Improving the Stability of Lithium Metal Anodes and Inorganic-Organic Solid Electrolytes

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Project ID: bat389

Overview

Timeline

- Start Date: Oct. 1, 2019
- End Date: Sept. 2020
- Percent complete: 30%

Budget

- Total budget: $848K
- FY19 funding: $400K
- FY20 funding: 448K

Partners/Collaborators

Venkat Srinivasan (ANL), modeling
Bryan McCloskey (UCB/LBNL), electrolyte characterization

Barriers Addressed

- Improved Energy Density:
  - Beyond Li-ion: enabling cells containing Li metal anodes
- Safety:
  - Li-metal based batteries have a long history of problematic dendrite growth which leads to internal shorts and thermal runaway

Relevance

Impact

Polymer electrolytes offer increased stability in lithium batteries in comparison to widely-used liquid electrolytes. We aim to synthesize hybrid organic-inorganic electrolytes with improved transport properties and greater stability against lithium metal for next-generation batteries.

Objectives

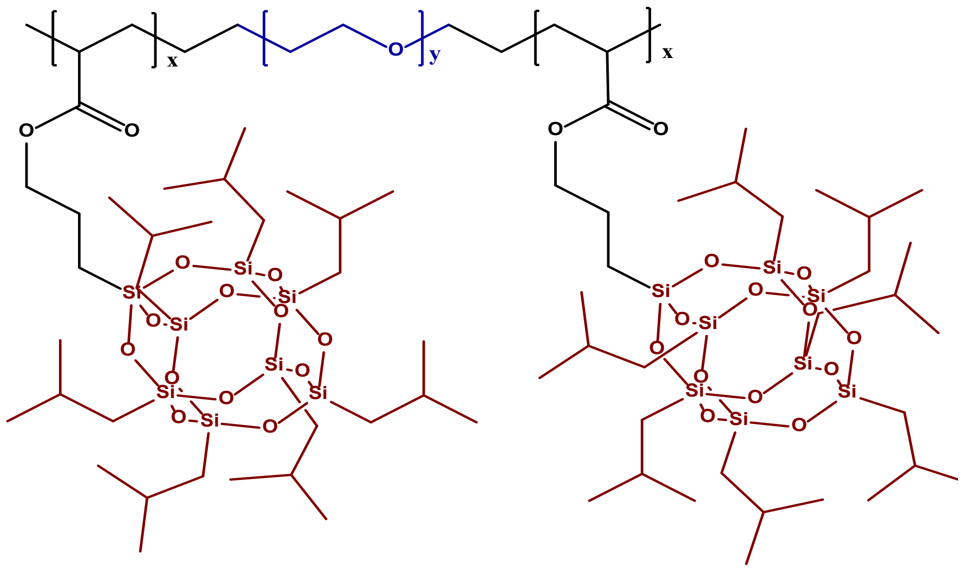
- Design and synthesize hybrid organic-inorganic electrolytes to enable lithium metal anodes.
- Create impurity-free lithium metal anodes.
- Full electrochemical characterization of electrolytes
- Provide cycling data for at least two POSS-containing block copolymer electrolytes.

Milestones

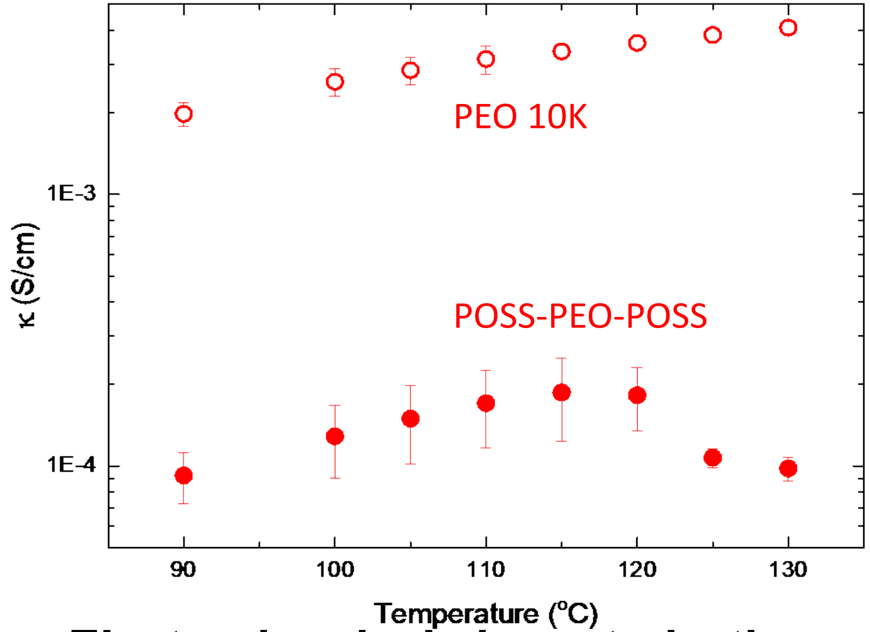
Date	Milestones	Status
December 2019	Synthesize a series of POSS-containing block copolymer electrolytes for electrochemical studies.	Completed
March 2020	Create impurity-free lithium layers	Completed
June 2020	Complete electrochemical characterization of POSS-containing block copolymer electrolytes	On track
September 2020	Provide cycling data for at least two POSS-containing block copolymer electrolytes.	On track

