Fundamental Studies of Lithium-Sulfur Cell Chemistry

PI: Nitash Balsara

LBNL

June 17, 2014

Project ID # ESS224

Overview

Timeline

- Project start: Oct 1 2013
- Project end: Sept 30 2017
- Percent complete: 30%

Barriers

- Barriers addressed
  - Energy density
  - Cycle life

Budget

- Total project funding
  - DOE share ($ 2,000,000)
  - Contractor share ($ 0)
- Funding FY13: $500,000
- Funding FY14: $500,000

Partners

- ALS, SSRL, Molecular Foundry, NRSC
- Lead Institution: LBNL

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.

FY13 Objectives: Obtain first computer simulation results of polysulfides and establish experimental fingerprints of polysulfides.

- Simulated X-ray Absorption Spectroscopy (XAS): Complete the first first-principles simulations of XAS spectra of polysulfides based on molecular dynamics simulations.
- Experimental Measurement of XAS Spectra: Complete first measurements of XAS Spectra of polysulfides.
- Mechanistic Insight: Compare simulations and experiments to obtain mechanistic insight into the redox chemistry of sulfur.
- Cell Design: Design *in situ* cell for studying redox reactions in sulfur cathode if XAS is a viable characterization tool.

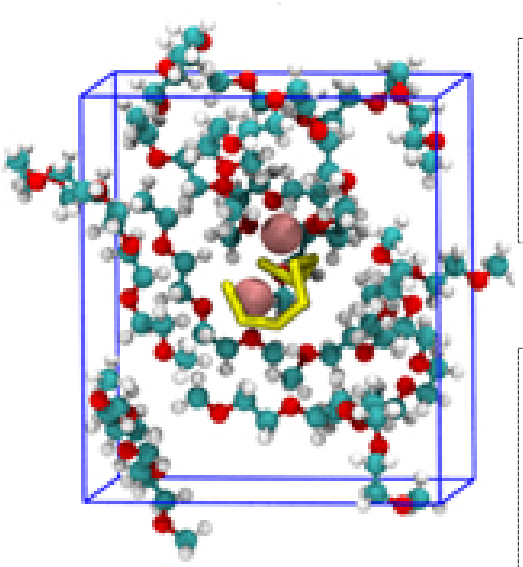
Milestones

Month/Year	Milestone or Go/No-Go	Description	Status
Dec, 2013	milestone	Theoretical calculations of polysulfide XAS by simulations	completed
Mar, 2014	milestone	Measurement of polysulfide XAS	completed
April, 2014	go/no-go	Viability of XAS for studying sulfur cathode	go
June, 2014	milestone	Design cell for *in situ* XAS measurements	on schedule
Sept, 2014	milestone	Synthesize binder and other components for *in situ* XAS experiments on sulfur cathode	on schedule

