Composite Electrolyte to Stabilize Metallic Lithium Anodes

OAK RIDGE National Laboratory

Xi (Chelsea) Chen, Beth Armstrong, Sergiy Kalnaus, Ritu Sahore, Andrew Ullman, Yiman Zhang, Nancy Dudney

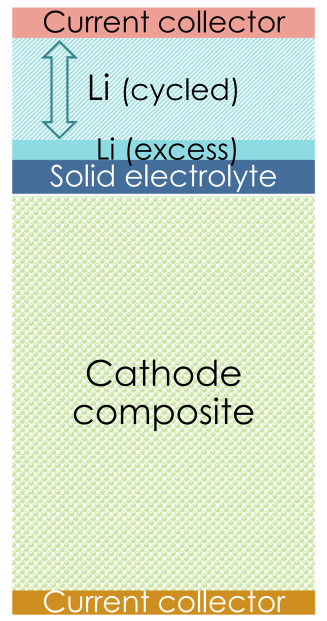
Project ID bat273

Overview – Composite Electrolytes to Stabilize Li Metal Anode

- Timeline
  - Start: October 2014
- Budget
  - \$400k FY20
  - \$400k FY21
- 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 and cost objectives.

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

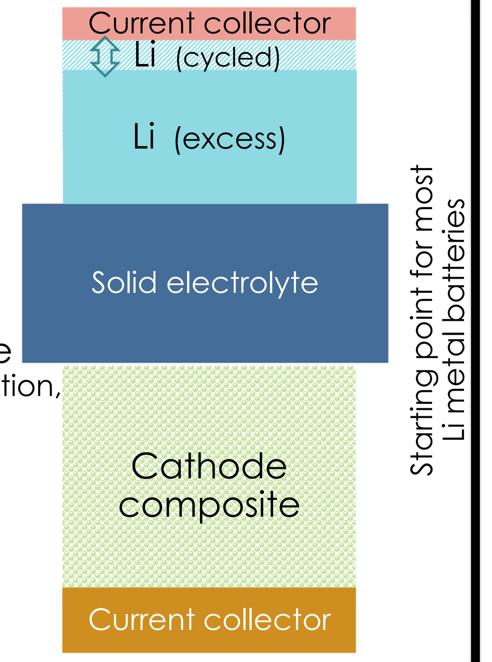


Objectives – Study, determine

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 - FY20-21

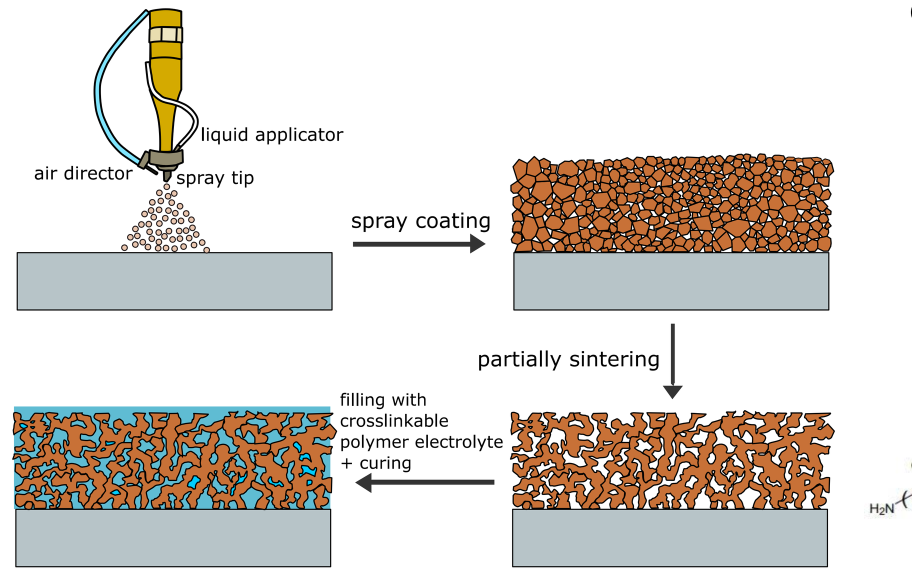
Milestones: FY20-FY21	Target:	Status:
Investigate the trade-off between **Li^+ transference number** and ionic conductivity of the gel composite electrolytes, and optimize it.	Q3 FY20	✓
Fabricate **full batteries** using NMC cathode, composite electrolyte, and Li-metal anode. Identify cell **failure mode**.	Q4 FY20	✓
Sinter and characterize porous LLZO network by different processes. (Room temperature conductivity > 10^{-5} S/cm)	Q1 FY21	80% complete
Compare polymer-LLZO ceramic composites with 4 different ceramic loadings. (Room temperature conductivity > 10^{-5} S/cm; Interfacial resistance with Li < 100 Ohm/cm^2)	Q2 FY21	80% complete
Elucidate the Li ion path through at least two distinct polymer-ceramic composites	Q3 FY21	50% complete
Measure Li^+ transference number with at least two different anion receptors.	Q4 FY21	50% complete
Make a robust, highly conductive, high cation transference number composite using LLZO based ceramics. Demonstrate cyclability with Li//Li symmetrical cells and NMC full cells.	Annual FY21	On track

