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, 2020
- End Date: Sept. 2021
- Percent complete: 70%

Budget
- Total budget: $623
- FY20 funding: $410
- FY21 funding: $217

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

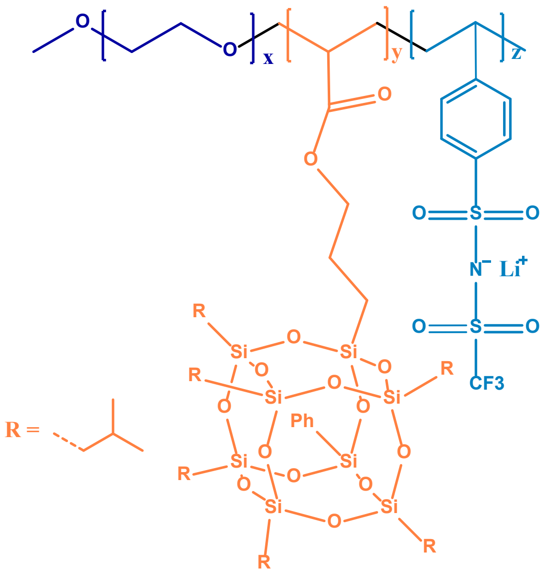
- Design and synthesis of POSS containing hybrid organic-inorganic single ion conductors.
- Develop the relationship between non-linear mechanical properties and ion transport in block copolymer electrolyte.
- Conduct in situ X-ray scattering experiments on Li symmetric cells to quantify polymer morphology in the presence of an applied field.
- Conduct X-ray tomography experiments on Li-polymer-Li symmetric cells to quantify dendrite growth

Milestones

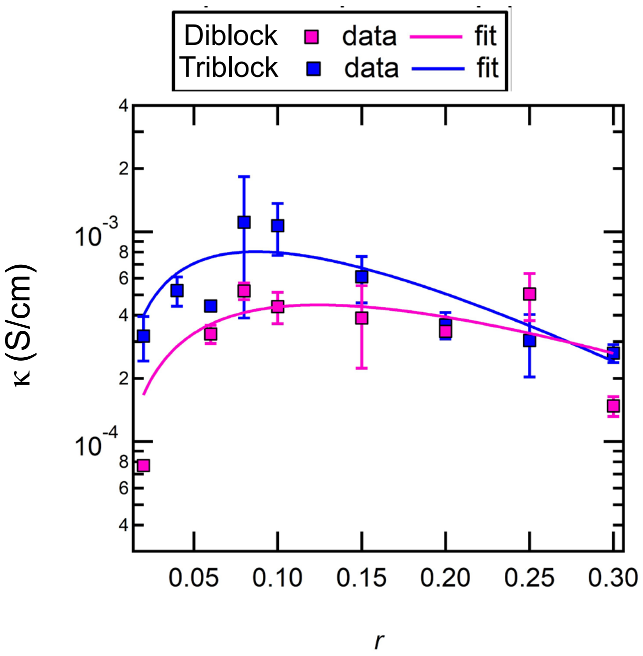
Date	Milestones	Status
December 2020	Synthesize at least 2 POSS-containing single ion conductors (SICs).	Completed
March 2021	Develop the relationship between non-linear mechanical properties and ion transport in solid block copolymer electrolytes	Completed
June 2021	Conduct in situ X-ray scattering experiments on Li-polymer-Li symmetric cells to quantify polymer morphology in the presence of an applied field	On track
September 2021	Conduct XRT experiments on Li-polymer-Li symmetric cells to quantify dendrite growth in block copolymer electrolytes	On track

Approach

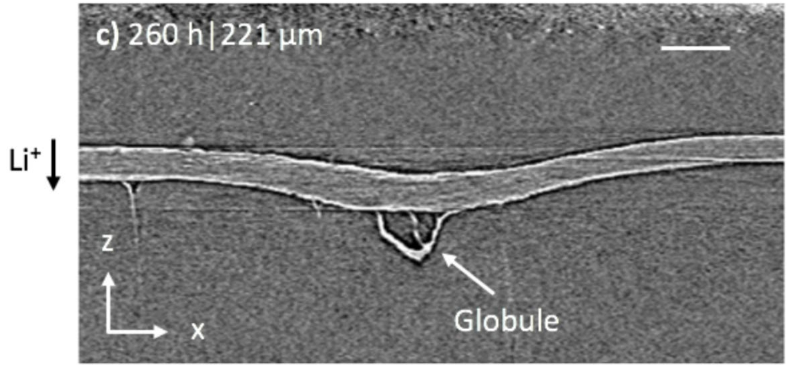
1. **Synthesize** hybrid copolymer single-ion electrolytes by incorporating monomers that contain covalently bonded salt and an inorganic component
2. **Characterize** the electrochemical morphological and mechanical properties of the block copolymer
3. **Visualize** the cell failure and dendrite growth using X-ray tomography



