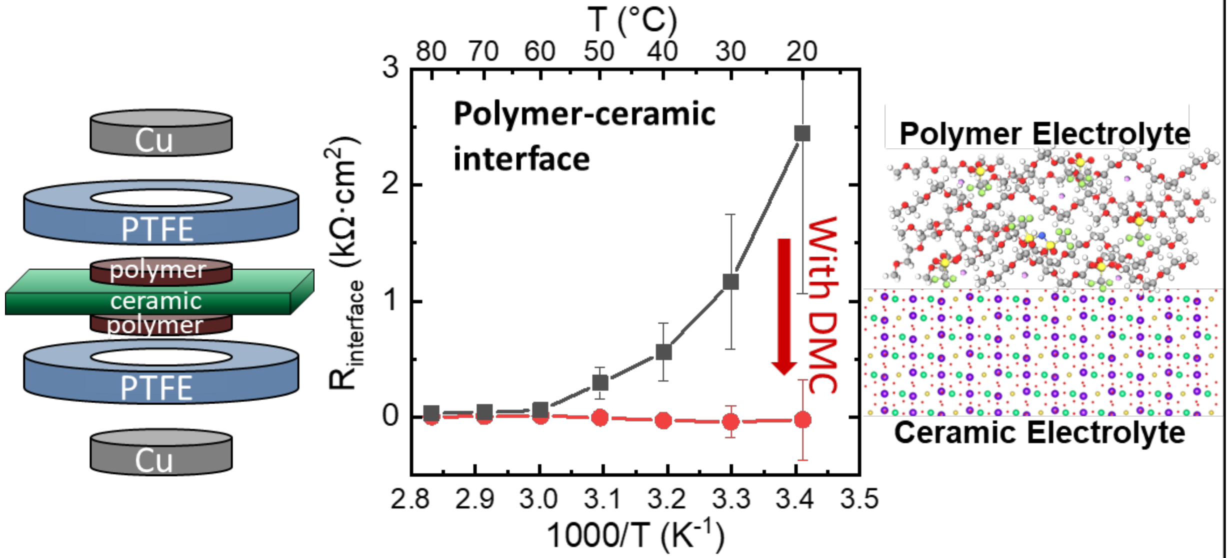


Composites are:

- PEO + LiTFSI + Ohara LiCGC™ particles
- Aqueous slurry
- ~20-30 μm thick, after pressing
- Up to 50 vol% ceramic, dispersed particles
- Dry ~10^{-8} S/cm, add TEGDME ~10^{-5} S/cm

A. S. Pandian, X. C. Chen*, J. Chen, B. S. Lokitz, R. E. Ruther, G. Yang, K. Lou, J. Nanda, F. M. Delnick, N. J. Dudney*, *Journal of Power Sources* **2018**, *390*, 153-164.

- **Challenge 2**: quantify and minimize interfacial resistance between polymer and ceramic electrolytes → trilayer model



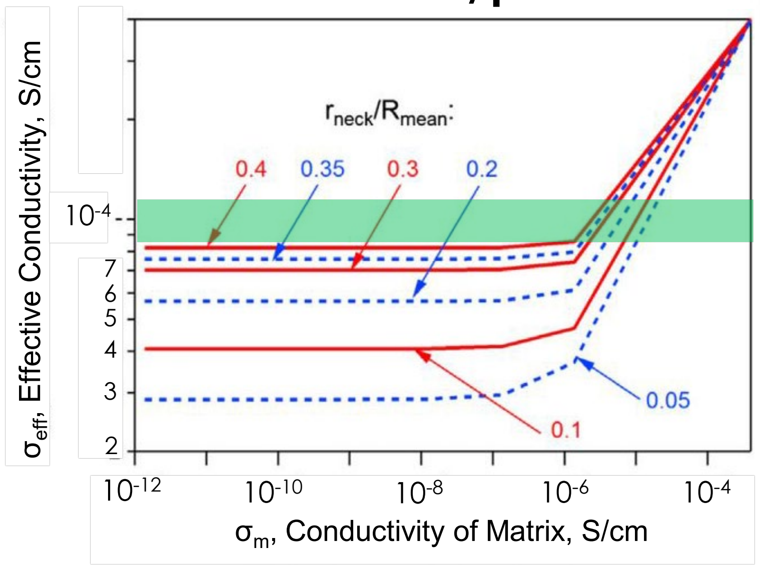
Are there other polymer electrolytes for better interfaces?

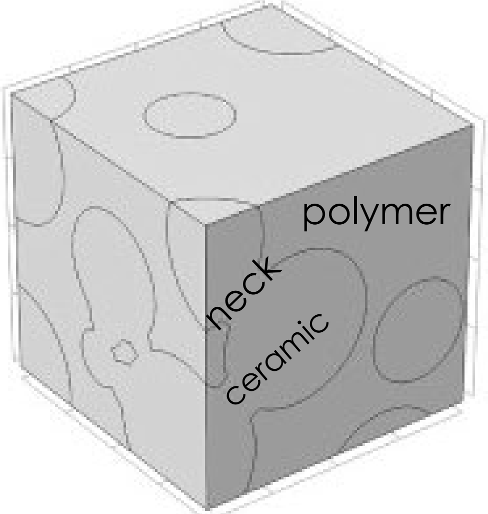
X. C. Chen*, X. Liu, A. S. Pandian, K. Liu, F. M. Delnick, N. J. Dudney*, *ACS Energy Letters*, **2019**, 4, pp 1080–1085.

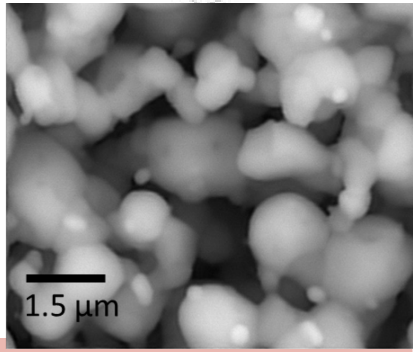
Composite Electrolytes to Stabilize Metallic Lithium Anodes: challenges and approaches

- **Challenge 3**: Fabricate composite to ensure connectivity of ceramic in composite

Critical geometry sintered neck radius/particle







Kalnaus, S., et al. *Journal of Power Sources* **2013,** *241*

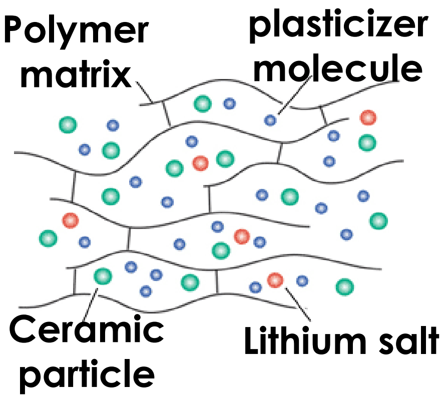
M. Palmer, et.al. N. Dudney, X. Chen, *A Three-Dimensional Interconnected Polymer/Ceramic Composite of as a Thin Film Solid Electrolyte*, Energy Storage Materials, 26, 242-249, **2020**

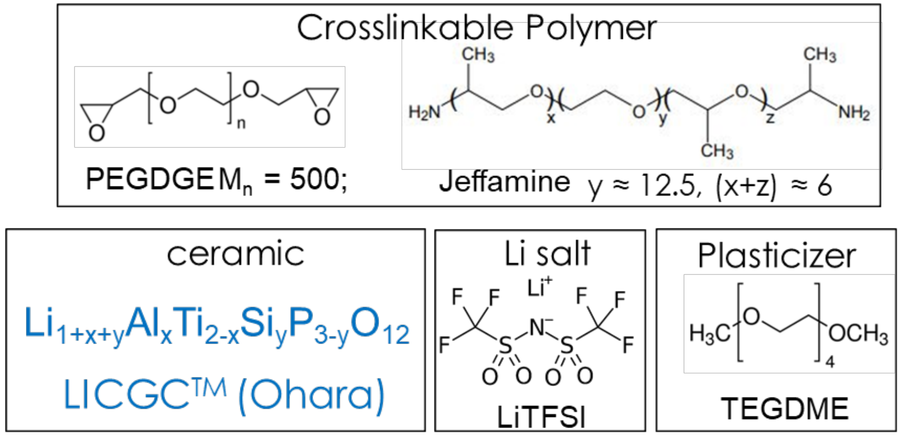
- **Challenge 4**: Integration to full cell with thin Li and dry cathode composite
- Complex
  - Li anodes, thin films – thick foils
  - Multiple electrolyte materials, used in combination
  - Abandoned homemade NMC cathodes (temporarily) → good source of optimized dry polymer composite with $LiFePO_4$ cathode.

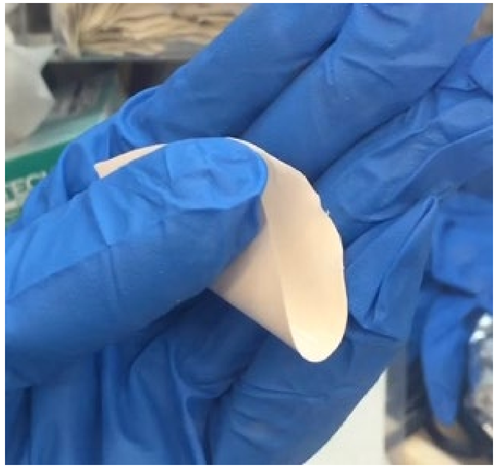
Improved polymers electrolytes

Preview new accomplishment

Crosslinked Gel Composite – achieves both high Li+ ion transport and mechanical properties when plasticized