Major Accomplishments

- Developed an aqueous spray coating technique as a facile fabrication method for thin composite electrolyte films with high ceramic loadings. (*J. Power Sources* **2018**, *390*, 153-164)
- Quantified the interfacial resistance for ion transport between model polymer and ceramic electrolyte (1.2 KΩ·cm²); Minimized the interfacial resistance (near zero). (*ACS Energy Letters* **2019**, *4*, 1080-1085)
- Developed a thin three dimensionally interconnected composite film with fast ion conducting path through the ceramic (ASR=70 Ω) and improved mechanical strength. (*Energy Storage Materials* **2020**, *26*, 242-249.)
- Fabricated a gel composite electrolyte with greatly improved cycling performance. The efficacy of ceramic fillers is discussed in depth. (*Journal of Materials Chemistry A*, **2021**, 9, 6555-6566)
- Used numerical modeling to understand concentration gradients in composite electrolyte with layered geometry and dispersed geometry.

A Three-Dimensional Interconnected Polymer/Ceramic Composite as a Thin Film Solid Electrolyte

Technical accomplishment: Overcoming ceramic interparticle resistance: the fabrication of a 3-dimensional interconnected composite

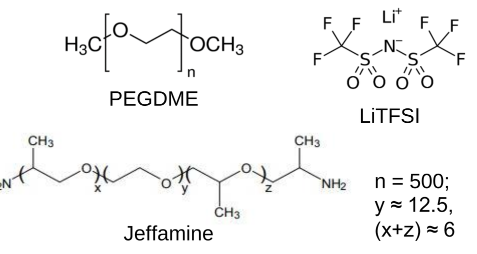


Ceramic: LICGC® powder

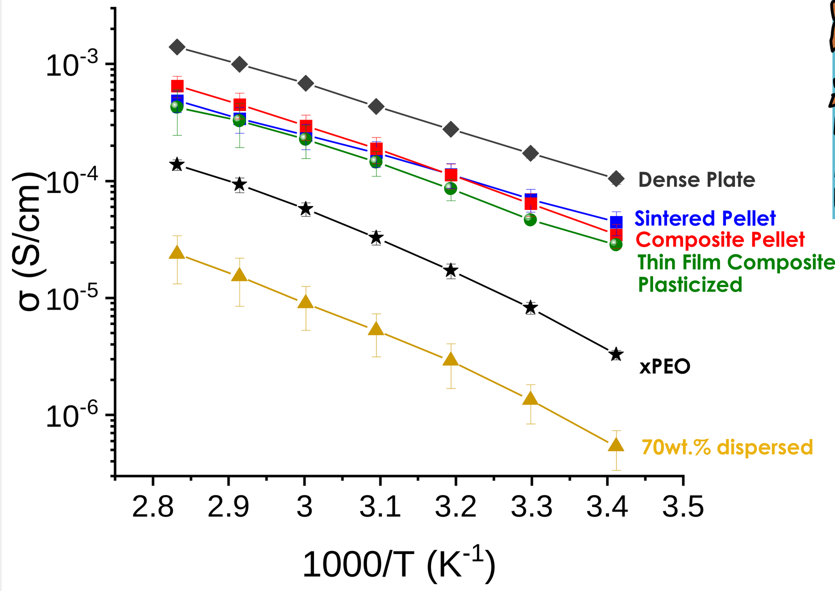
$Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$