Synthesis



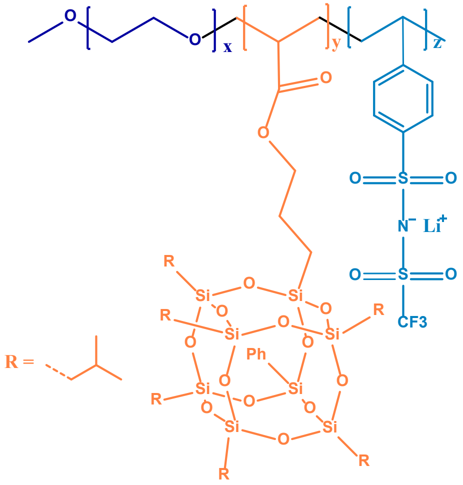
Electrochemical characterization

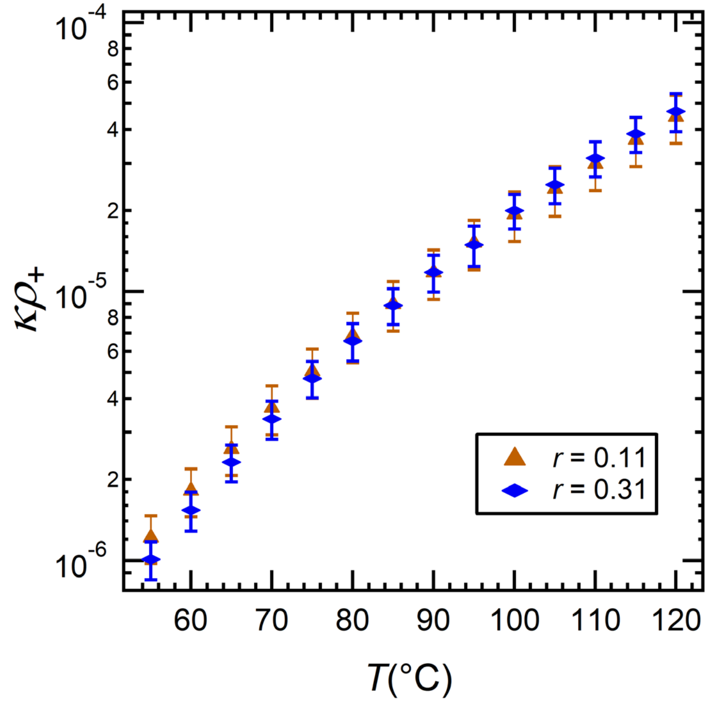


Visualization of the dendrite growth via X-ray tomography

Accomplishment: Synthesis and electrochemical study of single ion conducting hybrid copolymer electrolytes (SIC)

Poly(ethylene oxide) -b- Polyhedral oligomeric silsesquioxane -r- (trifluoromethane) sulfonimide stryrene





PEO-POSS-PSTFSILi	M_{PEO} (kg mol^{-1})	M_{POSS} (kg mol^{-1})	$M_{PSTFSILi}$ (kg mol^{-1})	*r*
5-2-4	5	1.9	4	0.11
5-2-11	5	1.9	11	0.31

- ❑ **All the electrolytes exhibit conductivity in the order of 10^{-5} S/cm at 90 °C**
- ❑ **The current fraction of r = 0.11 and 0.31 SIC was 0.963 ± 0.04 and 0.96 ± 0.04 respectively**