Approach

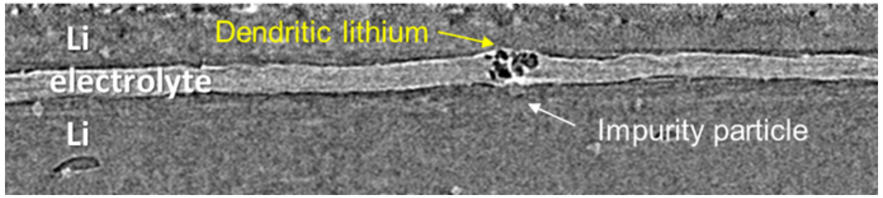
1. **Synthesize** hybrid copolymer electrolytes by incorporating monomers that contain an inorganic component and mixing with lithium salt
2. **Characterize** the electrochemical and mechanical properties
3. **Visualize** failure mode and dendrite growth using X-ray tomography



Synthesis



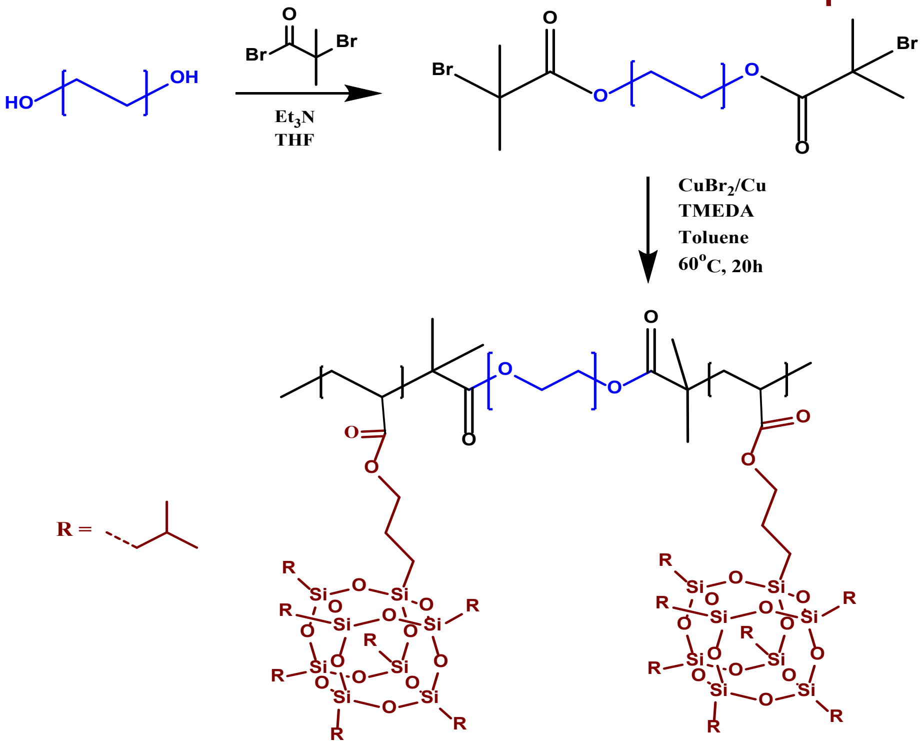
Electrochemical characterization



Visualization of dendrite short

Accomplishment: Synthesis of hybrid copolymer electrolytes

Polyhedral oligomeric silsesquioxane-b-Poly(ethylene oxide) -b- Polyhedral oligomeric silsesquioxane (POSS-PEO-POSS)



