Overview

Timeline
• Project start: Oct 1 2013
• Project end: Sept 30 2017
• Percent complete: 60%

Barriers
• Barriers addressed
  – Energy density
  – Cycle life

Budget
• Total project funding
  – DOE share ($ 2,000,000)
  – Contractor share ($ 0)
• Funding FY14: $500,000
• Funding FY15: $500,000

Partners
• ALS, SSRL, Molecular Foundry, NRSC
• Lead Institution: LBNL
Relevance and Objectives

Project Objective: To provide a fundamental science-based understanding of the products of redox reaction products (polysulfides) in a sulfur cathode, and enable rational design strategies to exploit the high energy density of lithium-sulfur cells.

FY15 Objectives: Elucidate thermodynamics of disproportionation using theoretical calculations coupled to ex situ XAS experiments. Build and cycle full cells for in situ XAS data acquisition and to study degradation mechanisms.

- Simulated X-ray Absorption Spectroscopy (XAS): Complete free energy calculations for polysulfide dianions and radical anions.
- In situ Cell for Measurement of XAS Spectra: Perform in situ measurements of XAS spectra of a Li-S cell.
- Mechanistic Insight: Compare simulations and experiments to obtain mechanistic insight into the redox chemistry of sulfur.
- Cathode and Cell Design: Build full all-solid Li-S cells with strategies for stabilizing the sulfur cathode.
## Milestones

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone or Go/No-Go</th>
<th>Description</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feb. 15, 2015</td>
<td>milestone</td>
<td>Experimental study of the effect of polysulfide concentration on XAS spectra</td>
<td>completed</td>
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<tr>
<td>May 20, 2015</td>
<td>milestone</td>
<td>Quantitative comparison of experimental and theoretical XAS spectra</td>
<td>completed</td>
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<tr>
<td>Aug. 23, 2015</td>
<td>milestone</td>
<td>Build and test cell for <em>in situ</em> XAS analysis.</td>
<td>completed</td>
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</table>
## Milestones

<table>
<thead>
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<th>Milestone or Go/No-Go</th>
<th>Description</th>
<th>Status</th>
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<tbody>
<tr>
<td>Dec, 15, 2015</td>
<td>milestone</td>
<td>Study radical anion formation in DMF and PEO by theory and experiment</td>
<td>completed</td>
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<tr>
<td>May 20, 2016</td>
<td>milestone</td>
<td>Perform in situ XAS tests of Li-S charge/discharge.</td>
<td>on track</td>
</tr>
<tr>
<td>Aug 23, 2016</td>
<td>milestone</td>
<td>First study of cycling behavior of all-solid Li-S cells</td>
<td>on track</td>
</tr>
</tbody>
</table>
Approach

• First implementation of a first-principles framework for understanding products in sulfur cathodes.

• Calculation of X-ray spectra of polysulfides based on molecular dynamics simulations and eXcited electron and Core Hole (XCH) method.

• Conduct complementary X-ray spectroscopy experiments to obtain molecular insight into the nature of polysulfide speciation and their fingerprints.

• Design lithium-sulfur cells with PEO electrolytes for enabling \textit{in situ} study of redox reactions at the sulfur cathode.

• Build lithium-sulfur cells that enable determination of capacity fade mechanisms and use this knowledge to build more stable sulfur cathodes.
Technical Accomplishment: Elucidated polysulfide radical presence in TEGDME

- UV-vis spectroscopy of TEGDME lithium polysulfide solutions ($\text{Li}_2\text{S}_{\text{mix}}$ is the overall stoichiometry of the lithium polysulfide)

- Peak at 617 nm indicative of radical species
Technical Accomplishment: Confirmed presence of radical species in TEGDME and PEO using EPR spectroscopy

- Electron paramagnetic resonance (EPR) spectroscopy of TEGDME polysulfide solutions
- EPR confirms presence of radical species in ether-based electrolytes
Technical Accomplishment: Thermodynamic modeling of radical formation

\[ \text{Li}_2\text{S}_x \rightarrow \text{LiS}_a + \text{LiS}_{a-x} \]

Take away: Disproportionation thermodynamics in diglyme (DGM) and dimethylformamide (DMF)
### Technical Accomplishment: Compared radical concentration in TEGDME versus DMF

<table>
<thead>
<tr>
<th>$\text{Li}<em>2\text{S}</em>{\text{xmix}}$</th>
<th>‘S’ concentration (mM)</th>
<th>Radical concentration (mM)</th>
<th>DMF</th>
<th>TEGDME</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10</td>
<td>0.61</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>0.91</td>
<td>0.06</td>
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<td>6</td>
<td>10</td>
<td>2.35</td>
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<tr>
<td>4</td>
<td>10</td>
<td>2.61</td>
<td>0.25</td>
<td></td>
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<tr>
<td>10</td>
<td>50</td>
<td>1.33</td>
<td>0.15</td>
<td></td>
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<tr>
<td>8</td>
<td>50</td>
<td>2.32</td>
<td>0.18</td>
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<tr>
<td>6</td>
<td></td>
<td>8.63</td>
<td>0.51</td>
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- Radical concentration obtained via Beer’s Law/UV-vis spectra

**Take away:** Radical concentration is an order of magnitude higher in DMF than TEGDME
Technical Accomplishment: Sulfur K-edge XAS used to probe DMF and TEGDME polysulfide solutions