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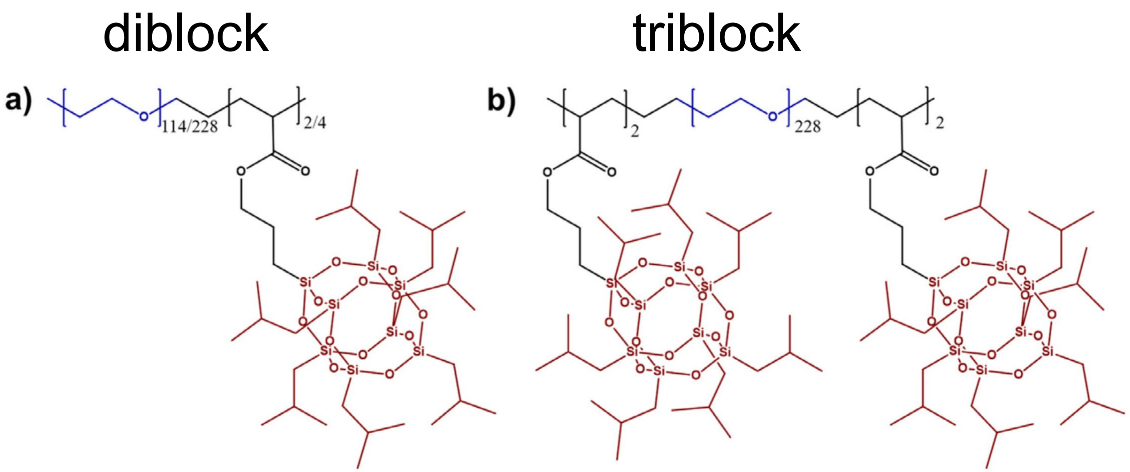
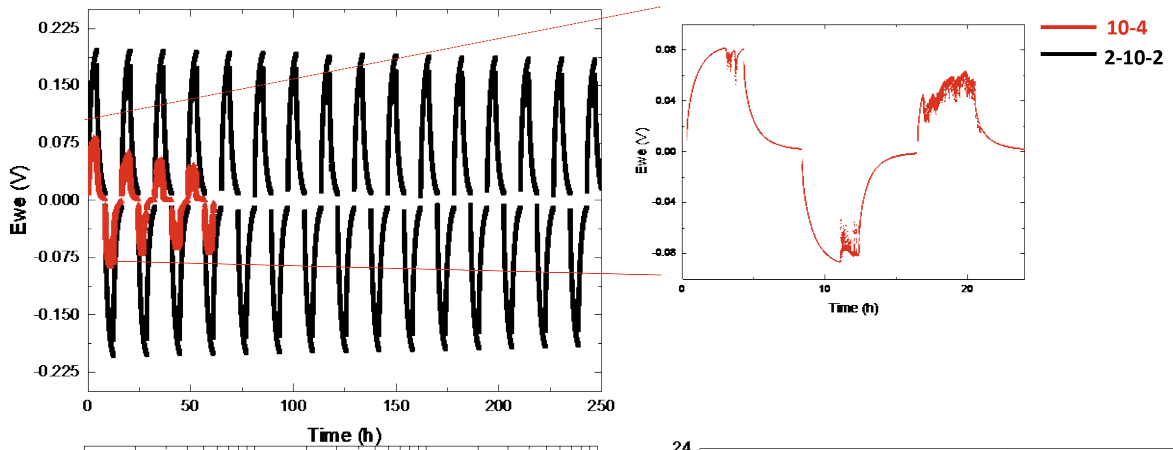
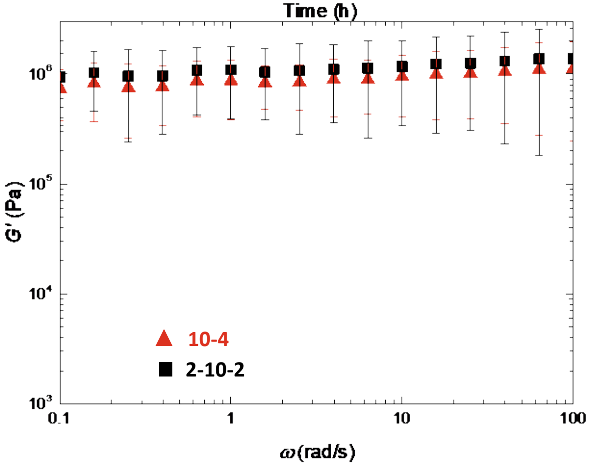
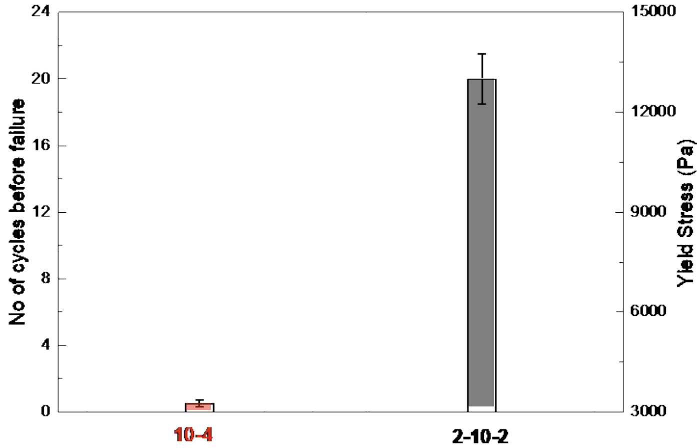
Accomplishment: Relationship between yield strength and dendrite resistance in polymer electrolytes