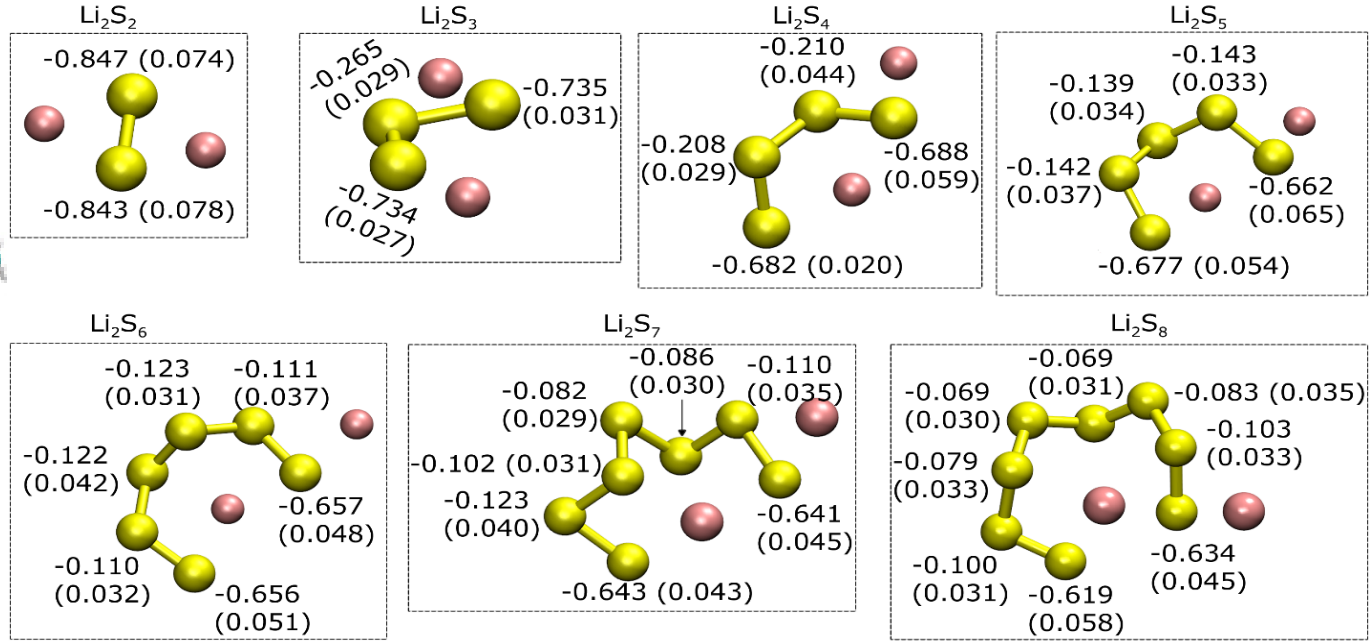
Approach

- 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.
- First use of Principle Component Analysis (PCA) to determine polysulfide dissociation without invoking any assumptions regarding the origin of XAS spectral features.
- Design lithium-sulfur cells for enabling *in situ* study of redox reactions at the sulfur cathode.
- Mechanistic insight will enable strategies of enhancing cycle life and energy density of lithium-sulfur cells being developed by OVT.

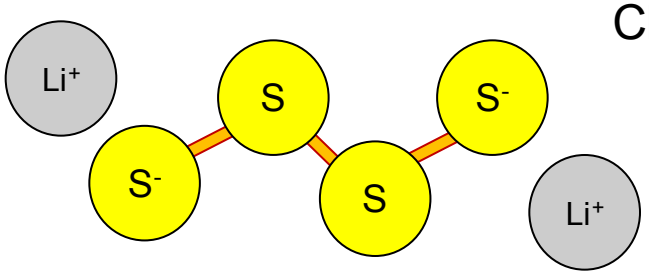
Technical Accomplishment: Charge Distribution in Polysulfides by Simulations



Typical simulation box



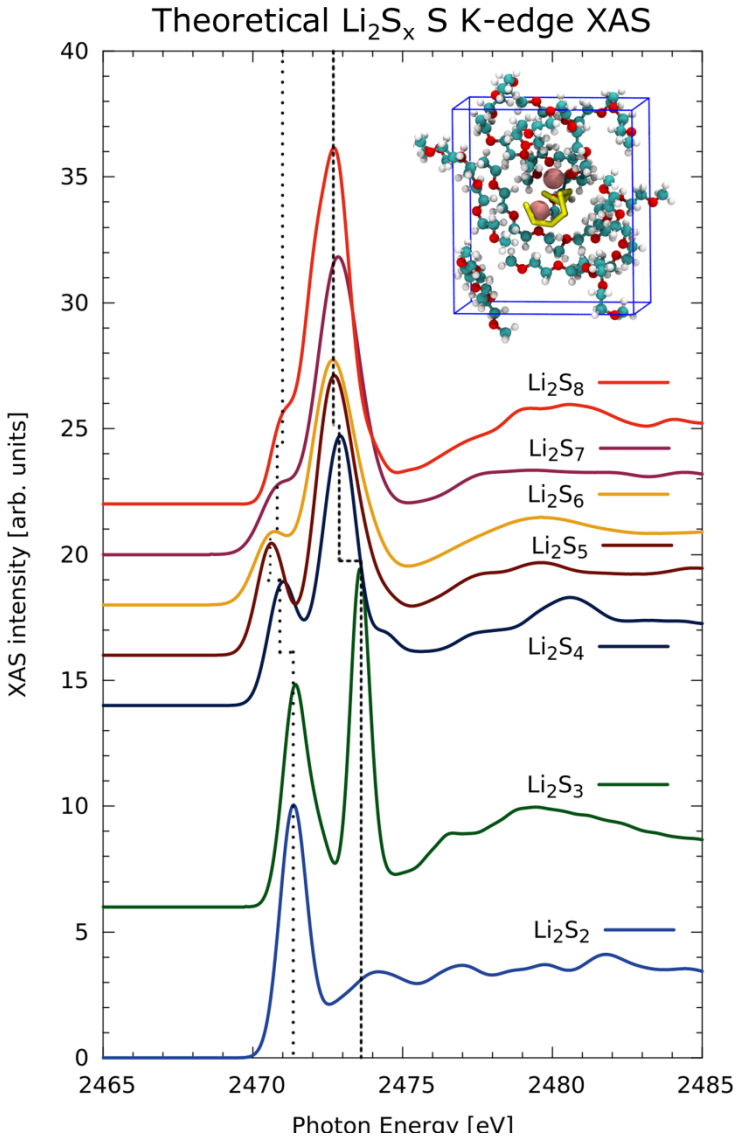
Charge distribution determined by simulation (uncertainty)