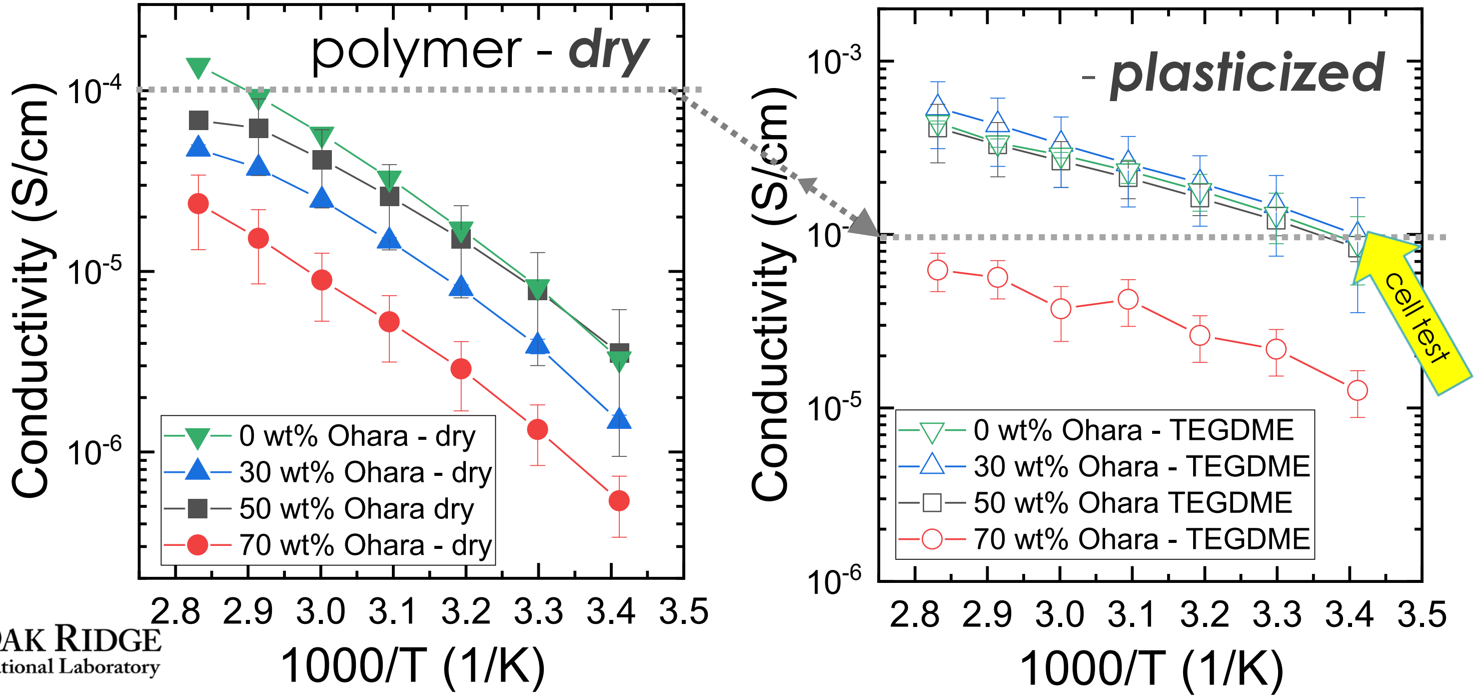


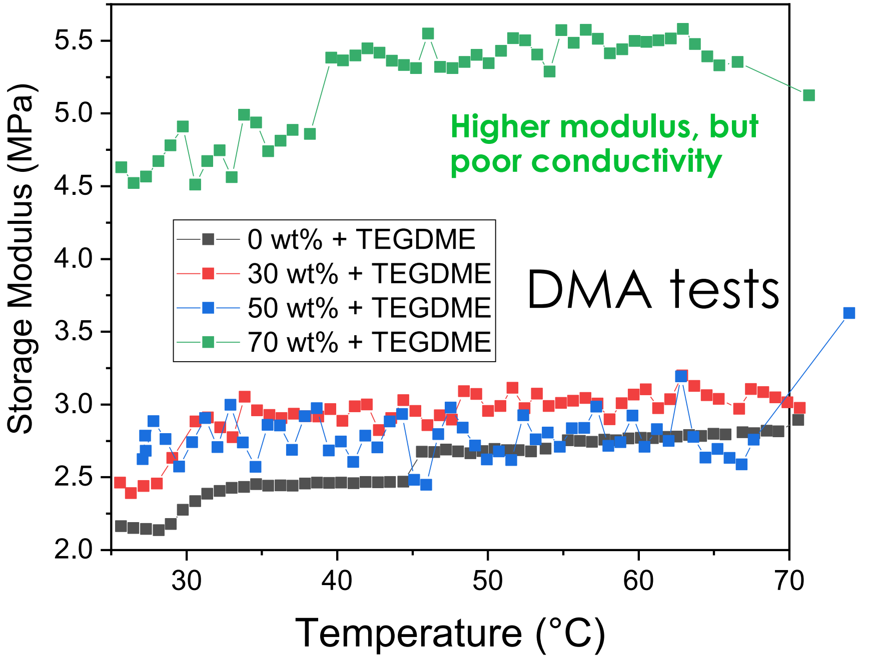




Good handling at 50wt%.

Brittle at 70wt%.

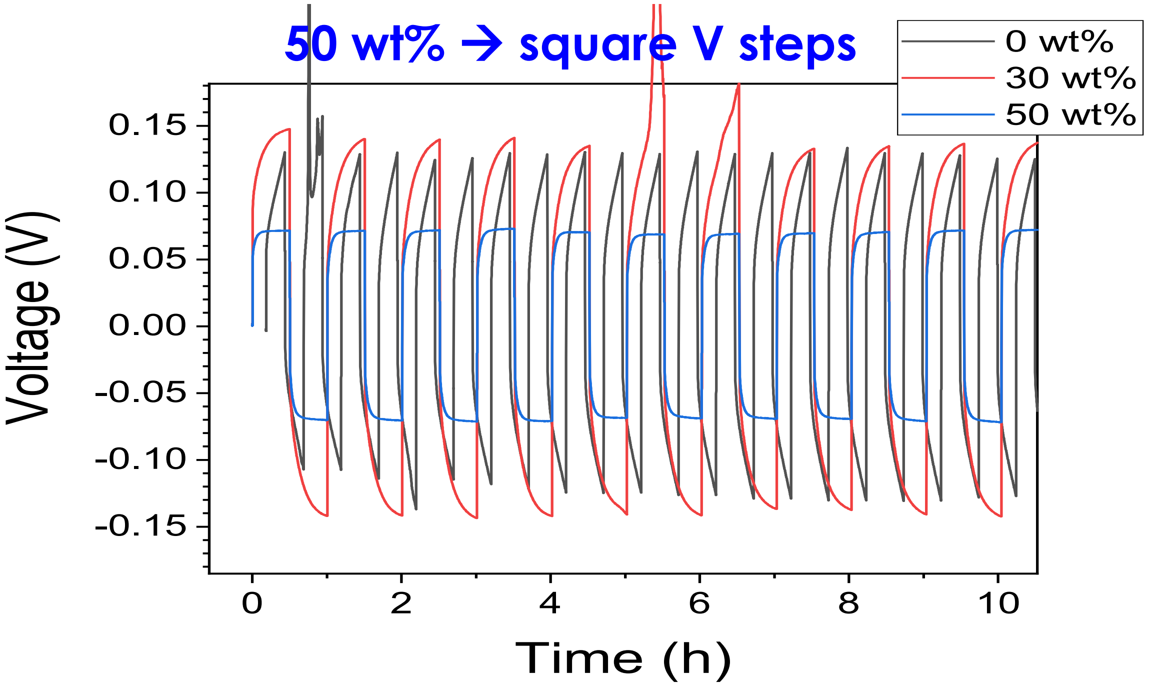




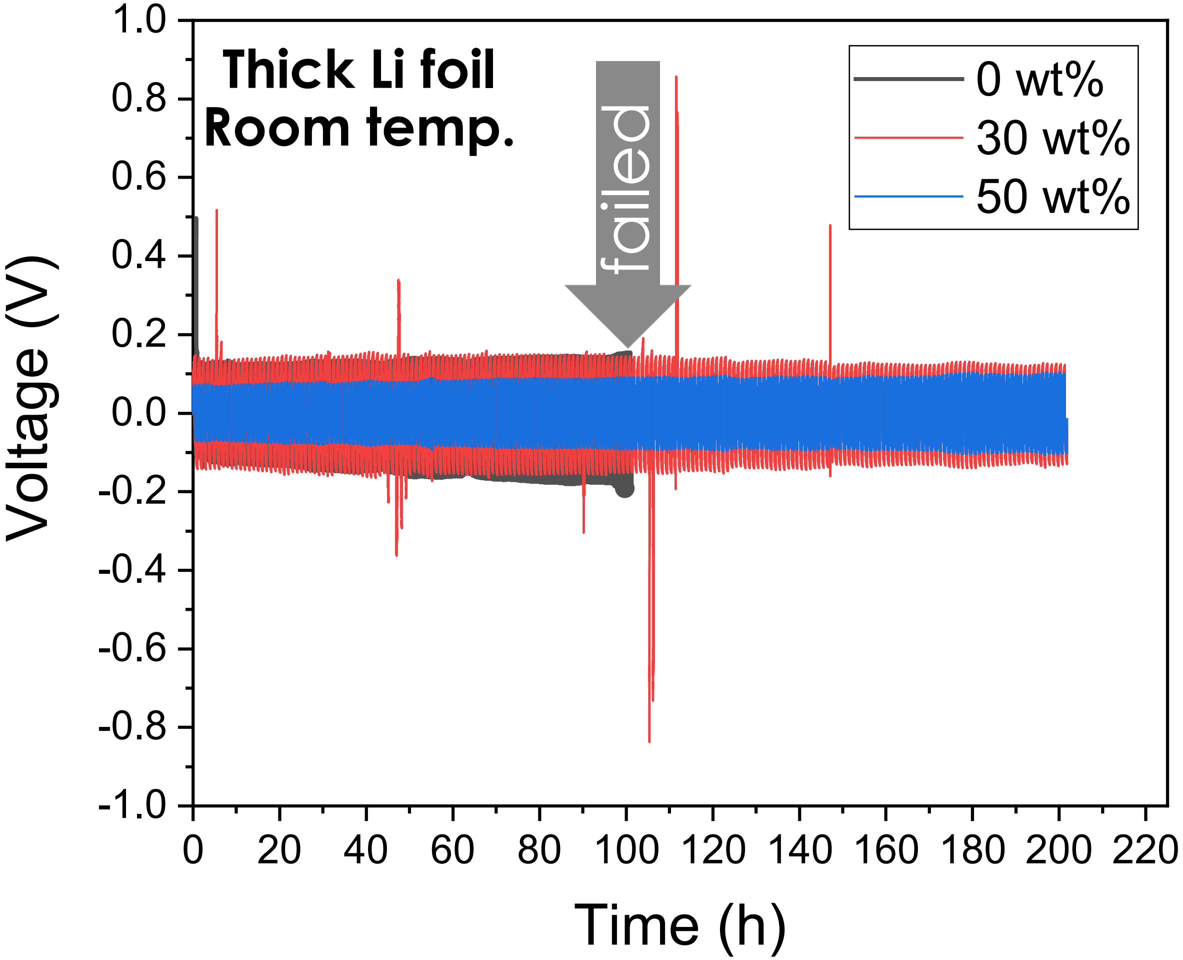
Crosslinked Gel Composite- Dispersed Ohara particles increases t_{Li+} and cycling stability, with good conductivity