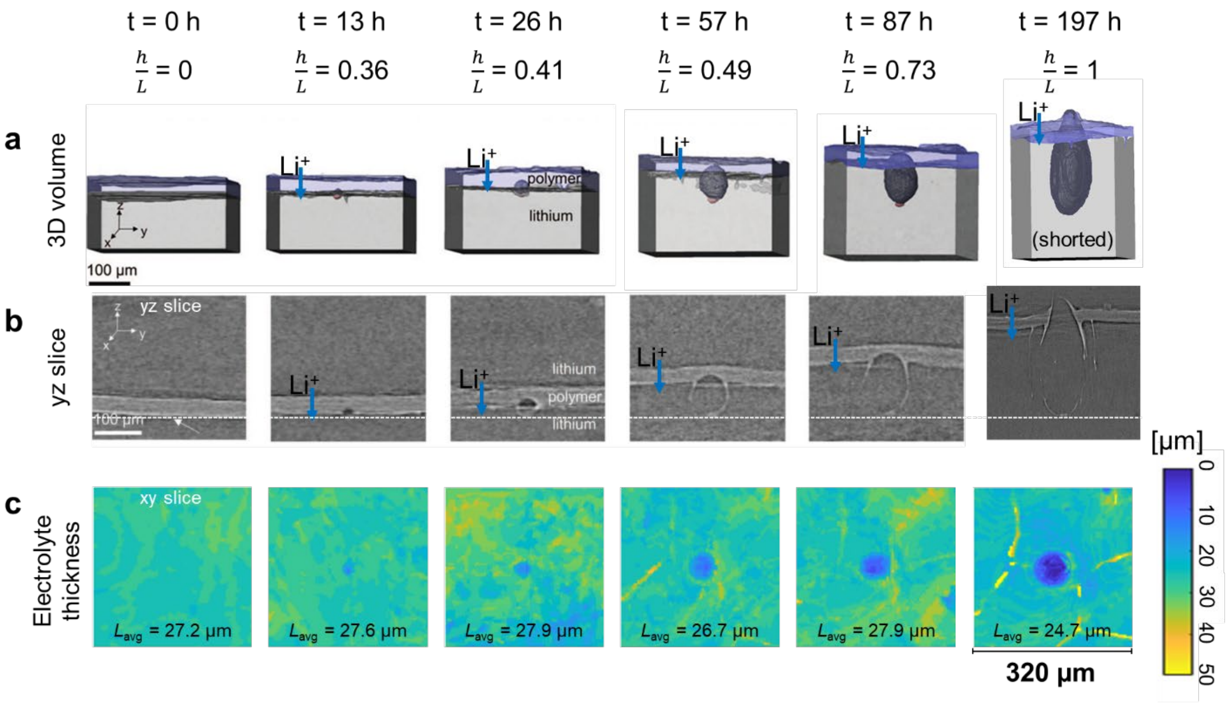


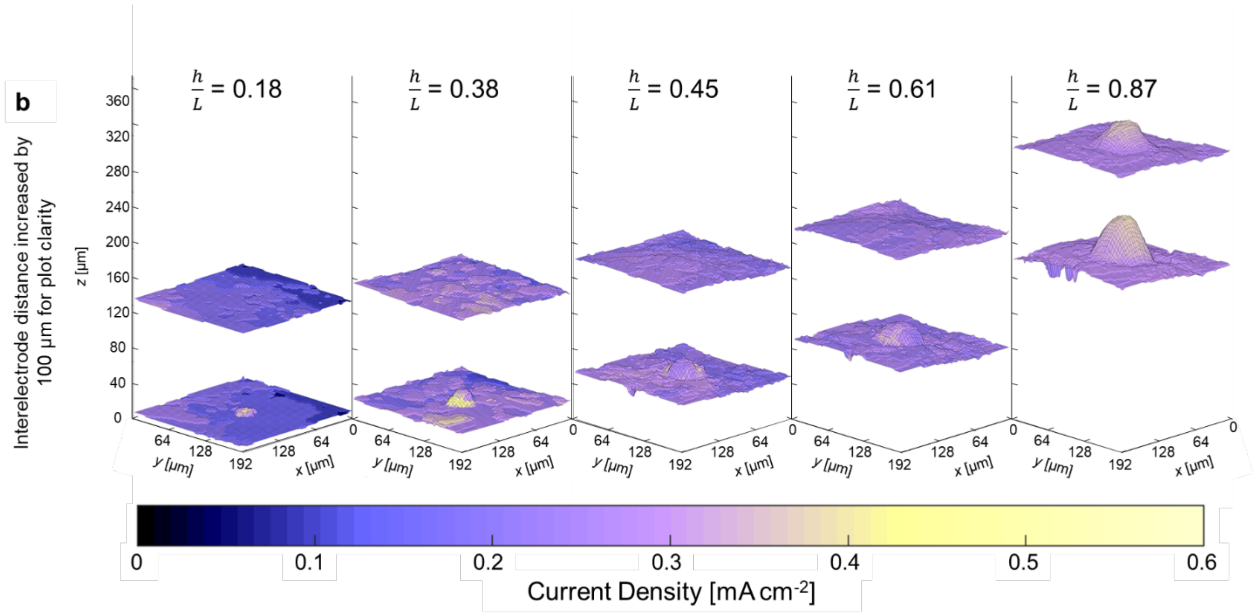




- **Two block copolymer electrolytes with the same modulus but very different yield strengths were cycled in symmetric lithium-lithium cells.**
- **Cycle life correlated with yield strength, not shear modulus; many theories suggest that modulus is the most important mechanical property for preventing dendrite growth.**

Accomplishment: X-ray tomography shows plastic deformation dominates lithium protrusion growth