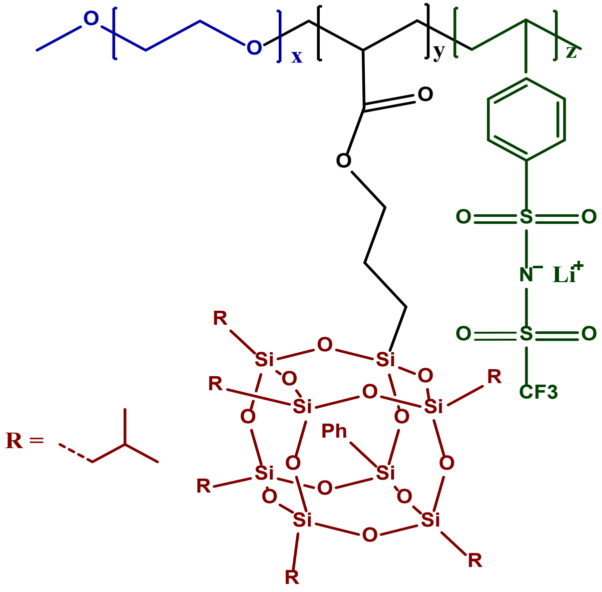
Synthesis schematic

Synthesized PEO-POSS and POSS-PEO-POSS copolymers

PEO-POSS	POSS units	M_{PEO} (kg mol^{-1})	M_{POSS} (kg mol^{-1})
5-2	2	5	1.9
10-4	4	10	3.7
2-10-2	4	10	3.7
5-35-5	10	35	9.2

- **We have synthesized a library of hybrid organic-inorganic copolymers for this study**
- **Electrolytes with salt concentrations 0.02< [Li]/[EO] < 0.30 will be prepared by mixing copolymers with lithium salt**