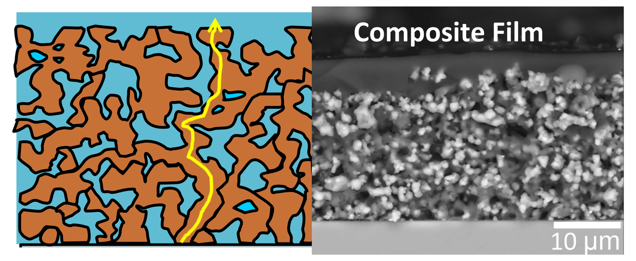
High Li^+ conducting ceramic (10^{-4} S/cm room temperature)
Air stable, Water resistant
Average size ~1 μm
NOT stable with Li metal

Polymer: xPEO



Ionic transport path in composite → through both the ceramic and the gel polymer

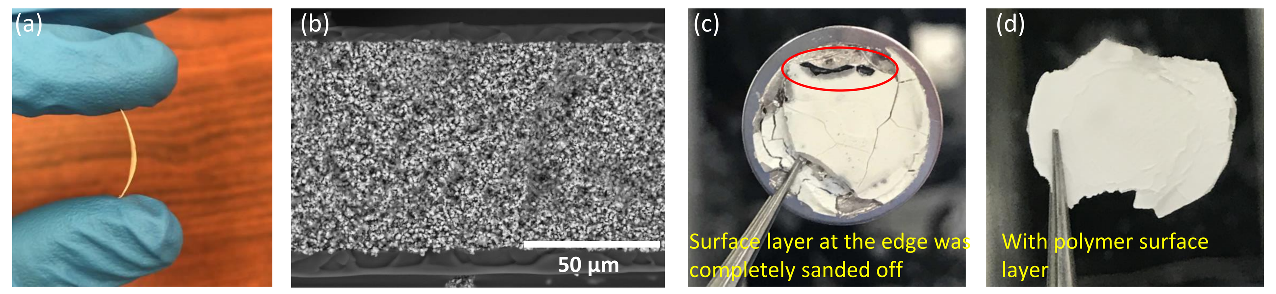


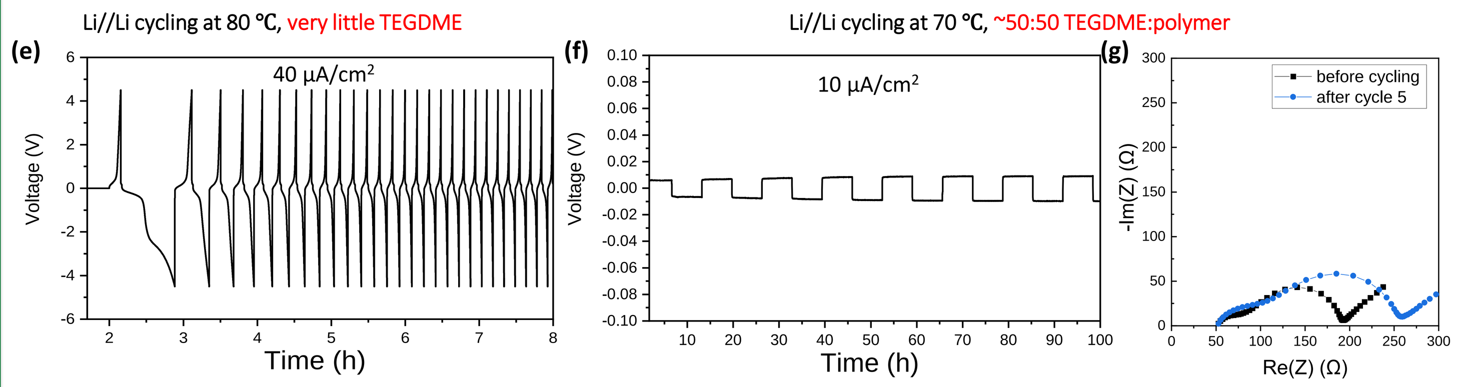


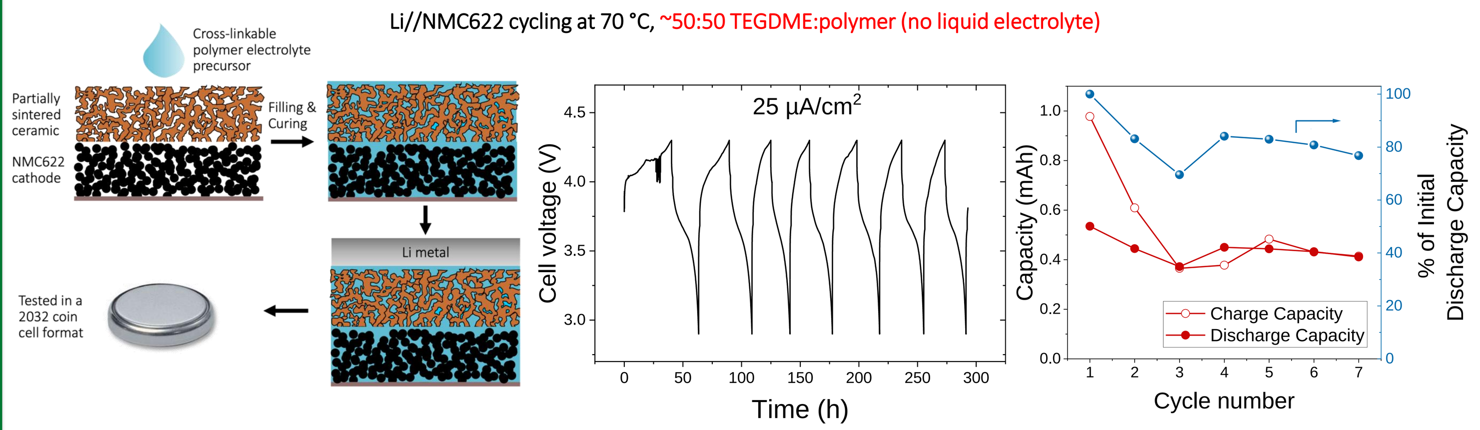
- **Sintered pellet and composite pellet: similar conductivity→ ion transport through the ceramic.**
- Plasticizer (TEGDME) effectively reduced the interfacial resistance between polymer surface layer and the composite.

Palmer, M. J.; Kalnaus, S.*; Dudney, N. J.; Chen, X. C.*, et. al. *Energy Storage Materials* **2020**, *26*, 242-249.

Technical accomplishment: Li symmetrical cell and full cell fabrication using the 3-dimensional interconnected composite