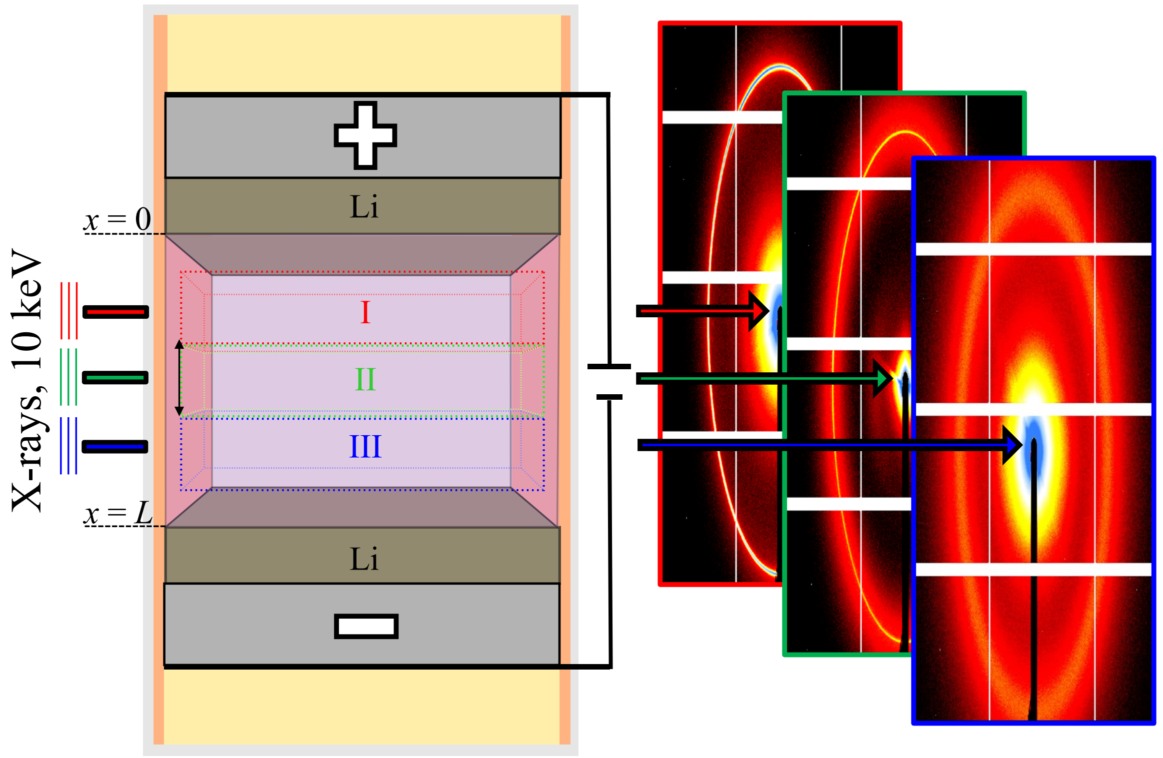


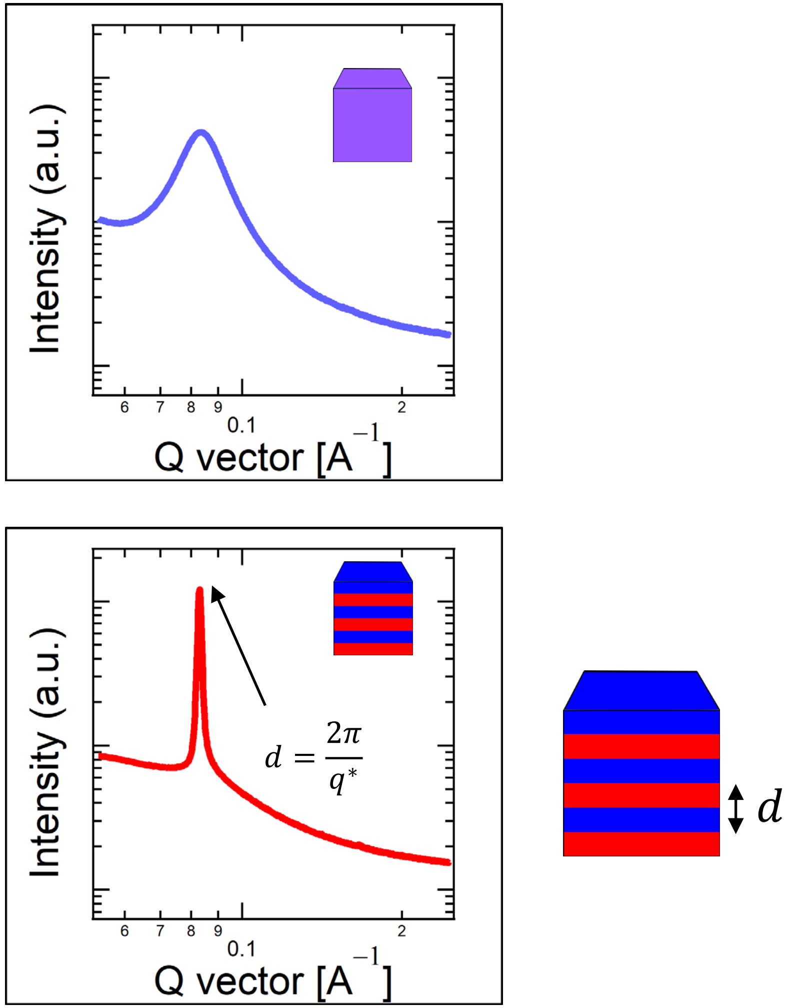


- ❑ **Images of the Li-polymer interfaces and local current density in 3D were obtained using X-ray tomography.**

- ❑ **Combining experiments with modeling, we show that plastic deformation of the electrode and electrolyte influences the evolution of mechanical stress reaction current density.**

Accomplishment: Custom designed cell for monitoring structure of PS-b-PEO electrolyte during polarization using X-ray scattering





- **Electrolyte was placed between Li electrodes in the custom designed cell**
- **Morphology was studied along the cell thickness using X-ray scattering**

Galluzzo, M. D. et al. *ACS Appl. Mater. Interfaces* 2020.