Accomplishment: Synthesis of single-ion conducting hybrid copolymer electrolytes



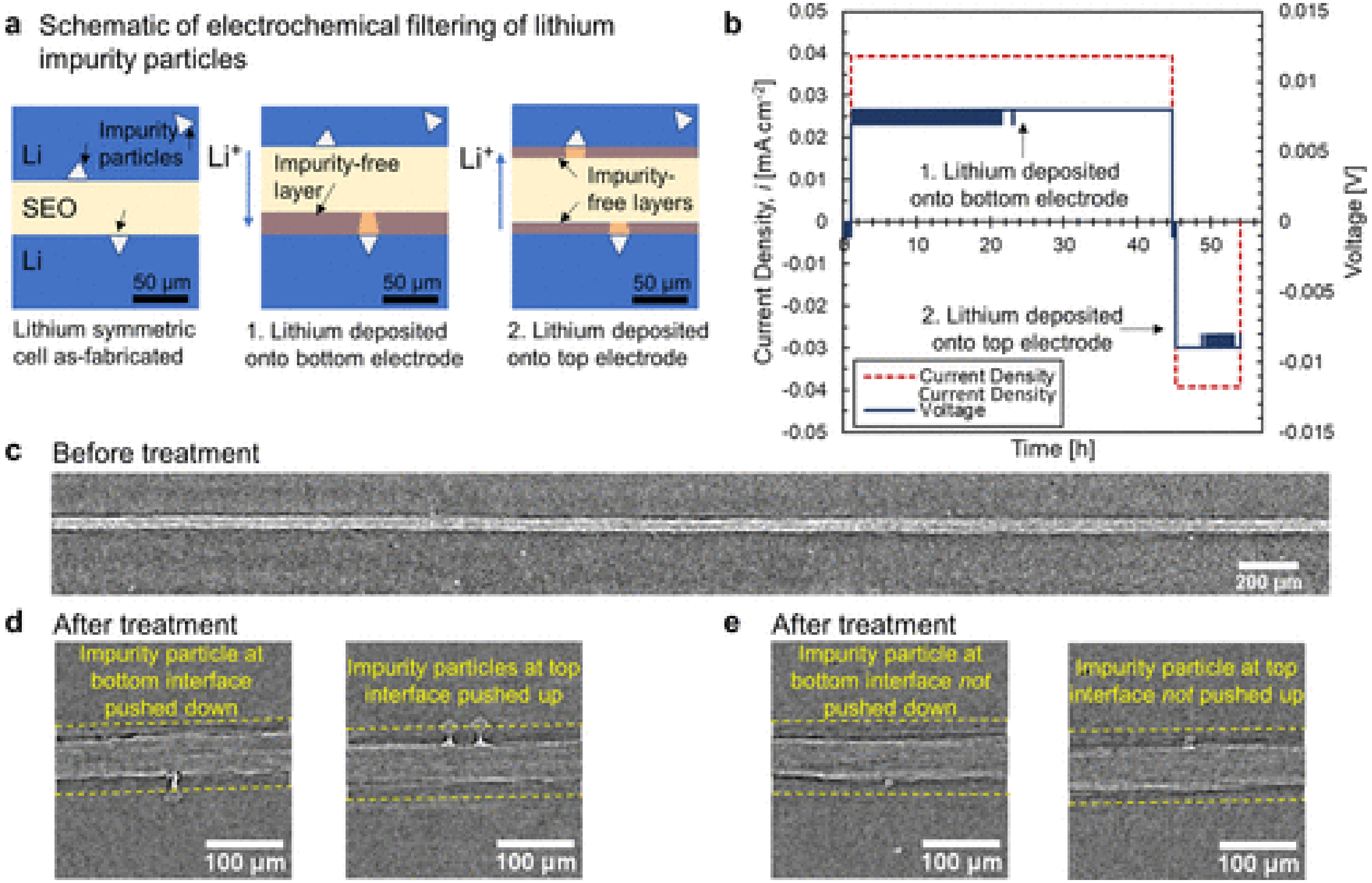
Single-ion conductor structure

Synthesized single-ion conductor polymers

PEO-POSS-PSTFSILi	M_{PEO} (kg mol^{-1})	M_{POSS} (kg mol^{-1})	$M_{PSTFSILi}$ (kg mol^{-1})	[Li]/[EO]
5-2-1	5	1.9	1	0.035
5-2-2	5	1.9	2	0.055
5-2-4	5	1.9	4	0.1
5-2-6	5	1.9	6	0.17
5-2-11	5	1.9	11	0.31

- **We have synthesized a library of hybrid organic-inorganic single-ion conducting copolymers**
- **Salt concentrations range: 0.035 < [Li]/[EO] < 0.31**

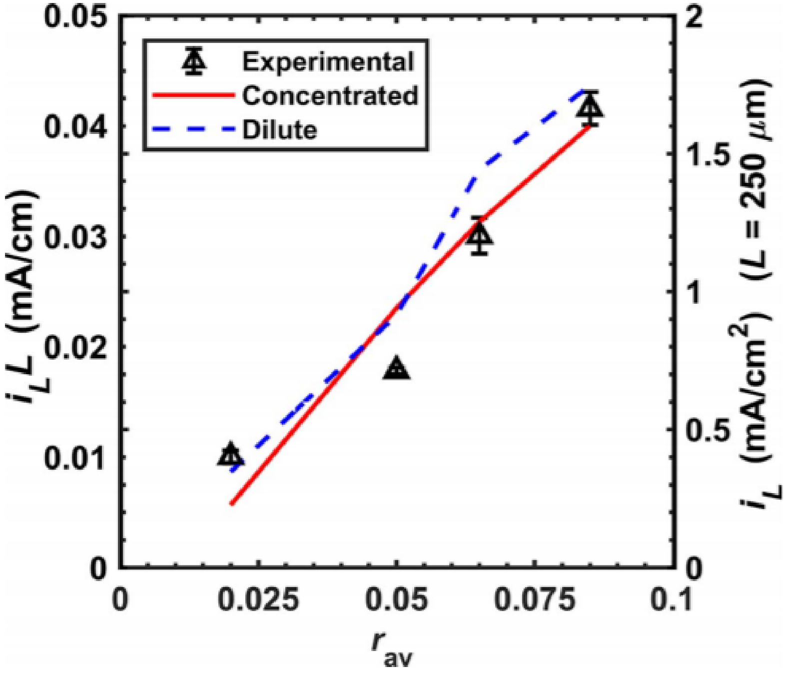
Accomplishment: Reducing impurities in lithium metal electrodes enabling extended cycling