Sulfur K-edge XAS of lithium polysulfides solutions

**DMF**

- **x = 6, DMF**
  - Radical species

**TEGDME**

- **x = 6, TEGDME**

**Take away:** Radical species are easily identifiable in chemically synthesized mixtures of polysulfides in DMF, but less noticeable in TEGDME.
Technical Accomplishment: Comparison of theoretical X-ray absorption spectra: DMF vs. diglyme (DGM)

Take away: More distinct features in DMF due to less structural fluctuations and electronic confinement

*XCH method: Prendergast and Galli, PRL, 96 215502, 2006
Technical Accomplishment: Calculated polysulfide stability in bulk electrolyte

$$Li_2S + \frac{(x - 1)}{8} S_8 + DGM \rightarrow Li_2S_{x(DGM)}$$

<table>
<thead>
<tr>
<th>Polysulfide</th>
<th>$\Delta G^*$ (kJ/mol)</th>
<th>Standard Deviation</th>
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<tr>
<td>s8</td>
<td>33.0</td>
<td>1.1</td>
</tr>
<tr>
<td>li2s2</td>
<td>67.2</td>
<td>1.3</td>
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<td>li2s3</td>
<td>54.3</td>
<td>1.2</td>
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<td>31.2</td>
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<td>li2s6</td>
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<td>li2s7</td>
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<td>li2s8</td>
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<tr>
<td>li2s</td>
<td>45.4</td>
<td>0.5</td>
</tr>
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**Take home:** Calculations confirm that longer chain polysulfides are more stable in the bulk.
Technical Accomplishment: Built modified Li-S cell to probe through anode side of Li-S cell

- Sulfur K-edge
- Advanced Light Source (ALS): beamline 9.3.1 and Stanford Synchrotron Radiation Lightsource (SSRL): beamline 4-3
- In situ: X-rays probed battery cathode during discharge
Rise of 2468-2469 eV XAS feature between 2.30-2.07 V suggests radical formation at early stage of discharge.
Technical Accomplishment: Built in situ XAS cell to directly probe cathode side of Li-S cell

1. Ultrathin Kapton film
2. O-ring
3. Spring
4. Stainless steel shim
5. Lithium metal
6. SEO/LiClO₄ electrolyte
7. Sulfur cathode
8. Aluminum mesh
Technical Accomplishment: Performed in situ XAS experiments to directly probe cathode during discharge

- Speciation of in situ XAS using theoretically calculated spectra now in progress
Technical Accomplishment: First All-Solid Li-S Cells Assembled

Carbon nanospheres impregnated with sulfur (C@S)

- **Anode**: Lithium metal
- **Electrolyte**: polystyrene-poly(ethylene oxide) (SEO) solid polymer electrolyte, LiTFSI
- **Sulfur Cathode**: Carbon black, Li2S8 or C@S x wt.% (x= 30, 50, 60), SEO/LiTFSI

**Take away**: Polysulfide shuttle not prevented by encapsulation
Technical Accomplishment: Battery failure mode analyzed by hard X-ray tomography

Active material
Li$_2$S$_8$

Typical C@S active material
C@S 50%

- **Anode**: Lithium metal
- **Electrolyte**: polystyrene-poly(ethylene oxide) (SEO) solid polymer electrolyte, LiTFSI
- **Sulfur Cathode**: Carbon black, Li2S8 or C@S x wt.% (x = 30, 50, 60), SEO/LiTFSI

**Take away**: Cell capacity fades mainly due to formation of an insulating layer on the Li metal anode, rather than degradation of the sulfur cathode. Need to protect the anode and improve confinement strategy.
Technical Accomplishment: Structure, thermodynamics, and spectroscopy of encapsulated sulfur in graphite electrodes

\[ \Delta XPS(S_8[\text{graphene}]-S_8[\text{xtal}]) = -0.3\text{eV} \]
\[ \Delta E(\text{peak}) = -0.5\text{ eV} \]

Sulfur in Carbon nanochannels

Take away: XAS can differentiate between surface and bulk sulfur species
Collaborators

- David Prendergast (Molecular Foundry, LBNL): Key co-PI on project in charge of theory and simulations. Advisor of post-doc BATT Program post-doc, Tod Pascal, Within VT program.
- Kevin Wujcik and Rita Wang: graduate students advised by PI. Within VT program.
- Ethan Crumlin (ALS): XAS measurements.
- Miquel Salmeron (Materials Sciences Division, LBNL): X-ray spectroscopy experiments. Outside VT program.
- Jeffrey Reimer (UC Berkeley): Electron paramagnetic resonance spectroscopy.
Remaining Challenges and Barriers

- Determine species formed during cycling at different C-rates and in different cell configurations.

- Simulations of polysulfides under electrochemical potential.

- Use fundamental knowledge to build a better lithium-sulfur battery.
Summary

- Elucidated the stability of radical polysulfide species in ether-based solvents using XAS, UV-vis, EPR, and theoretical calculations.
- Established our approach of using first-principles molecular dynamics simulations to determine charge distribution and X-ray absorption spectra of polysulfide species (radical anions and dianions).
- Used simulations and in situ experiments to determine species formed during first discharge.
- Begun studies on solid Li-S cells with sulfur confinement.
Future Work

- Continue *in situ* cell studies to determine reaction products as a function of C-rate.
- Design simulations to study electrochemical reactions in sulfur cathode.
- Use fundamental knowledge to build a lithium-sulfur cell with long cycle life and high energy density.