Transference number measurement

Samples	t_{Li+}
Gel polymer	0.20
Gel with 30wt% LICGC™	0.16
Gel with 50 wt% LICGC™	0.44



Li//Li symmetrical cell cycling

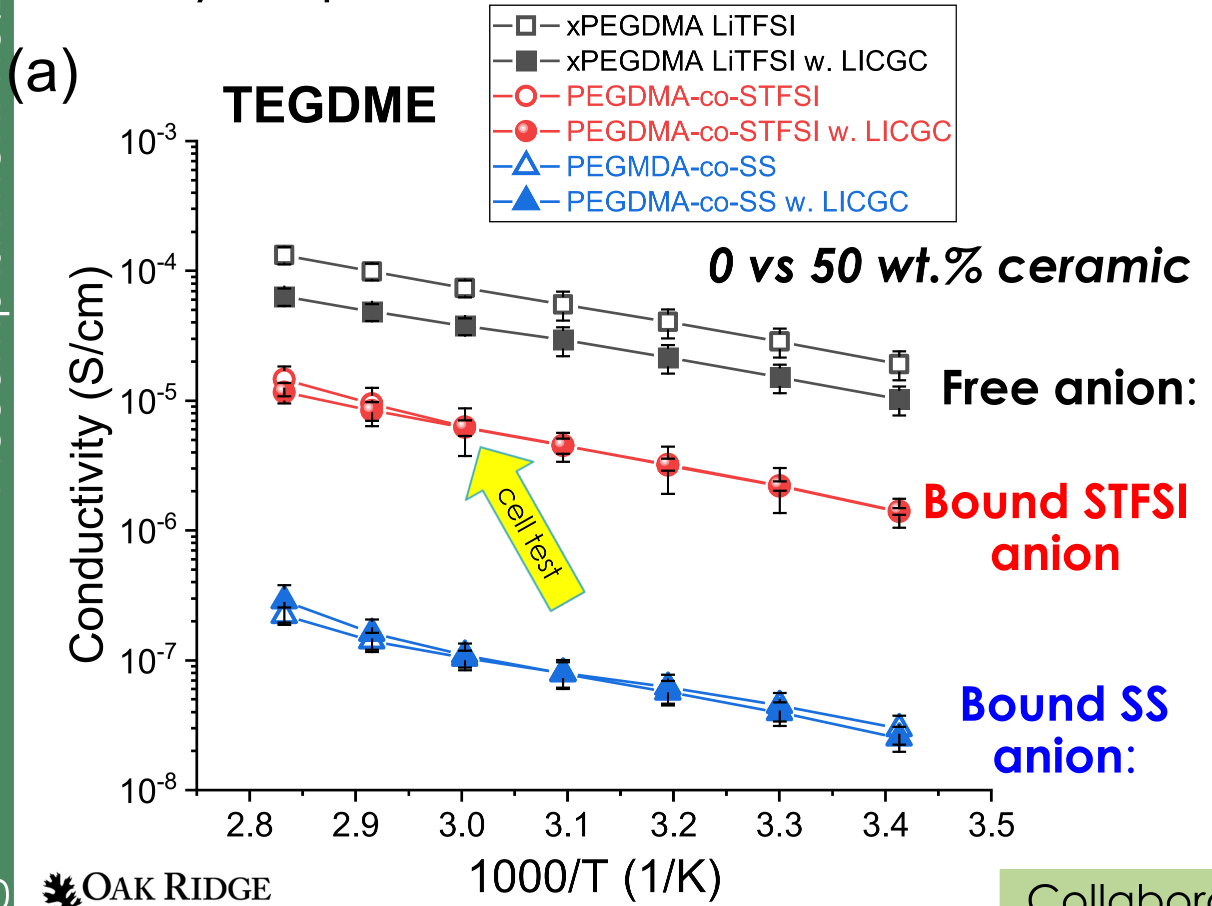


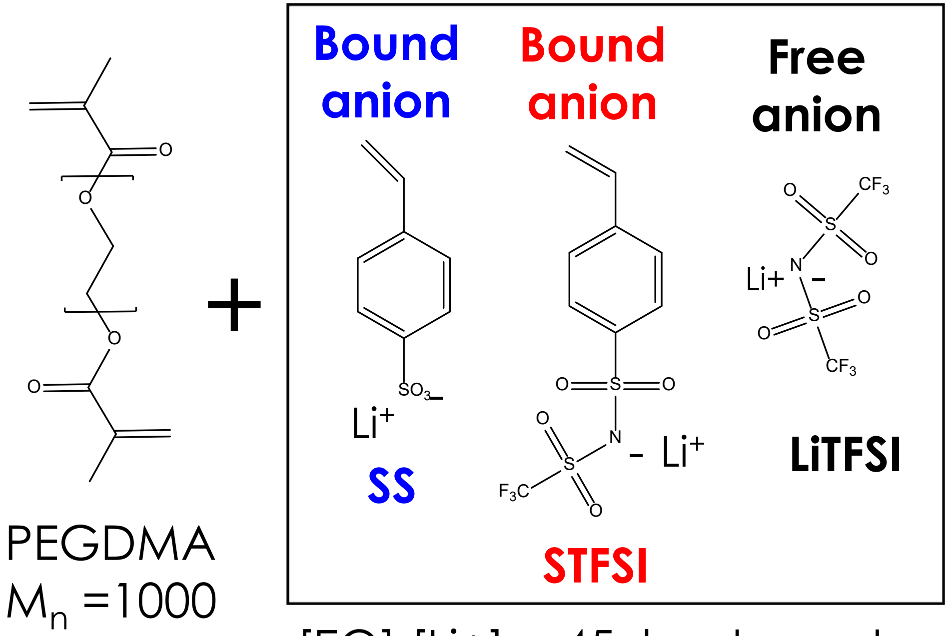
Y. Zhang and Chen, Xi et al. unpublished results

Single-ion composite (SIC) – can have large ceramic loading, but plasticizer needed for high conductivity

- TEGME plasticizer (50-100X) increased conductivity
- 50wt.% ceramic does not impede conductivity of dry or plasticized SIC

But poor ionic conductors ~1μS/cm





[EO]:[Li+] = 45, kept constant

Ceramic = $Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$
LICGC™ (Ohara) powder

Collaboration with Jennifer Schaefer, manuscript submitted, in review

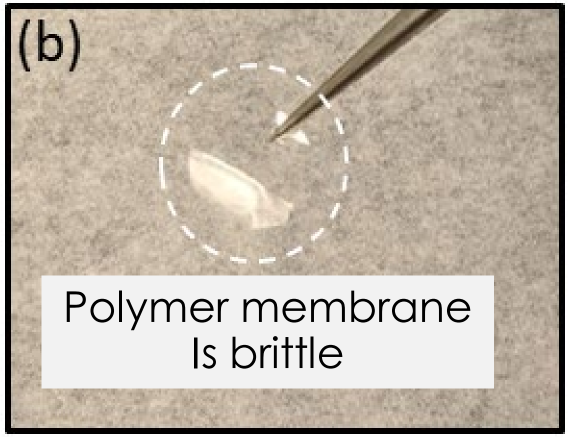
Single-ion gel composite – good t_{Li+}, stable Li/Li cycles, and handability is good

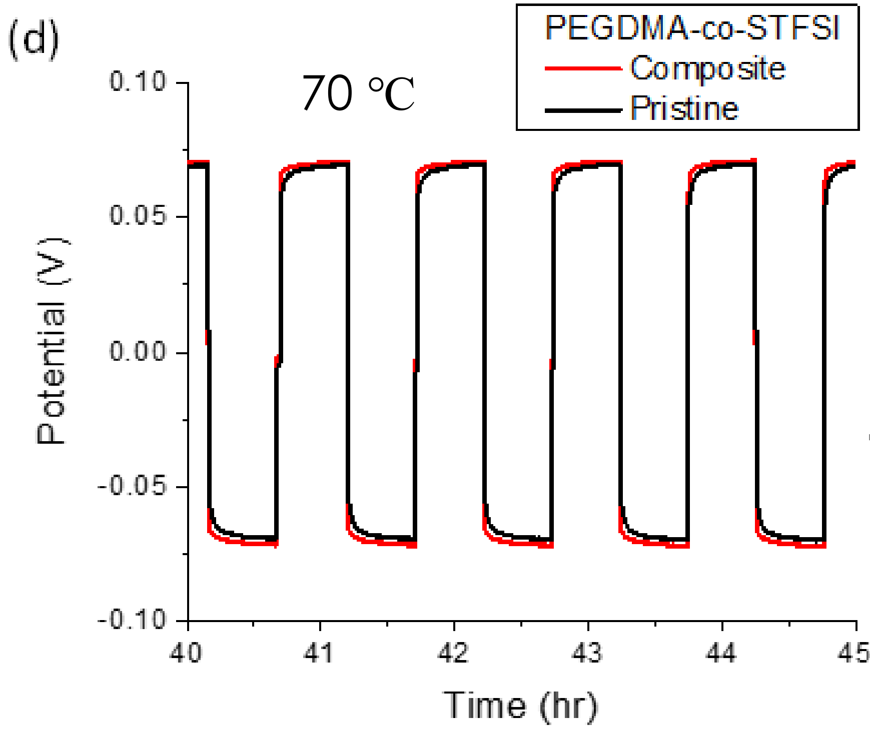
Transference number

Samples all gel polymers	t_{Li+}
Single ion polymer – STFSI anion	0.90
Single ion polymer – STFSI anion + 50 wt% LICGC™	0.88
Polymer with free LiTFSI salt	0.28
Polymer with free LiTFSI salt + 50 wt% LICGC™	0.56

Single ion gel polymer vs composite:
- similar conductivities,
- similar transference numbers
- composite mechanically more robust