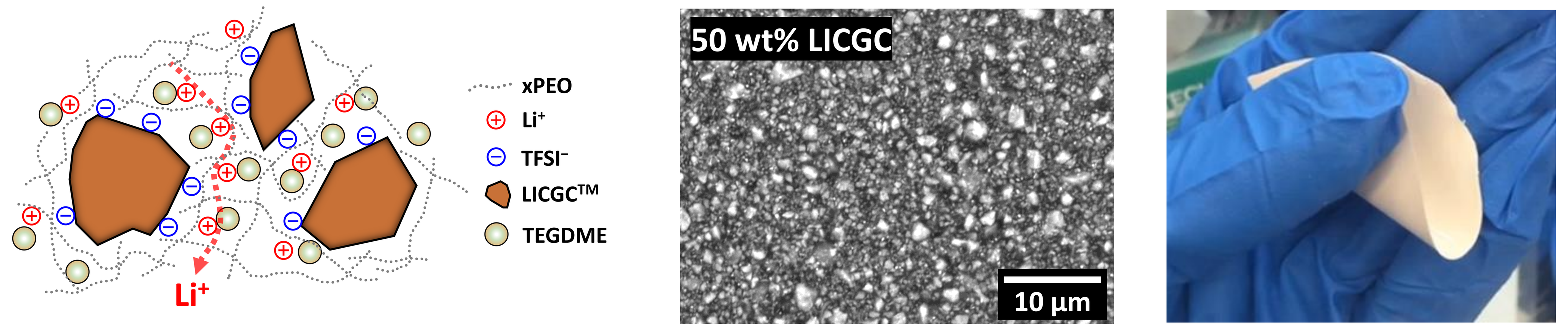






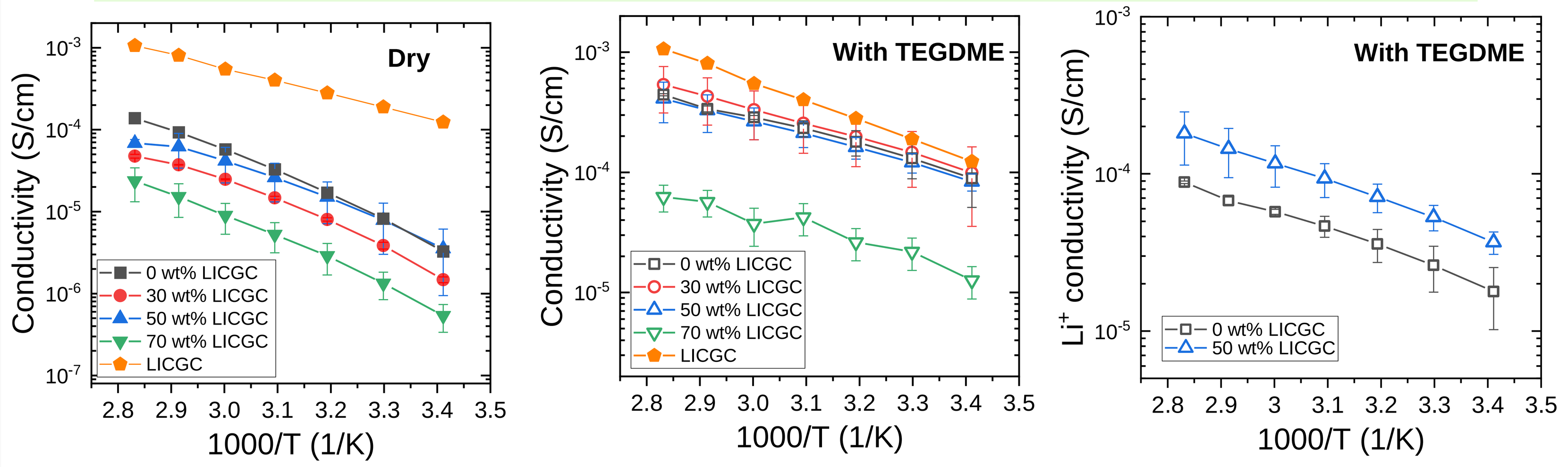
Gel Composite Electrolyte - An Effective Way to Utilize Ceramic Fillers in Lithium Batteries