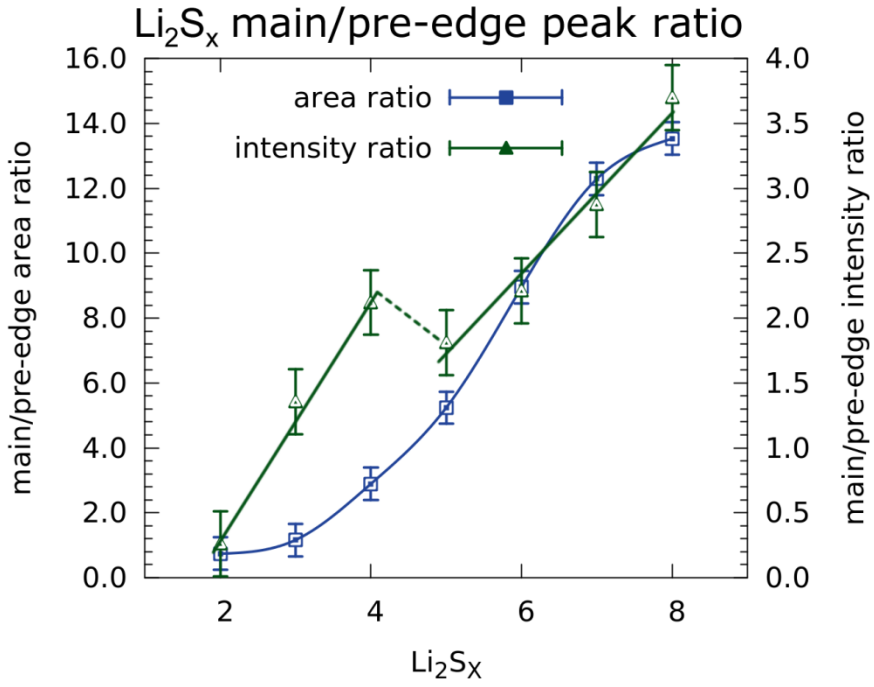


Assumed charge distribution

Take-home: Usual assumption that only terminal sulfur atoms are charged (-1 charge) is not valid due to partial charges on other S atoms and charged transfer to electrolyte.

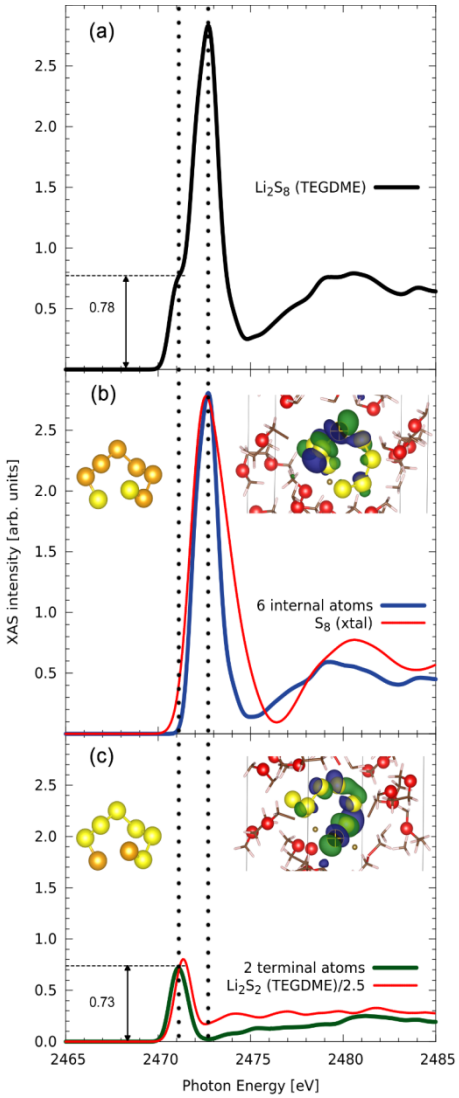
Technical Accomplishment: Polysulfides X-ray Absorption Spectra by Simulations





Take-home: Main edge to pre-edge intensity ratio provides a "fingerprint" of polysulfide, but the relationship is non-linear.