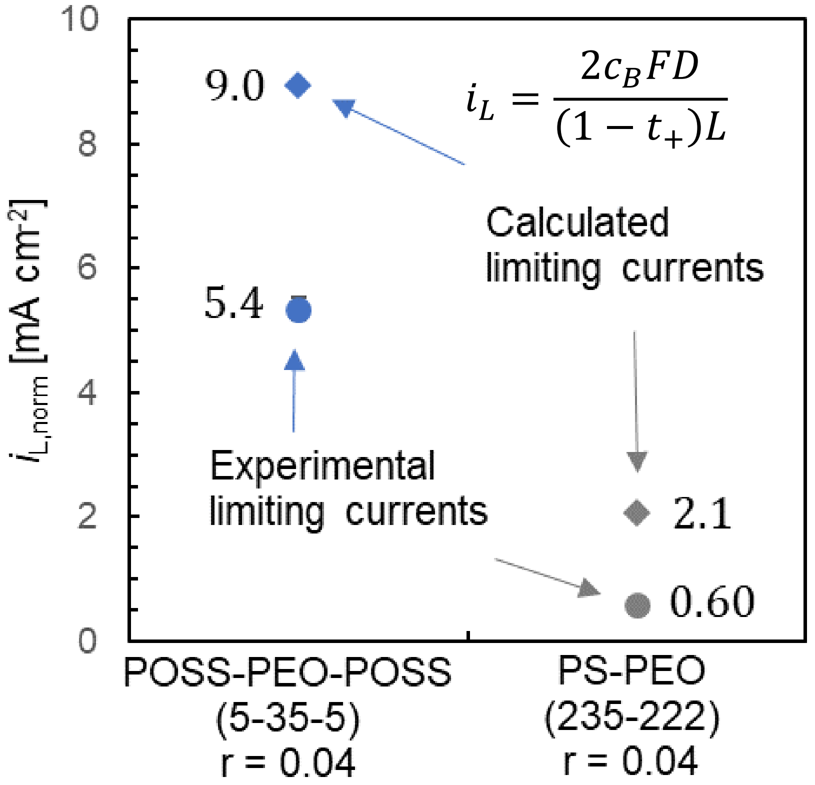


- ❑ **Stable deposition is obtained at by cycling at low current density (0.04 mA cm^{-2})**
- ❑ **This method will be used to pre-treat lithium cells to extend cycle life at high current density.**

Maslyn, J. A., Frenck, L., Loo, W. S., Parkinson, D. Y., & Balsara, N. P. "Extended Cycling through Rigid Block Copolymer Electrolytes Enabled by Reducing Impurities in Lithium Metal Electrodes." *ACS Applied Energy Materials* 2.11 (2019): 8197-8206.

Accomplishment: Limiting current of POSS-PEO-POSS electrolytes





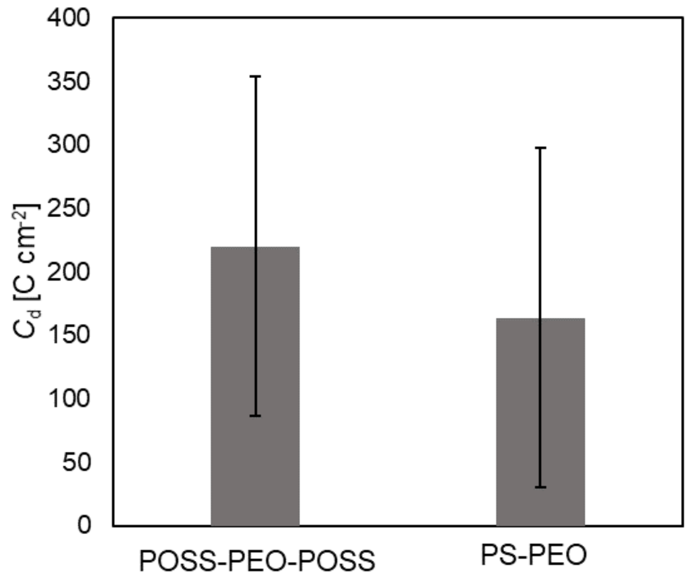
	POSS-PEO-POSS	PS-PEO
$\phi_{EO, neat}$	0.81	0.48
D [cm²/s]	9.42E-8	2.31E-8
$t_{+,SS}$	0.117	0.0628
morphology	lamellar	lamellar

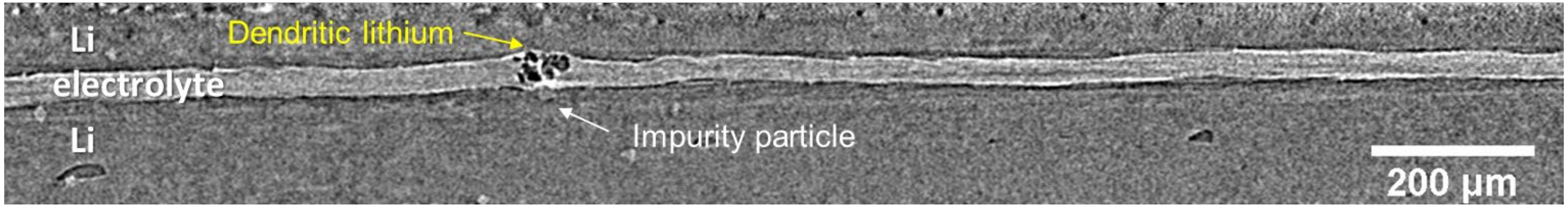
- **The theoretical limiting current can be accurately determined using dilute or concentrated solution theory**
- **The POSS-PEO-POSS hybrid triblock electrolyte show higher limiting current compared to PS-PEO due to favorable transport properties.**

Gribble, D. A., Frenck L., Shah, D. B., Maslyn, J. A., Loo, W. S., Mongcopa, K. I. S., Pesko, D. M., & Balsara, N. P. .(2019). Comparing Experimental Measurements of Limiting Current in Polymer Electrolytes with Theoretical Predictions. *Journal of the Electrochemical Society*, *166*(14), A3228-A3234.

