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

Nitash P. Balsara, Principal Investigator
Lawrence Berkeley National Laboratory
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Project ID: bat389

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Overview

Timeline
• Start Date: Oct. 1, 2020
• End Date: Sept. 2021
• Percent complete: 70%

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

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

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

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

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**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 styrrene

![Chemical Structure]

<table>
<thead>
<tr>
<th>PEO-POSS-PSTFSILi</th>
<th>$M_{PEO}$ (kg mol⁻¹)</th>
<th>$M_{POSS}$ (kg mol⁻¹)</th>
<th>$M_{PSTFSILi}$ (kg mol⁻¹)</th>
<th>$r$</th>
</tr>
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<tbody>
<tr>
<td>5-2-4</td>
<td>5</td>
<td>1.9</td>
<td>4</td>
<td>0.11</td>
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<tr>
<td>5-2-11</td>
<td>5</td>
<td>1.9</td>
<td>11</td>
<td>0.31</td>
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</table>

- 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 $0.963 \pm 0.04$ and $0.96 \pm 0.04$ respectively
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

\[ d = \frac{2\pi}{q^*} \]
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.
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
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**

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.

**Presentations**
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.