Breaking the usual tradeoff





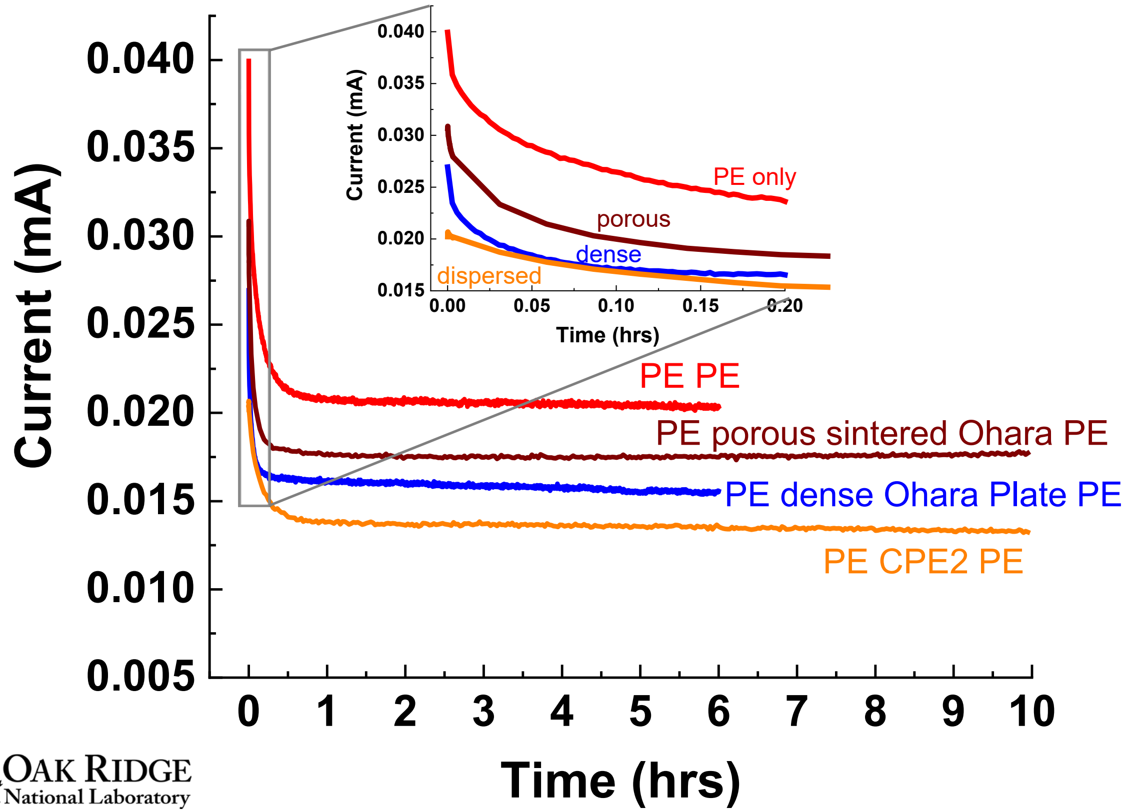
On for 100 hours, cycles

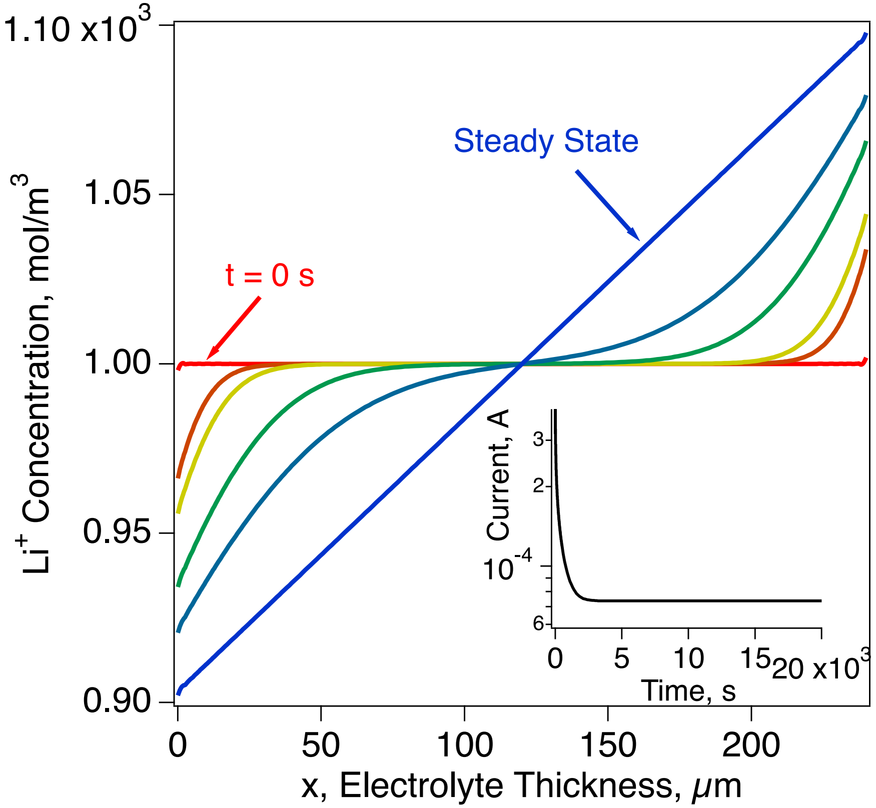
Accomplishment

Collaboration with Jennifer Schaefer, manuscript submitted, in review

Transference and Li//Li polarization getting a closer look

- Observations of chronoamperometric relaxation with EIS
  - Adding ceramic particles changes the t_{Li}^+ for PE (via Bruce Vincent)
  - A SIC blocking layer change kinetics
- Models to assess the relaxation kinetics are being developed





Simulation for Li/PE PE/Li cell

Details given in supplement slides

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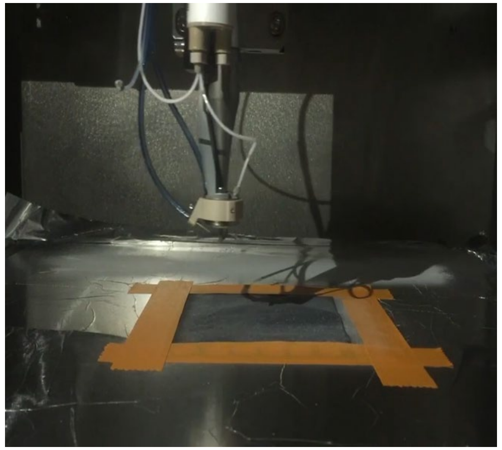
Gel electrolytes with dispersed ceramic particles – perspective, next steps

- Benefits: Many ways to tune
  - Single ion conductors may alleviate Li dendrites
- Challenges:
  - Balance of mechanical properties and ion transport, typical tradeoff
  - Cycling tests at practical currents and temperatures
  - Fabrication and integration of thin (~20μm) membranes
- Future work: Build on what is deduced for ion distribution in CPE:
  - Understand polarization in CPE, tradeoff with conductivity.
  - Assess at microscale, the CPE stability with Li.

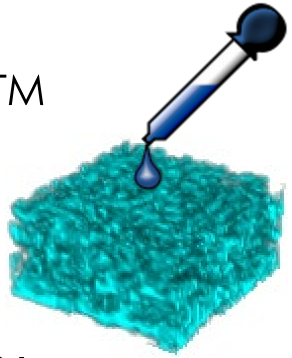
Porous sintered ceramic composites

Composites replacing dispersed ceramic particles with sintered particle → best for transport and robust mechanics



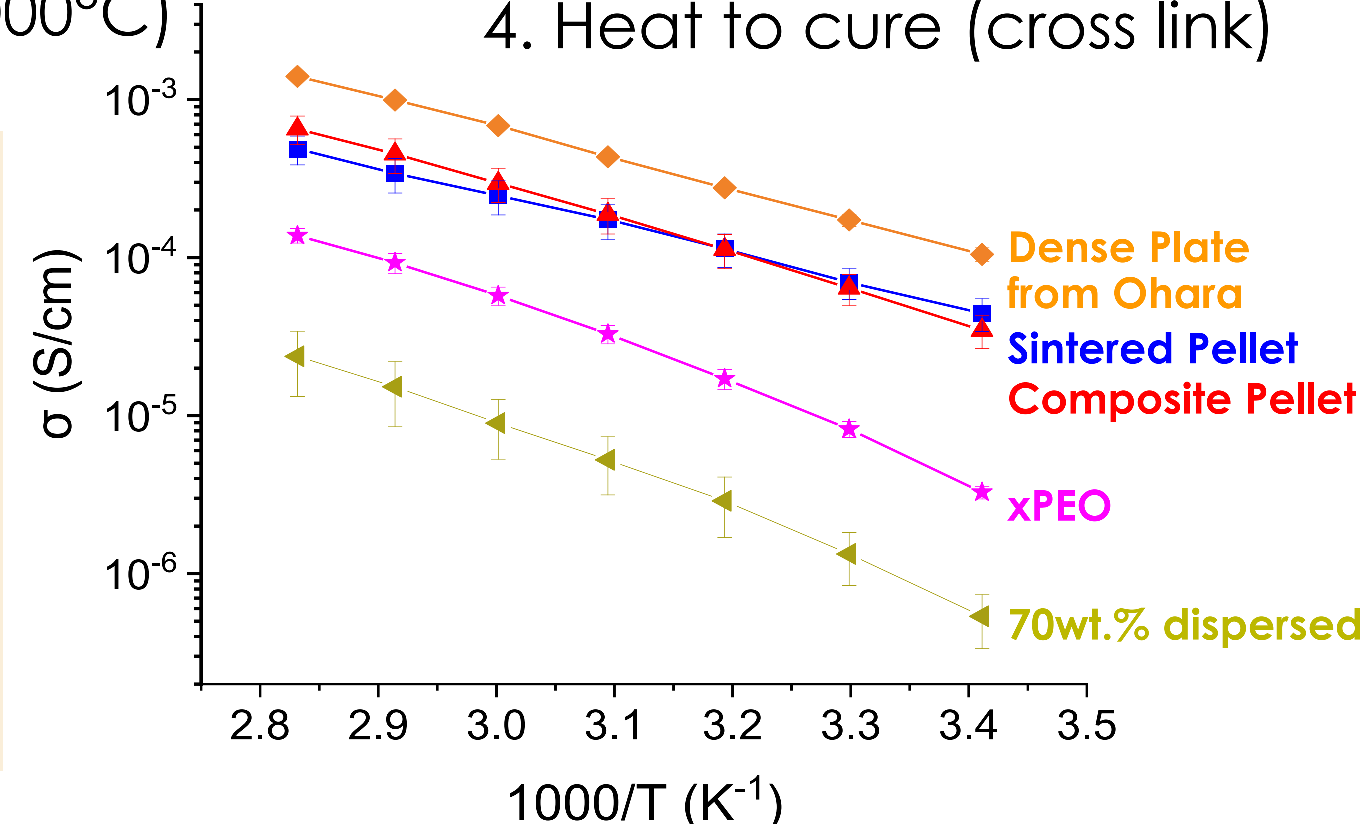
1. Spray coat LICGC™ powder suspension.