Crosslinkable PEO-based Gel Composite Electrolytes – components and morphology

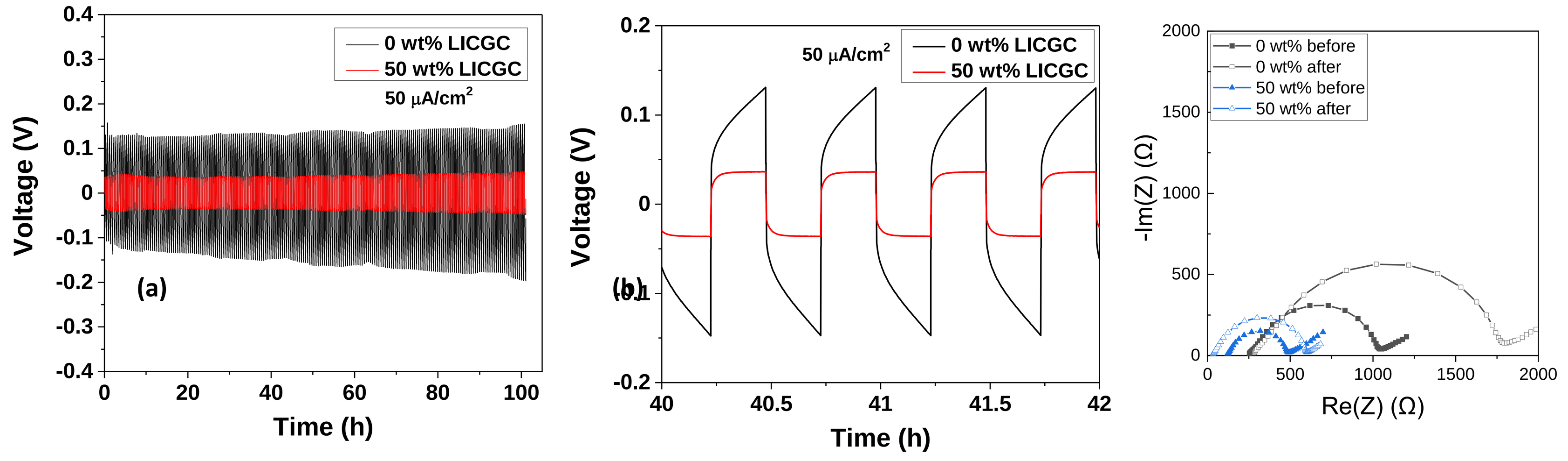


- A gel composite electrolyte is fabricated, using crosslinked PEO matrix, LiTFSI salt, TEGDME plasticizer and doped-lithium aluminum titanium phosphate particles (LICGC™) fillers.
- The incorporation of the LICGC particles into the membrane improves its handleability – more flexible, less sticky, can be made thinner.

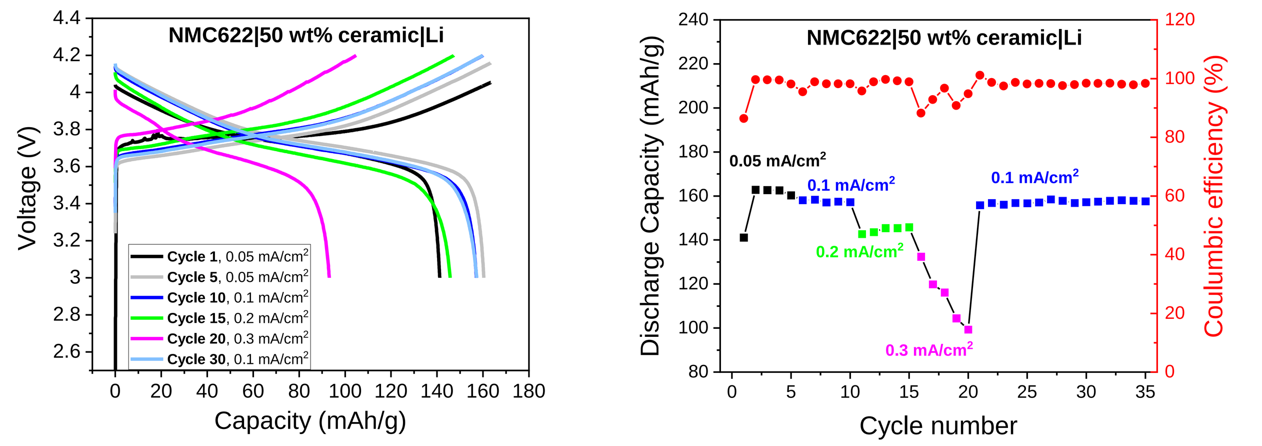
Conductivity: in the dry state, composites present decreased conductivity; in the gel state, composite with 50 dry wt% LICGC has similar overall conductivity and 2-fold increase in Li^+ conductivity



Li symmetrical cell cycling: gel composite electrolyte has lower overpotential, lower interfacial impedance and quickly reaches steady state