Technical Accomplishment: Molecular Underpinnings of Polysulfides XAS



Full Li_2S_8 spectrum

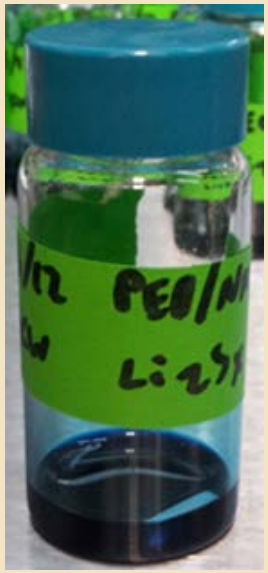
Internal S atom contribution

Terminal S atom contribution

Take-home: Main edge due to internal S atoms. Pre-edge due to terminal S atoms.

Technical Accomplishment: Established Protocol for Experimental Measurement of Polysulfides XAS

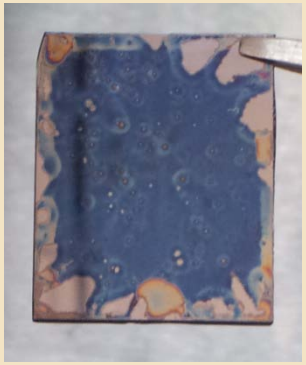
Solution preparation



Only Li:S ratio is specified

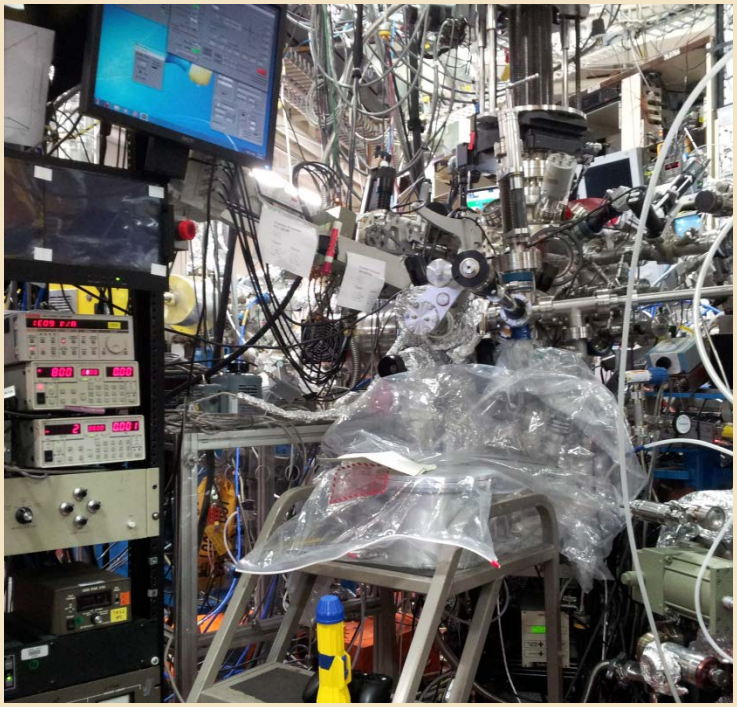
- Li_2S
- S_8
- Polymer electrolyte
- Solvent

Spin coating



- Spin coated thin films
- (PEO/SEO & Li2Sx)
- Ellipsometry (200 nm thick sample)