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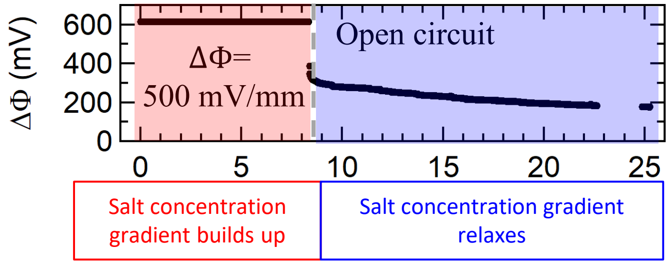
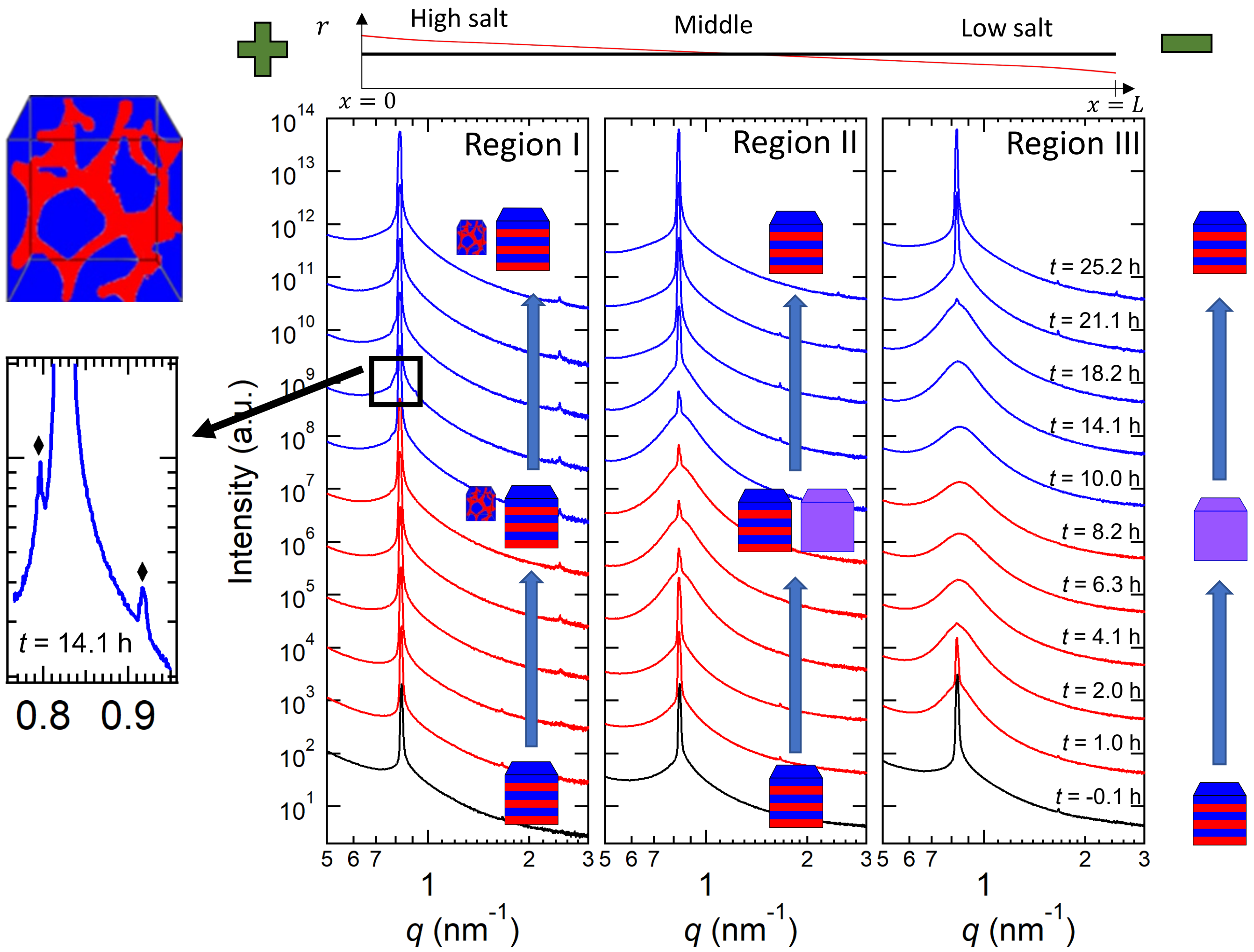
Accomplishment: Simultaneous electrochemical and SAXS experiments to understand mechanisms of ion transport

Experiment: **Apply a constant potential for 8.3 h, then switch the cell to open circuit**



- **On polarizing the electrolytes, concentration gradient develops**
- **This leads to change in polymer morphology along the cell –new phases not present in the unpolarized cell form when current flows.**



Response to Reviewers' Comments

This program was not reviewed in 2020.