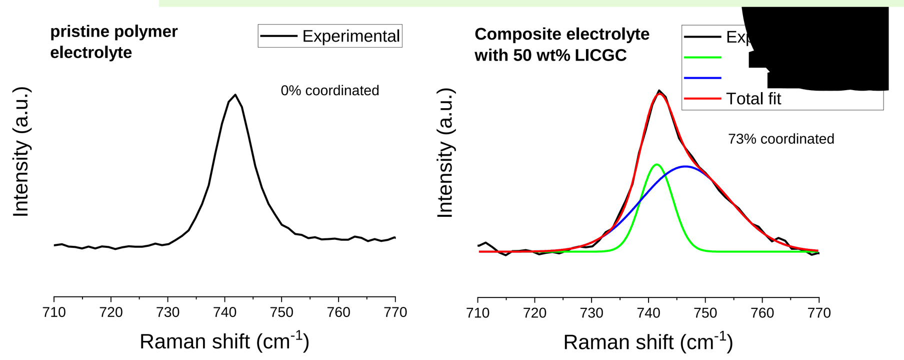
Full cell performance at room temperature



Li^+ transference number

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

Underpinnings of the gel composite electrolyte's superior performance

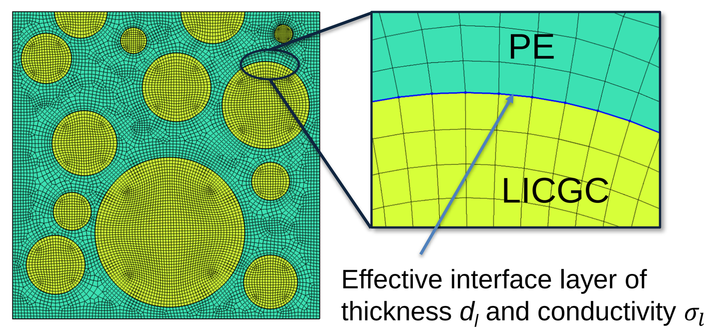


- LICGC™ serves as an anion receptor and immobilizes TFSI⁻, leading to significantly increased t_{Li+};
- Simultaneously, it promotes Li^+ dissociation and enhances Li^+ mobility due to increased plasticizer to Li^+ ratio.
- The simultaneous Li^+ transport promotion and TFSI⁻ immobilization leads to greatly improved cell cycling performance.