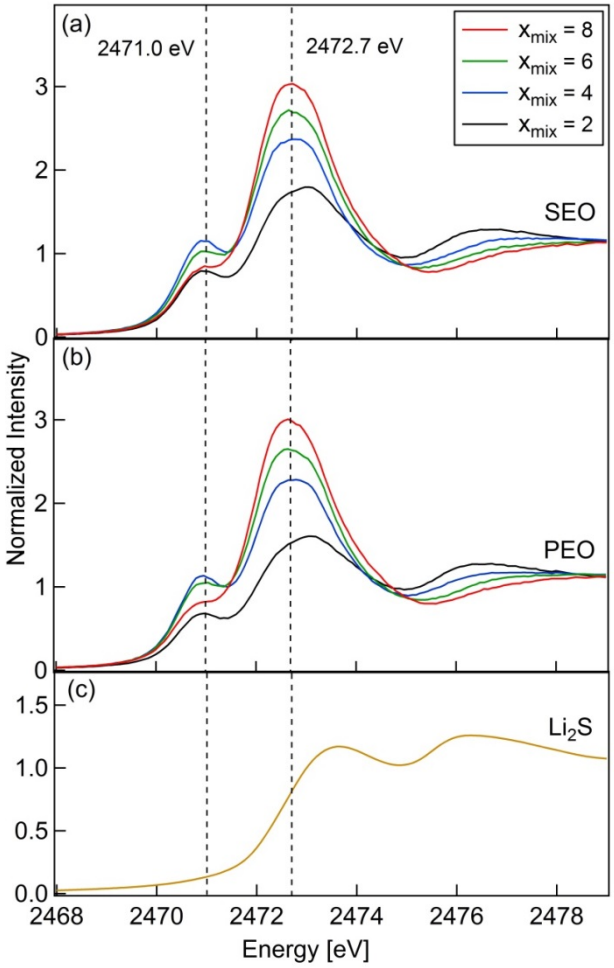
X-ray absorption spectroscopy



- Sulfur K-edge

$$Li_2S + [(x_{mix}-1)/n]\cdot S_8 \rightarrow Li_2S_{xmix}$$

Technical Accomplishment: Experimental Polysulfides X-ray Absorption Spectra



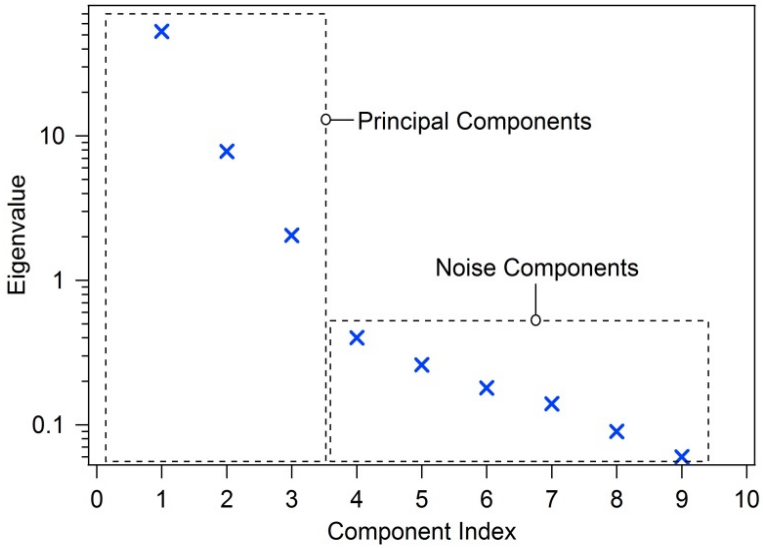
Polysulfides in a block copolymer electrolyte

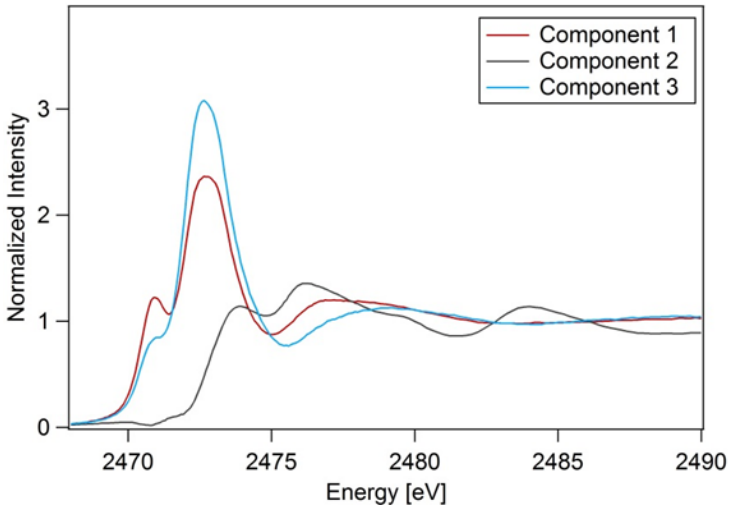
Polysulfides in a homopolymer electrolyte

Li_2S crystal spectrum (reference)

Take-home: Experimental XAS data similar to simulation-based predictions.