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 the essential factors that lead to localization of current at the dendrite tip on a lithium electrode.
- Designing new polymer electrolytes to mitigate the effects of localized current density.
- Develop robust in situ methods for studying changes in the electrolyte structure under high current density conditions.
- Designing soft materials that will enable hitting the DOE target of 1 mS/cm and a transference number above 0.5.

Proposed future research

- Combining theoretical limiting current, limiting current measurements, nonlinear viscoelastic measurements, and complete electrochemical characterization to determine current distribution during dendrite growth.

- Understanding the effect of block copolymer composition and morphology on the limiting current measurement.

- Design new ion-conducting polymer electrolytes with improved conductivity, transference, and electrochemical stability at different potentials.

- Continue to work on polymer electrolytes to reach the DOE target of 1 mS/cm and improve all transport properties

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

Summary

- Synthesized new single ion organic inorganic hybrid block copolymer and determined electrochemical properties.
- New understanding the relationship between mechanical properties, particularly yield strength, and dendrite growth.
- Identified mechanism of protrusion growth in block copolymer electrolytes by electrochemical methods and X-ray microtomography.
- Visualized salt concentration gradients and morphological changes in polymer electrolyte by X-ray scattering.

Publications and presentations (FY20-21)

Publications

- Galluzzo, M. D.; Loo, W. S.; Wang, A. A.; Walton, A.; Maslyn J.A.; Balsara, N.P. "Measurement of Three Transport Coefficients and the Thermodynamic Factor in Block Copolymer Electrolytes with Different Morphologies" *J. Phys. Chem. B* **2020**, *124*, 5, 921
- Didier, D.; Villaluenga, I.; Jiang, X.; Chang, Y. H.; Parkinson, D. Y.; Balsara, N. P. "Lithium-Sulfur Batteries with a Block Copolymer Electrolyte Analyzed by X-ray Microtomography". *Journal of The Electrochemical Society* **2020**, *167*, 060506.
- Chakraborty, S.; Jiang, X.; Hoffman, Z. J.; Sethi, G. K.; Zhu, C.; Villaluenga, I.; Balsara, N. P. "Reversible Changes in the Grain Structure and Conductivity in a Block Copolymer Electrolyte" *Macromolecules*, **2020**, *53*, 5455
- Galluzzo, M.D.; Loo, W. S.; Zhu, C.; Schaible, E.; Balsara, N. P. "Dynamic Structure and Phase Behavior of a Block Copolymer Electrolyte under dc Polarization" *ACS Appl Mater & Inter*, **2020**, *12*, 57421
- Maslyn J, A.; McEntush K.D.; Harry, K.J.; Frenck, L.; Loo, W. S.; Parkinson D. W.; Balsara, N. P. Preferential Stripping of a Lithium Protrusion Resulting in Recovery of a Planar Electrode" *J. Electrochem. Soc*. **2020**, *167* 100553

Presentations

- Galluzzo, M.D. and Balsara, N.P., "Predicting Electrolyte Performance in Lithium Metal Batteries at Low and High Current Densities". In PRiME **2020** (ECS, ECSJ, & KECS Joint Meeting). ECS.

Critical assumptions and issues

- Creating dry electrolytes that are compliant is essential for enabling lithium metal anodes.
  - We aim to experimentally determine all of the relevant properties: conductivity, current fraction, transference number, diffusion coefficient, thermodynamic factor, limiting current, linear and non-linear rheological properties, and impurity effects.
- The full electrochemical and mechanical characterization can reveal molecular underpinnings of cell failure
  - We will quantify lithium dendritic growth using X-ray tomography experiments
- A systematic study of the incorporation of inorganic moieties in polymers is promising to improve cycle-life and safety of lithium metal based batteries.
  - We will explore different chemical compositions and single-ion conducting electrolytes to improve transport properties of compliant electrolytes.