2. Sinter at high temperature (1000°C)



3. Add cross-linkable polymer (Jeffamine + PEGDGE) + LiTFSI under vacuum

4. Heat to cure (cross link)



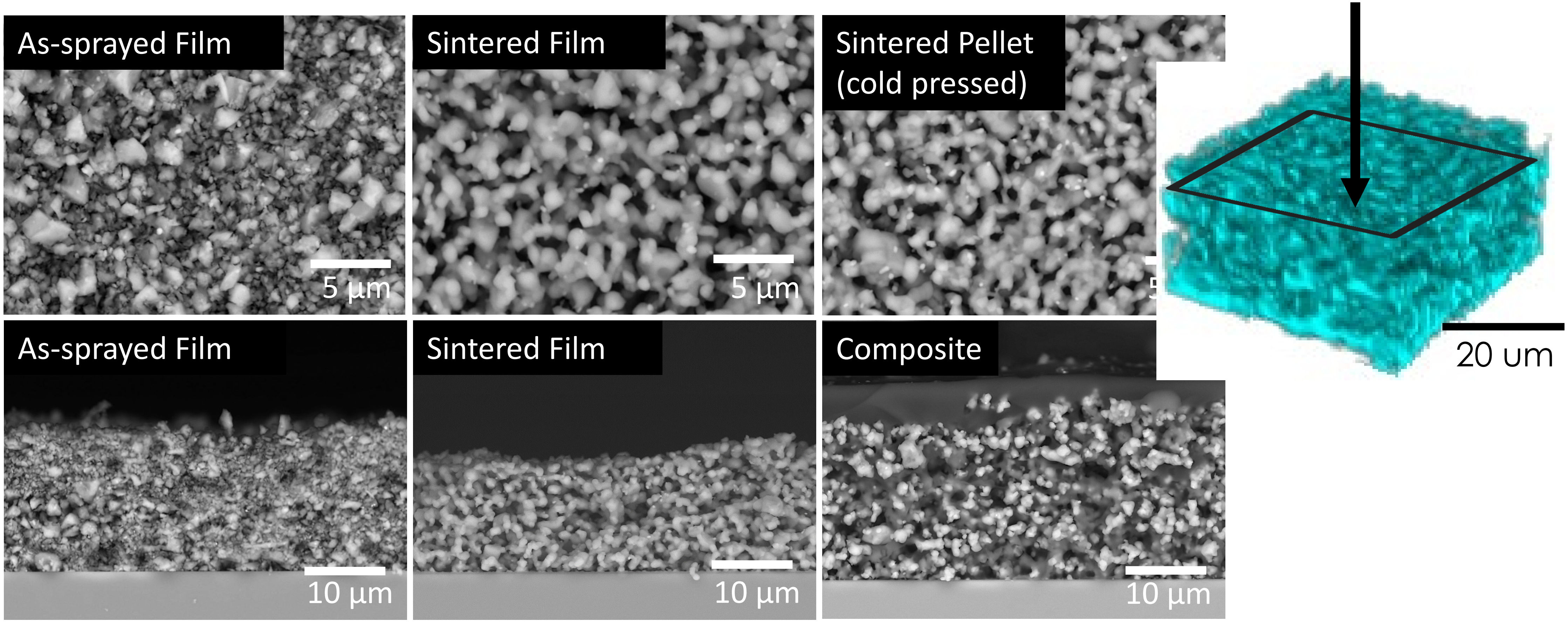
Properties

- 77wt.%, 61vol% ceramic
- Conductivity 10^{-4} S/cm
  - Li^+ path through ceramic phase
  - Grain boundaries are not barriers
- Dry xPEO+LiTFSI phase is resistive
  - Polymer is chemical & mechanical protection

Sintered structure of the ceramic film and composite

Top view

Edge view

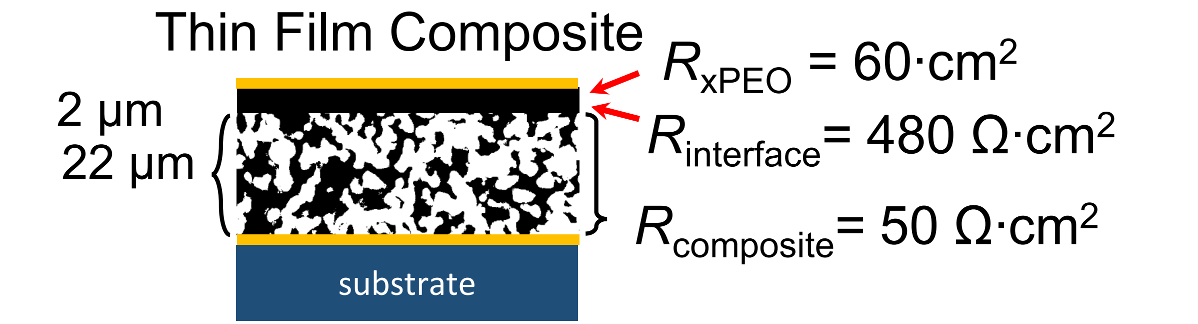


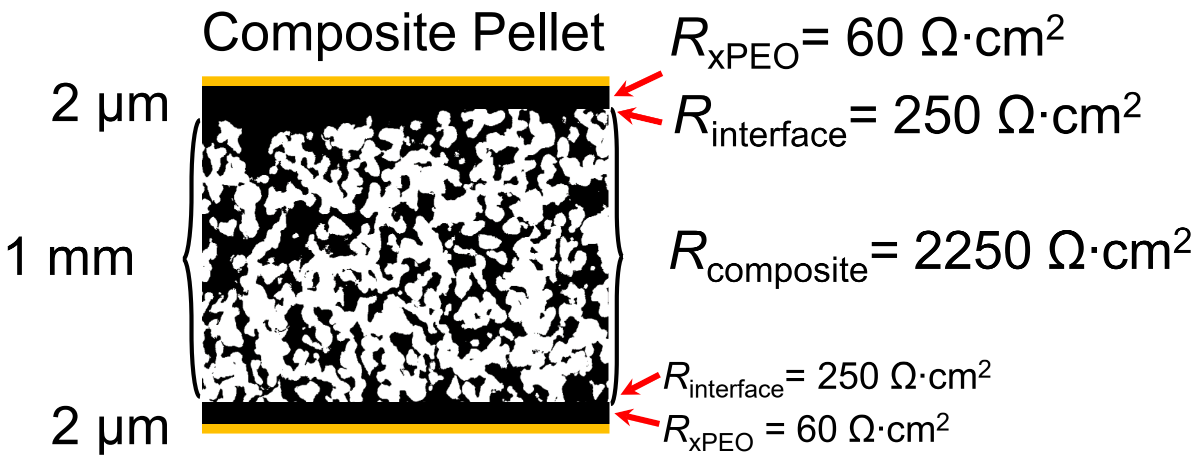
- Sprayed ceramic → uniform close packed particles
- X-ray tomography → homogeneous, partially sintered, fully connected
- Polymer overfill → adds buffer layer for Li contact, but also resistance

Sintered CPE pellets tested for Li cycles and mechanics

Polymer overlayer

- Needed for $Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$
- Dominates resistance of thin film

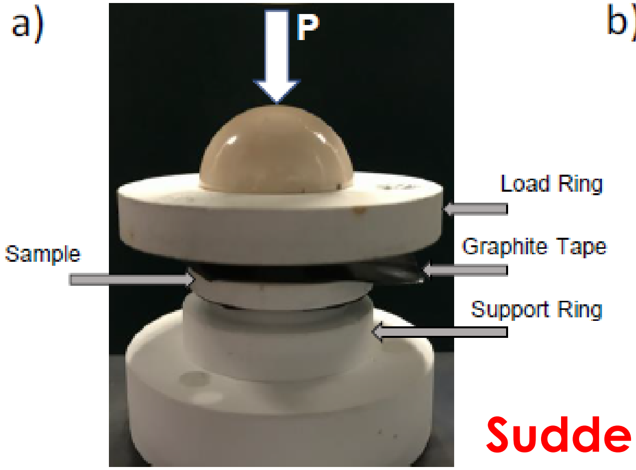




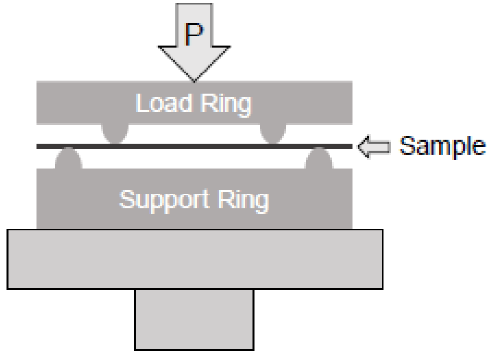
Equi-biaxial flex strength test

- Crack initiates at center of pellet
- Polymer bears some of load

a)

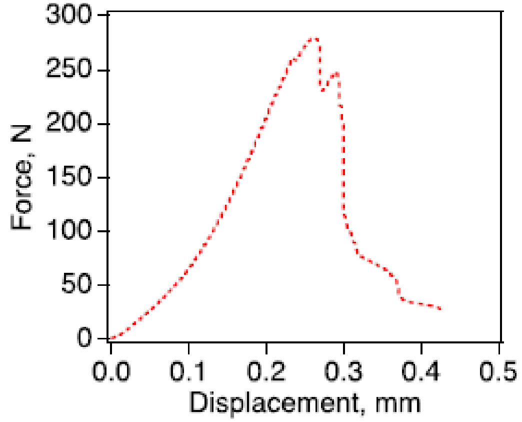


b)