Chen, X. C.*, et. al. *Journal of Materials Chemistry A*, **2021**, 9, 6555-6566

Understanding Transport in Composite Electrolytes Using Numerical Modeling

Model describes diffusion, migration and LICGC/PE interface

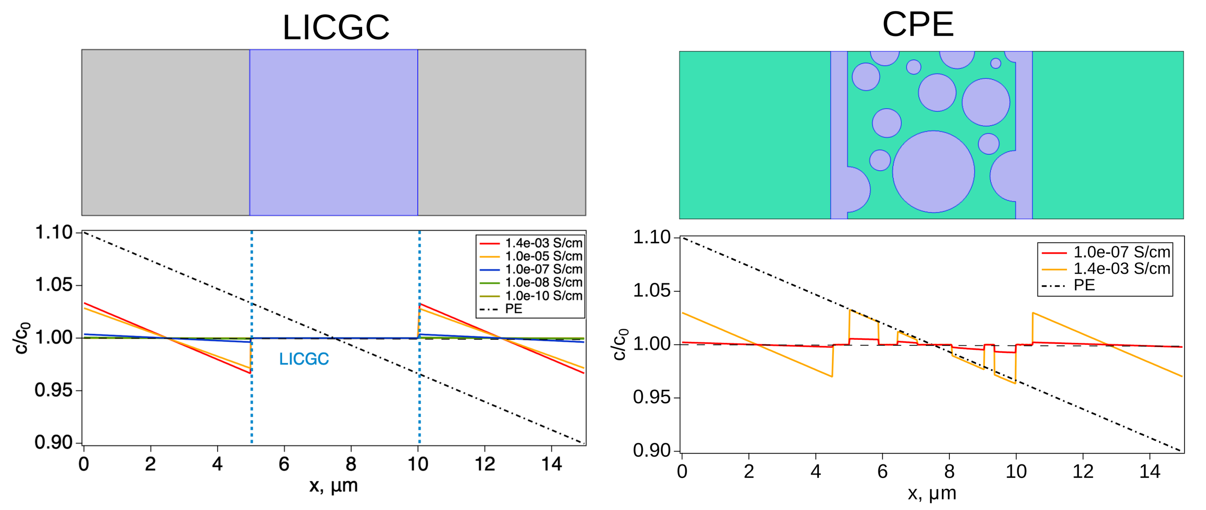


Nernst-Plank equations

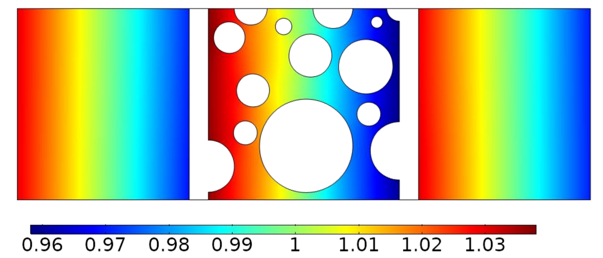
$$N_+ = -z_+u_+Fc_+\nabla\phi - D_+\nabla c_+$$
$$N_- = -z_-u_-Fc_-\nabla\phi - D_-\nabla c_-$$
$$\frac{\partial c_+}{\partial t} = -\nabla N_+$$
$$\frac{\partial c_-}{\partial t} = -\nabla N_-$$

Presence of single ion conductor reduces concentration gradient under 10 mV applied potential

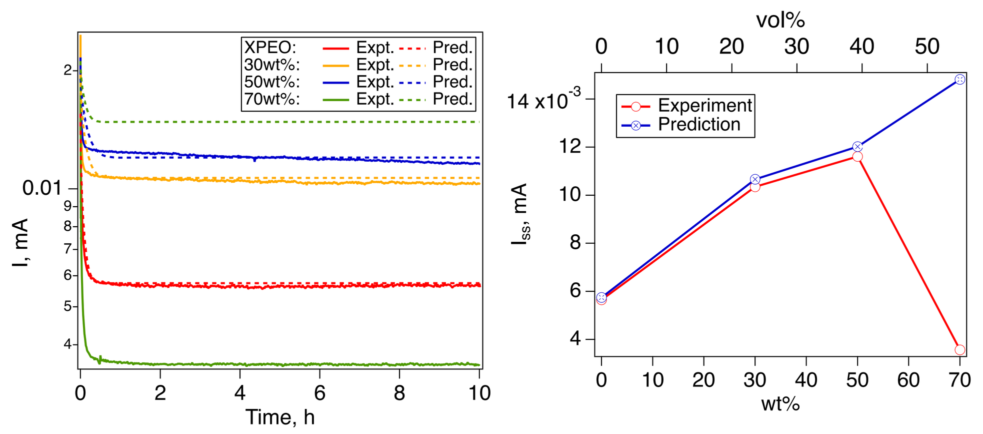
Mid-section concentration profiles



2D normalized concentration profile in PE



Chronoamperometry to determine steady state current and transient behavior

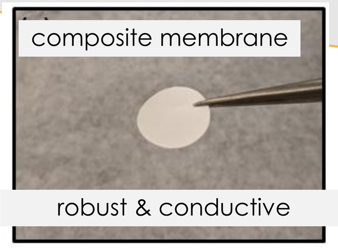


Steady state current in CPE

Summary and Future Work: CPE of new materials/processing → path to SSB

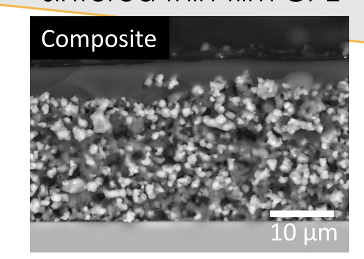
Focus on high energy density. Thin Li and electrolytes with good interfaces.

Gel composite electrolyte



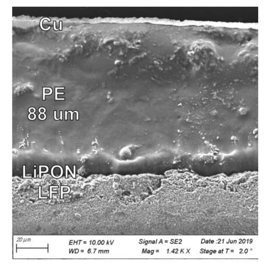
Future work
- Explore different anion receptors;
- Studying Li plating/stripping morphology through heterogeneous electrolyte

Highly conductive sintered thin-film CPE



Future work
- replace the LICGC ceramic to LLZO
- Optimize the integration with cathode

Li-free anode to achieve max energy density



Future work
- Processing to form/integrate ultra thin Li