Accomplishment: Cycling characteristics of PEO-POSS electrolytes

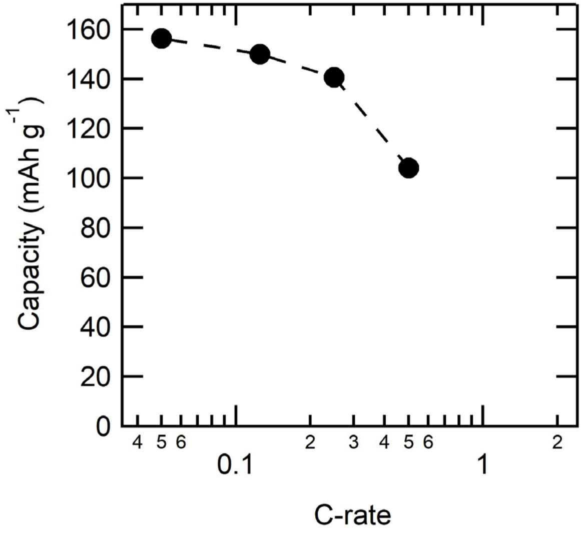
	POSS-PEO-POSS	PS-PEO
$\phi_{EO,\ neat}$	0.81	0.48
D [cm^2/s]	9.42E-8	2.31E-8
$t_{+,SS}$	0.117	0.0628
morphology	lamellar	lamellar

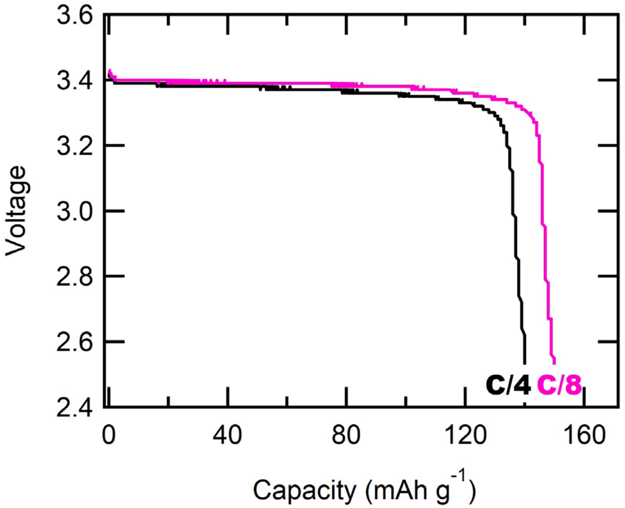


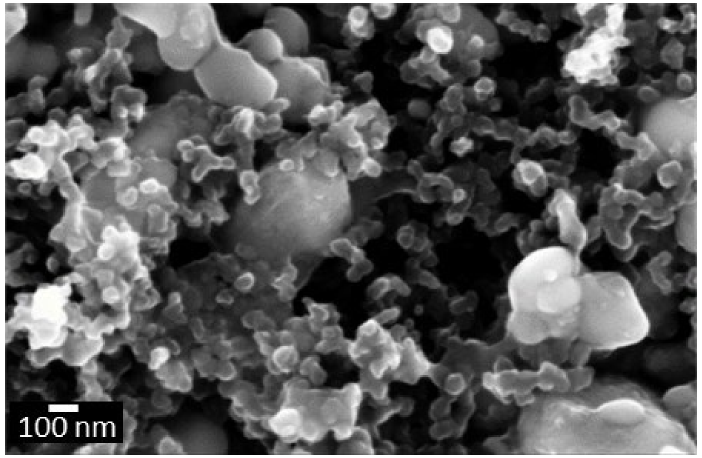


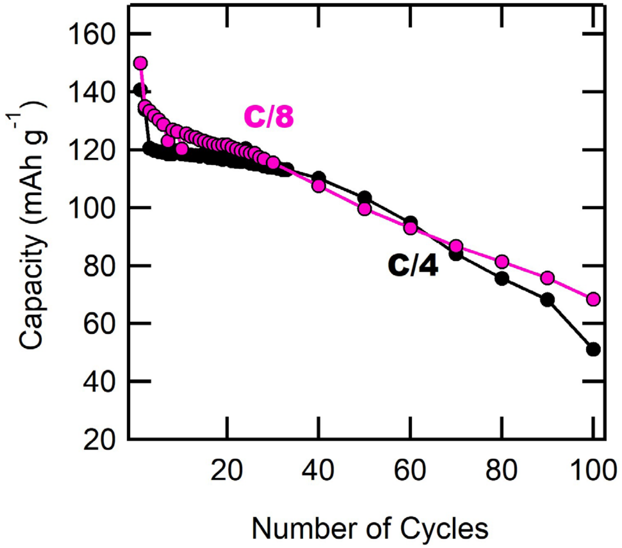
- ❑ **Despite the much higher molecular weight and lower conducting phase volume fraction of the all-organic (PS-PEO) electrolyte, the cycle life is improved in the hybrid organic-inorganic electrolyte (POSS-PEO-POSS)**
- ❑ **Failure mode is due to impurities in the lithium metal. Removal of impurities will likely to improve cycling performance.**