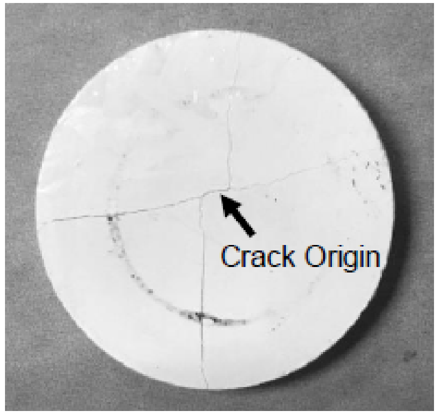


Sudden brittle failure avoided.

c)

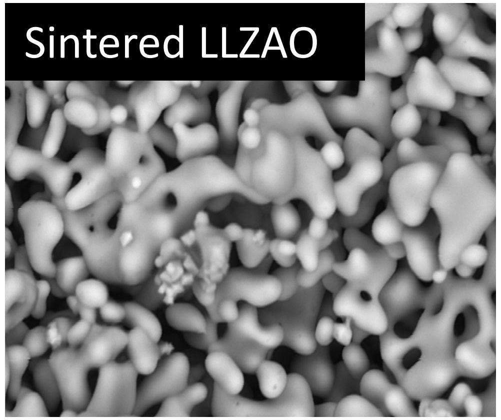


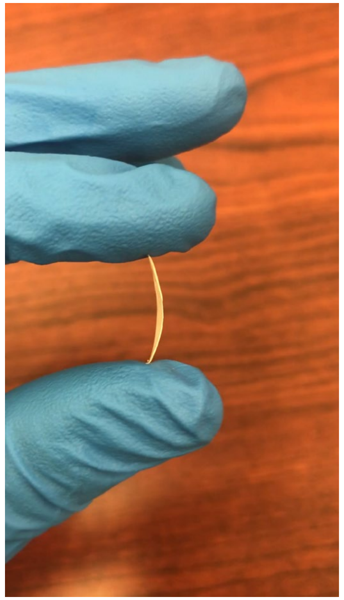
d)



Porous sintered composite electrolytes – perspective, next steps

- Benefit: high room-temperature conductivity, mechanically robust
- Challenge: high temperature required to sinter ceramics
- Future work: Focus on thin membranes
  - Alternate materials, processing
  - Test without polymer interface
  - Li/Li symmetrical cell testing
  - Co-sinter with cathode





Fabricating and cycling full cells

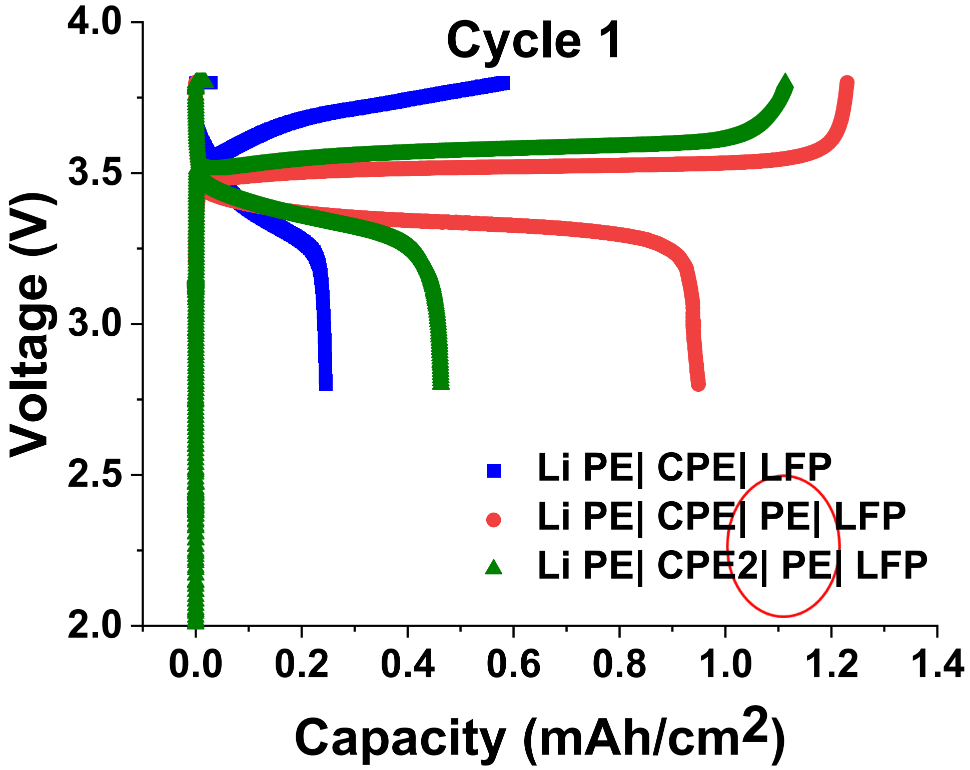
$LiFePO_4$ on Cu dry composite cathode + **Solid Electrolyte** layers of composites, polymers, ceramics + **Li metal** Thick foil or thin film from vapor

Challenges and Next steps

Soft polymer is "stopgap" filler between composites with high ceramic loading (LFP and CPE) and at Li interface

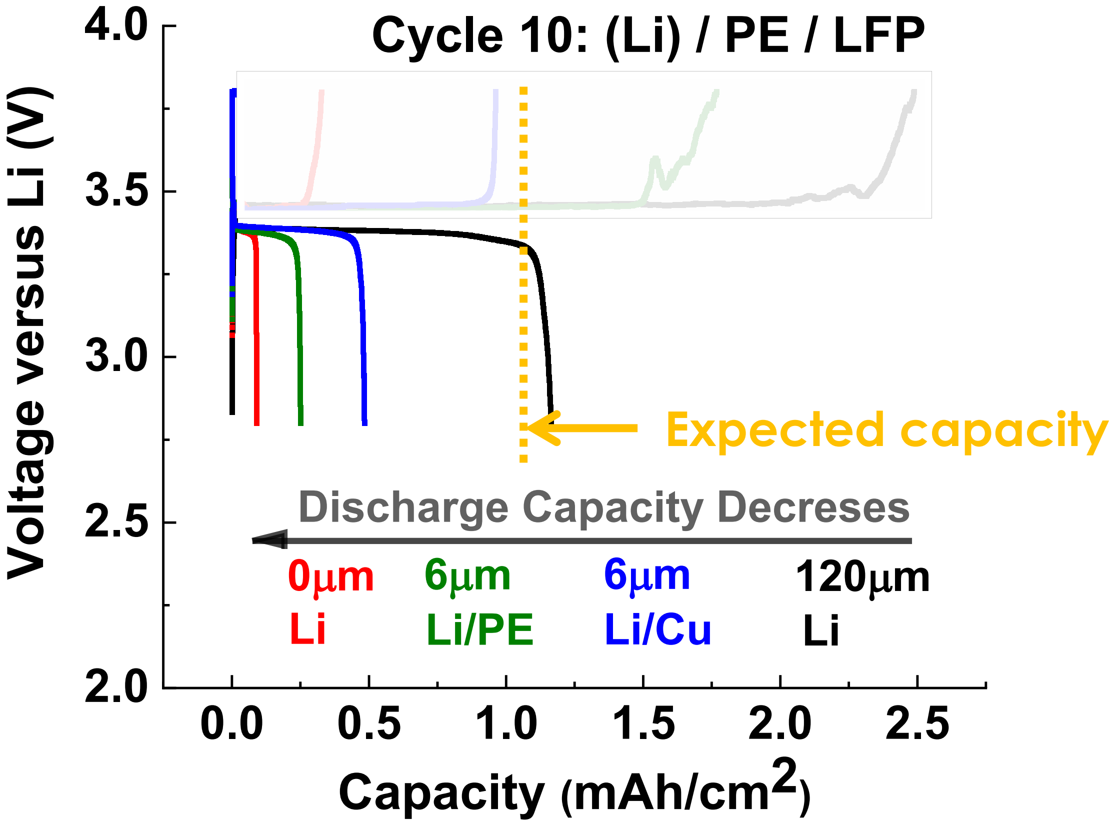
Thin polymer electrolyte (PE) fills gaps at rough LFP / CPE interface

- Improves contact, but adds cell resistance



Reducing excess Li, clearly shows if capacity is fading. Here at cycle 10.

- Is Li loss due to physical isolation ? OR
- Is Li loss due to chemical reaction ?



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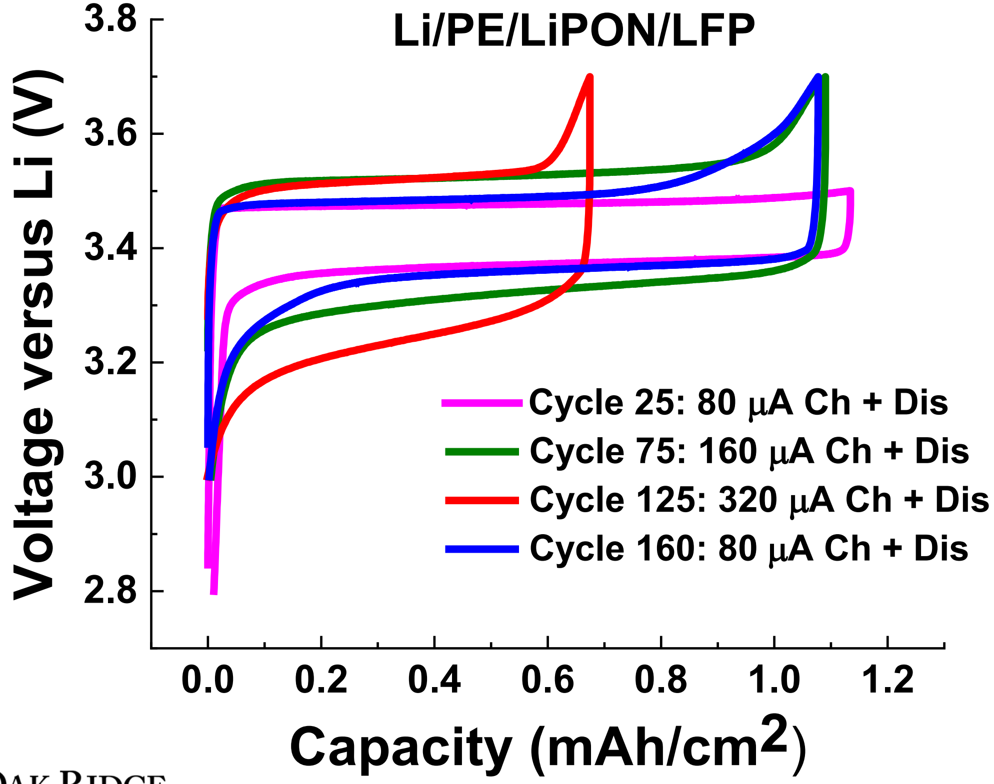
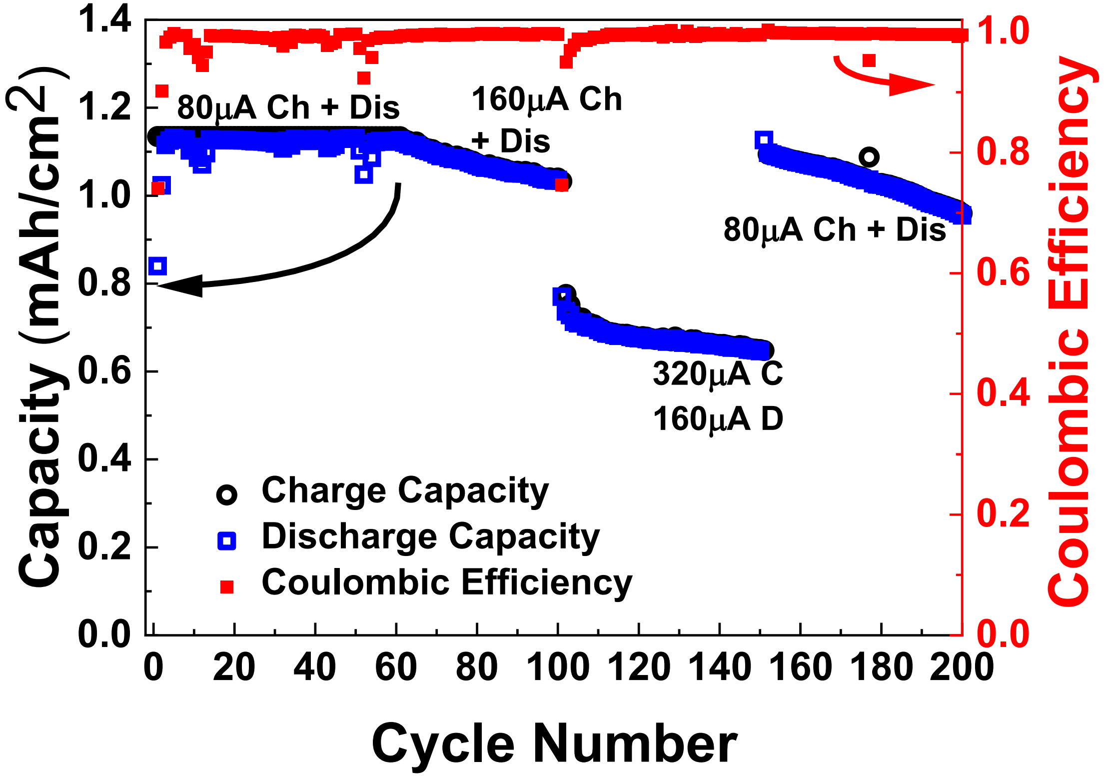
Accomplishment

Single ion conduction layer (Lipon) → best cycling to date

- Motivated by work of J. Christensen and N. Craig (Bosch)
- Here stable (although resistive) cell with Lipon sputter-coated cathode
- Long cycling. Also seen for very thick PE (~300μm) and thick Li

Li / PE / Lipon (0.3μm) / LFP cathode

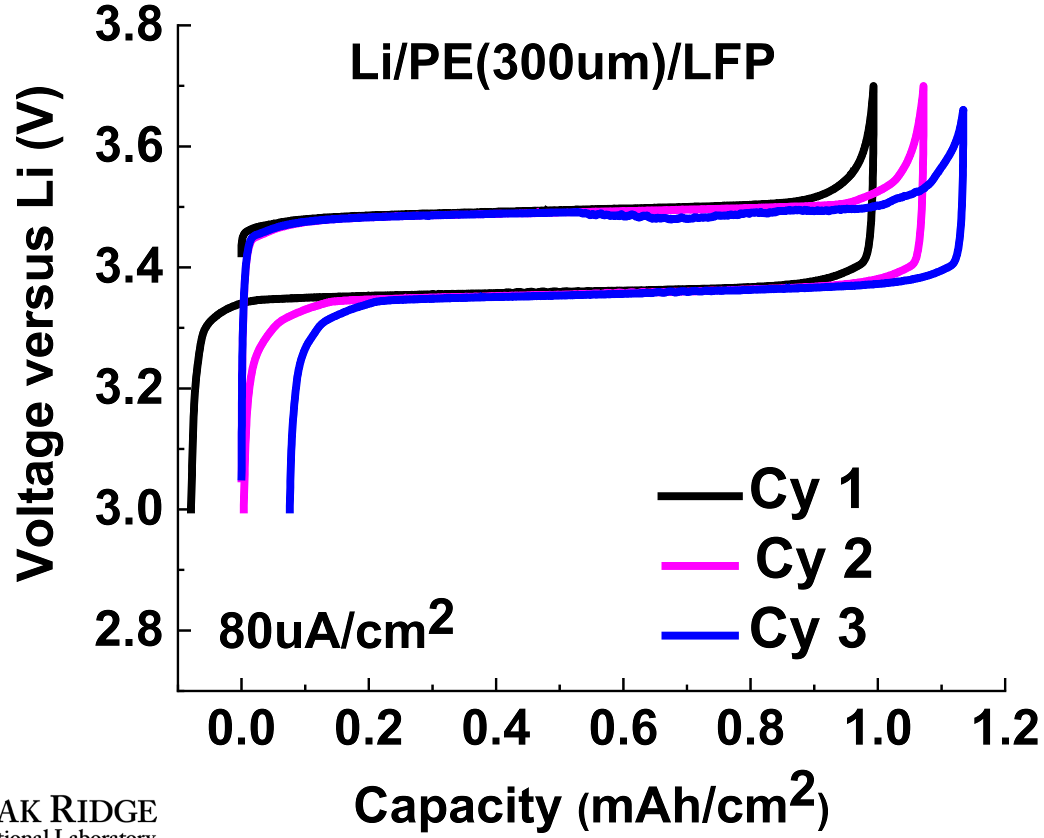




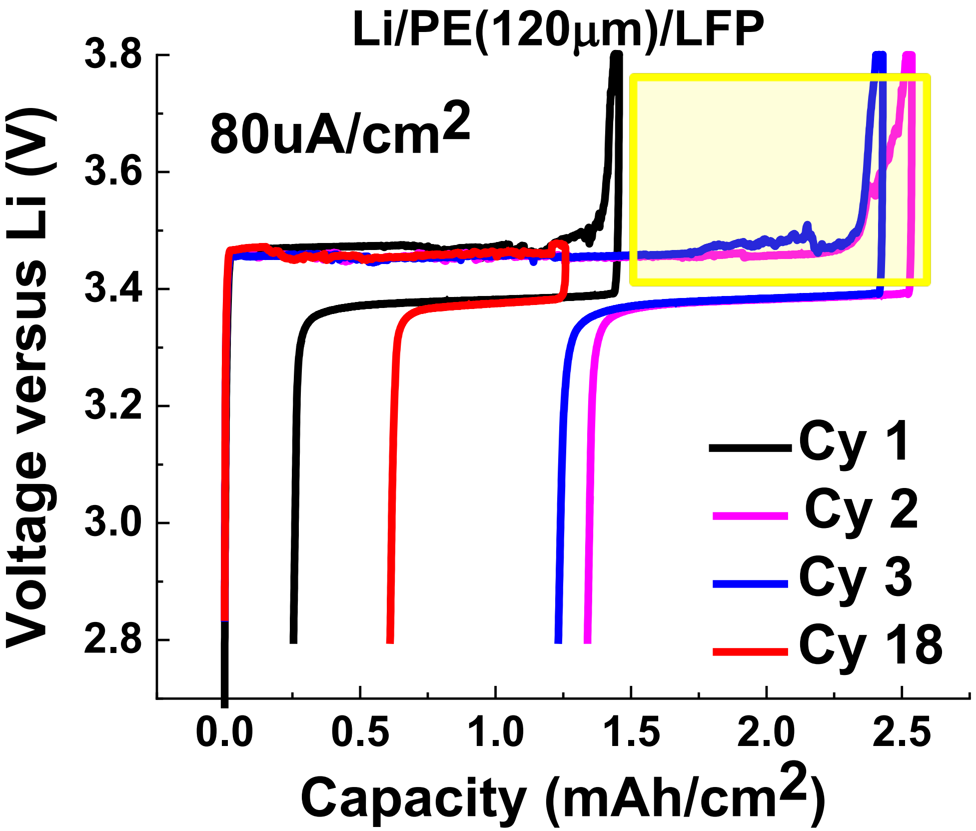
Overcharging is observed – assessing mechanism(s)

- Over-charge can exceed $LiFePO_4$ capacity (1.1mAh/cm^2) by 2-3X.
- Could this be soft lithium shorts?
- Depends on cell layouts and PE thickness, *reproducibly*.