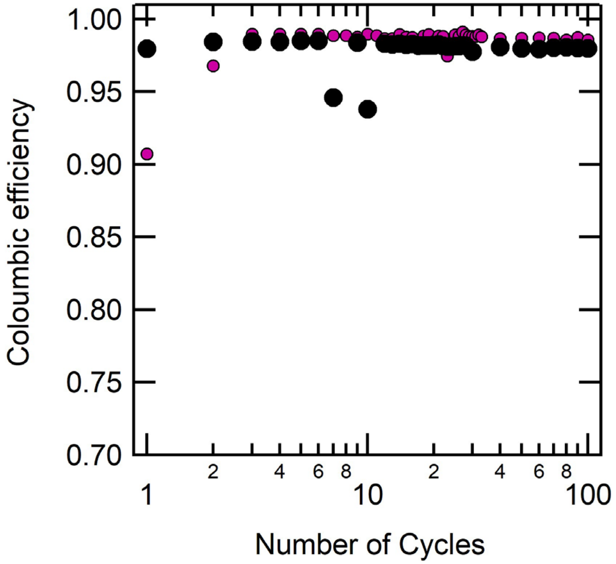
Accomplishment: Cycling full cells containing POSS-PEO-POSS electrolytes











- ❑ Full electrochemical cells are prepared with $LiFePO_4$/carbon/POSS-PEO-POSS/LiTFSI cathodes and lithium metal anodes
- ❑ Though capacity fade is high, coulombic efficiency remains close to 0.98 for 100 cycles

Response to Reviewers' Comments

Comment 1: *The reviewer said that a composite electrolyte is a good way to go for the achievement of Li-metal anodes in solid electrolytes. The project is well-designed and feasible.*

Response: We thank the reviewer for acknowledging the significance and design of this project.

Comment 2: *The reviewer said that the work approach is a very nice balance of synthesis of new materials, advanced characterization including microscopy and spectroscopy (e.g., NMR and impedance spectroscopy), and a reasonable theoretical component. The reviewer pointed out that by focusing the approach on a couple of key aspects of understanding the nature and dynamics of the solid-solid Li metal/solid polymer electrolyte interface, the project design is efficient and likely to produce the most significant results. Indeed, in the first half of the 1-year project, there have been few if any problems or limitations with the basic approach, and a series of significant results has been obtained in a short period of time. The reviewer said that the only "complaint" is that some initial full cell testing would have been helpful to include to get an early indication if Li-Li metal cycling really is a good model system for understanding the nature of the Li dendrite issue with polymeric solid-state electrolytes (SSEs) like the one developed in this project.*

Response: We thank the reviewer for complimenting the progress of the project to date. We agree that full cell performance is important, and have begun this task as shown on slide 10.

Comment 3: *The reviewer noted that the approach is to develop new ceramic-polymer composite electrolytes to enable Li metal anodes, to identify failure modes at Li-metal anodes using synchrotron hard X-ray tomography, and to study the Li-metal/electrolyte interface by spectroscopy and impedance*.

Response: We agree with this reviewer's summary of the project.

Collaboration and Coordination with Other Institutions

- Venkat Srinivasan (ANL)
  - Collaborator
  - National Laboratory
  - Within VTO
  - Modeling of lithium dendrite growth
- Bryan McCloskey (UCB/LBNL)
  - Collaborator
  - University, National Laboratory
  - Within VTO
  - Electrolyte electrochemical characterization

Remaining challenges and barriers

- Determining all of the factors that lead to localization of current at the dendrite tip on a lithium electrode.
- Can impurity-free lithium electrodes improve cycling?
- Designing soft materials that will enable hitting the DOE target of 1 mS/cm.
- What can we say about the behavior of Li metal electrodes in full cells based on what we learn from Li/Li symmetric cells?

Proposed future research

- Combining theoretical limiting current, limiting current measurements, nonlinear viscoelastic measurements, and complete electrochemical characterization to determine current distribution during lithium dendrite growth
- Compare experiments with calculations based on the full Newman model
- Improve methodologies to purify lithium
- Study the cycling characteristics of purified lithium electrodes in optimized hybrid electrolytes
- Continue to work on polymer-based composites to reach the DOE target of 1 mS/cm and improve all transport properties
- Begin work on understanding lithium dendrite formation in full cells

Any proposed future work is subject to change based on funding levels.