Normal cycling to expected capacity



Over charge capacity of cycles 2, 3



Accomplishment - ongoing

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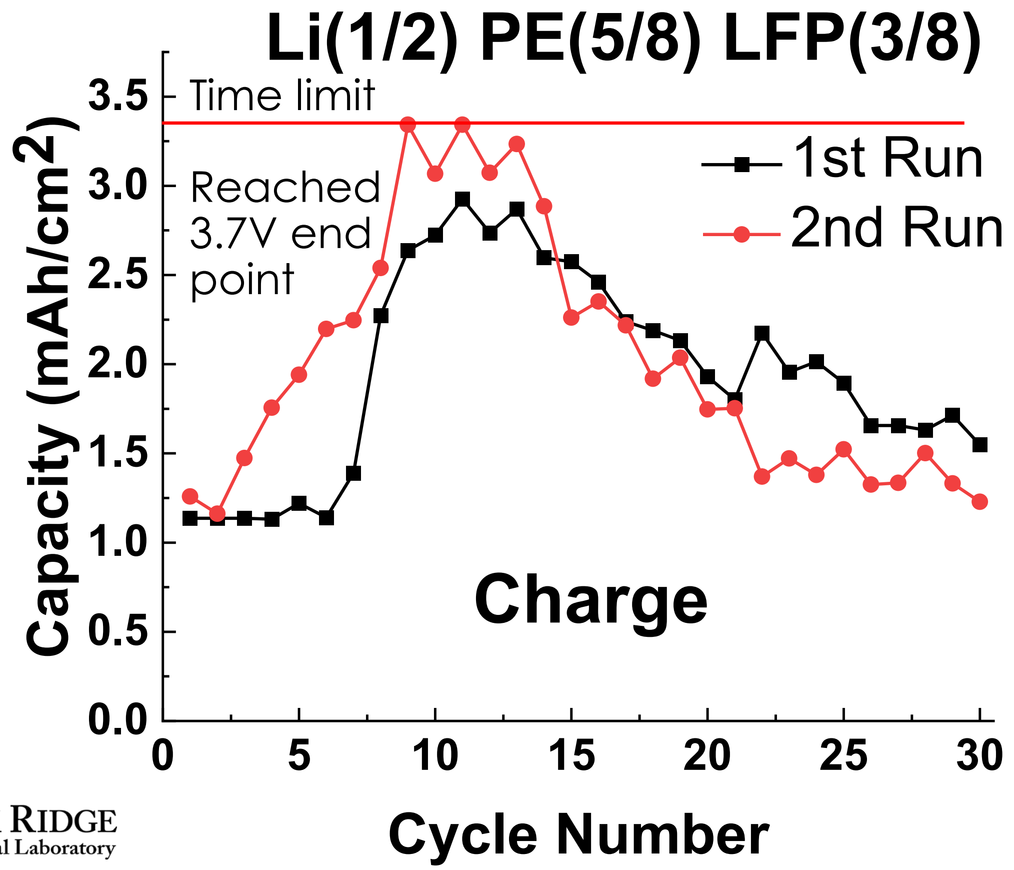
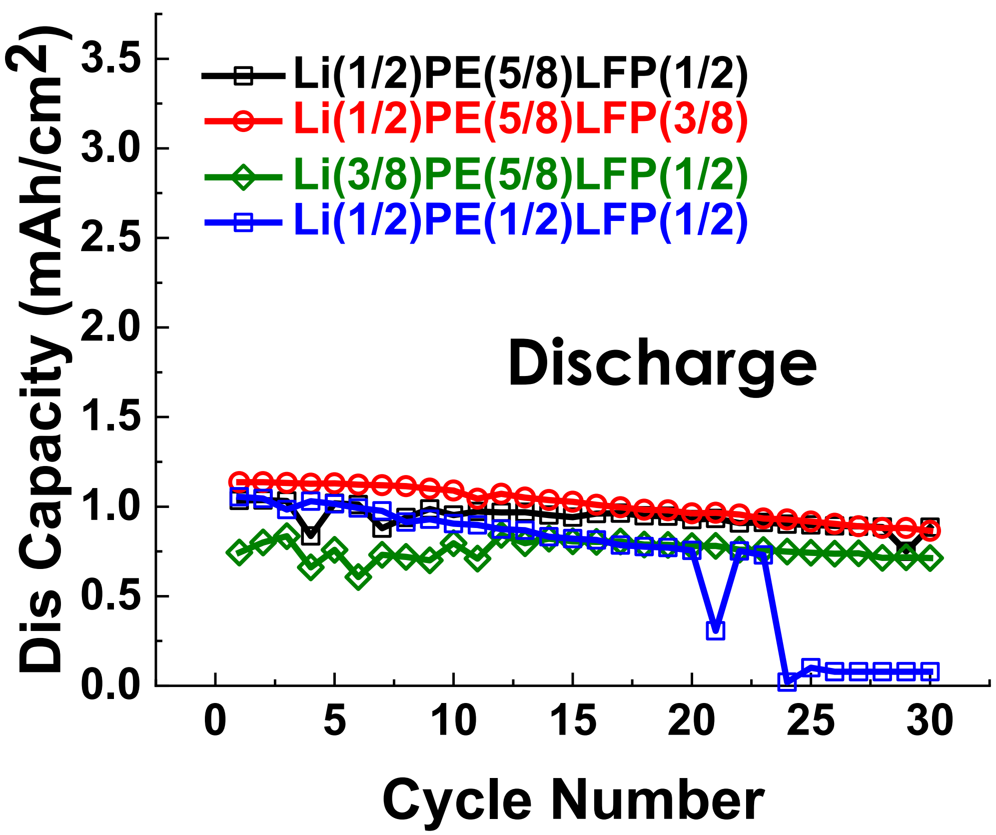
Overcharge related to cell design – dimensions, thickness

- Observations in coin cells
  - Overcharge related to electrode areas → suggests edges are more sensitive
  - Discharge cycles are well behaved → no major damage
  - Similar to Homann et al. (Sci. Rept. 2020) → attributed noise to Li micro-dendrite





Full cell fabrication and cycling – perspective, next steps

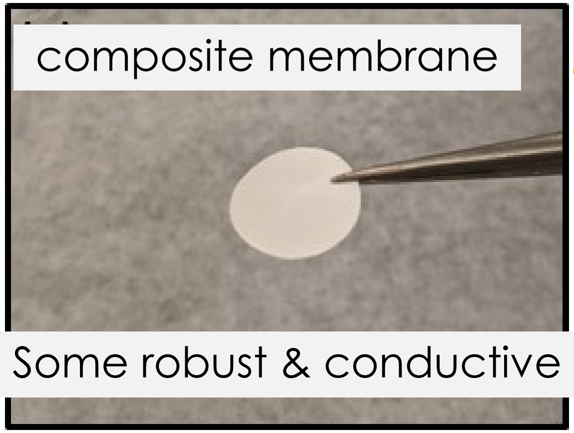
- Benefit: Initial work with $LiFePO_4$
  - allowed isolation of Li aging, and focus on electrolyte research
- Challenge
  - Identify processes leading to Li loss, degradation
  - Test cycling with practical thicknesses, temperatures, larger layouts
- Future work
  - Test with HE/HV NMC 622 cathodes.
    - Homann et.al. (2020) – PEO based PE should be stable to 4.6V
  - Assess advantages of incorporating SIC electrolyte, best location
  - Alternate processing to form interfaces, eliminate soft-fill layers

Summary- CPE of new materials/processing → path to SSB

Focus on high energy density. Thin Li and electrolytes with good interfaces.

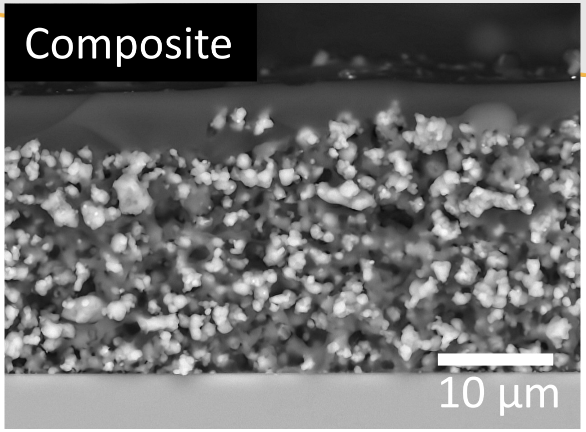
Summary with future work

SIC or crosslinked gel with high ceramic loading



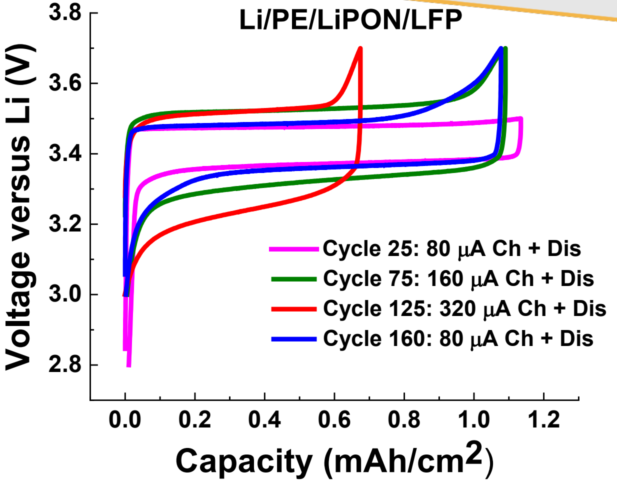
Future work
- Tune materials & interfaces ~ free Li^+
- Polarization in composite
- Reduce thickness

Highly conductive sintered thin-film CPE



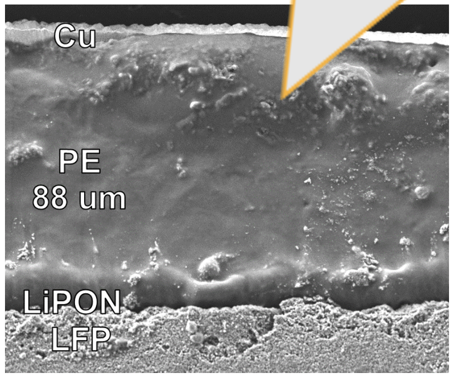
Future work
- Microstructure ~ Li dendrites
- Low temp sintering of thin ceramic
- Integrate with cathode

Integration into cell balancing ASR and stability



Future work
- Aging processes at Li interface
- Effective SIC use
- Reduce SE thicknesses
- HE cathode evaluation

Li-free anode to achieve max energy density



Future work
- Processing to form/integrate ultra thin Li

Technical backup slides

- Details of polarization model

Setup of model (for review slides only is needed)

- In order to explicitly include the double layer at the electrode surface we solve Poisson's equation for potential change due to distribution of charge carriers in electrolyte

$$-\epsilon\nabla^2\phi = F(c_+ - c_-)$$

- Fluxes of charge carriers in the electrolyte are modeled using Nernst-Plank equations

$$N_+ = -z_+u_+Fc_+\nabla\phi - D_+\nabla c_+$$
$$N_- = -z_-u_-Fc_-\nabla\phi - D_-\nabla c_-$$

- Mixed boundary conditions need to be prescribed at the electrode surfaces (z = 0 and z = L)

$$\phi(0) - \lambda_s\nabla\phi(0) = 0$$
$$\phi(L) + \lambda_s\nabla\phi(L) = V,$$

- Evolution of concentration of charge carriers in time (mass balance)

$$\frac{\partial c_+}{\partial t} = -\nabla N_+$$
$$\frac{\partial c_-}{\partial t} = -\nabla N_-$$