Summary

- Synthesized a new class of hybrid organic-inorganic composite polymer electrolytes and single-ion conducting electrolytes
- Working toward complete characterization of electrical, mechanical, and morphological properties of PEO-POSS electrolytes.
- Successfully removed impurities from lithium metal anodes to enable extended cycling
- Direct identification of failure modes in composite electrolytes by electrochemical methods and X-ray microtomography.
- Exploring the relationship between limiting current, cell lifetime and dendrite growth.

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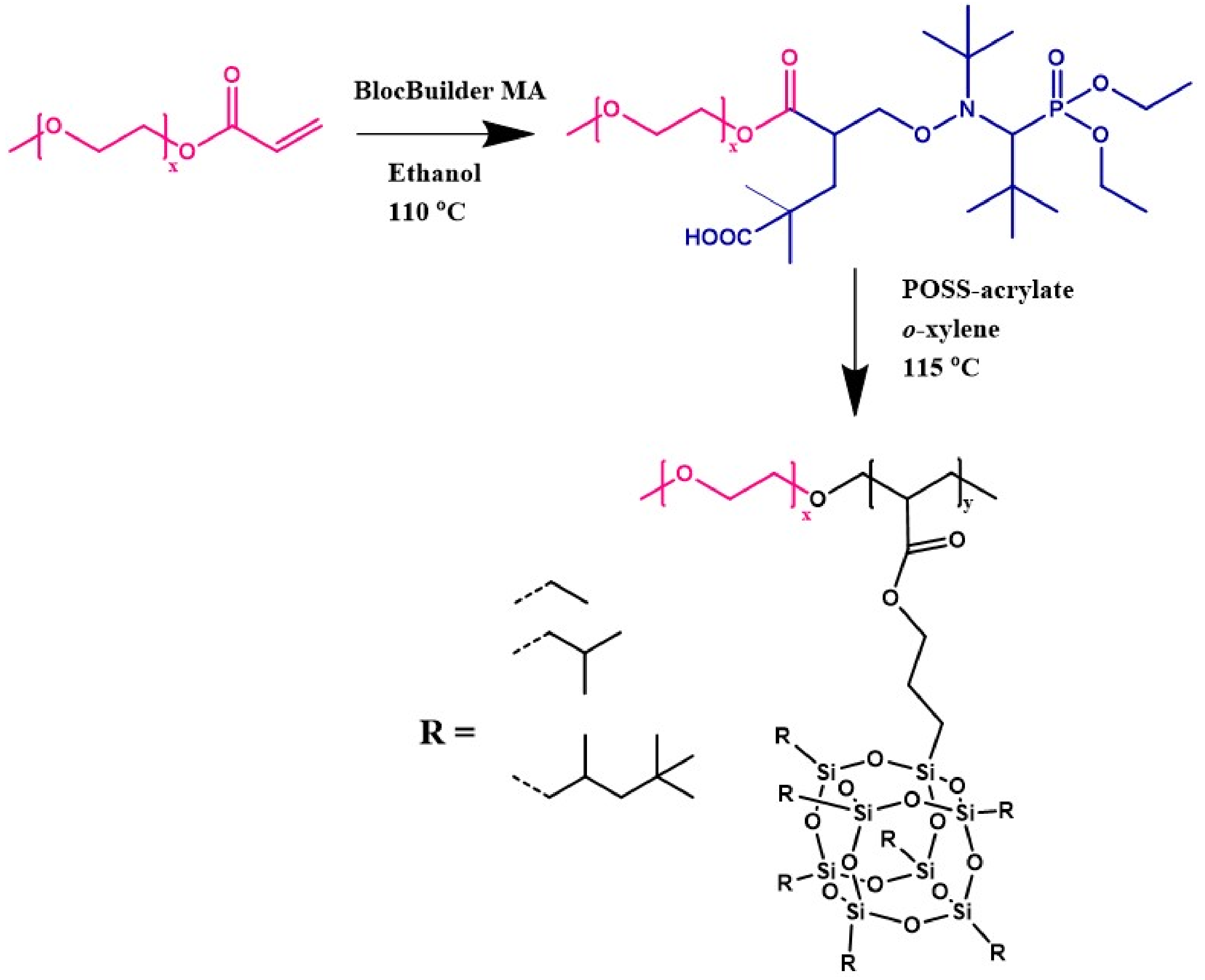
Technical Back-up Slides

Synthesis of PEO-POSS diblock copolymer electrolytes



G.K. Sethi, H.Y. Jung, W.S. Loo, S. Sawhney, M.J. Park, N.P. Balsara, and I. Villaluenga, accepted, ***Macromolecules*, 2019**.