Technical Accomplishment: First PCA Analysis of Polysulfide XAS

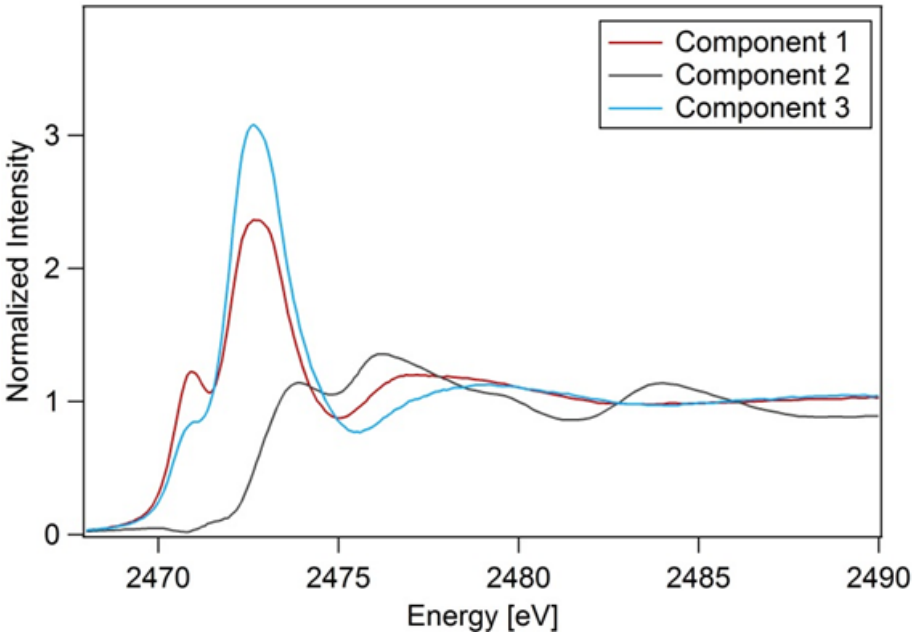




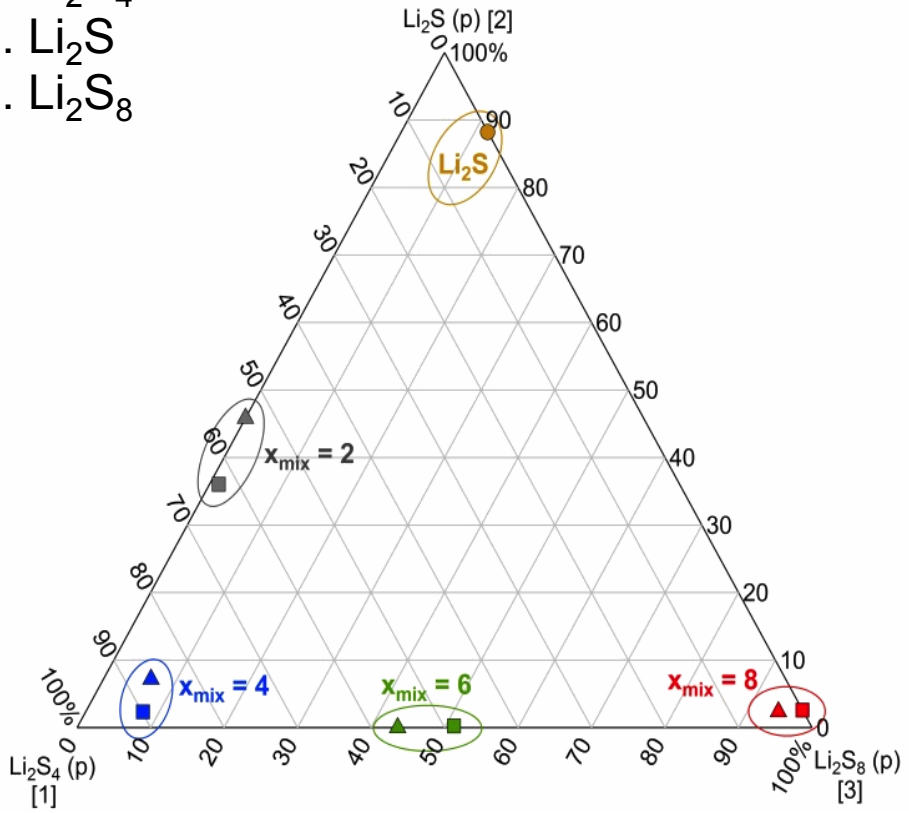
- Principle Component Analysis (PCA) of XAS Spectra makes no assumption regarding the number of underlying species.
- PCA analysis of polysulfide data indicates the presence of **only three principle components**.

Take-home: PCA –based spectra of the three principle components (left) have been determined by statistical analysis alone with no simplifying assumptions.

Technical Accomplishment: PCA-based Analysis of Polysulfide Dissociation

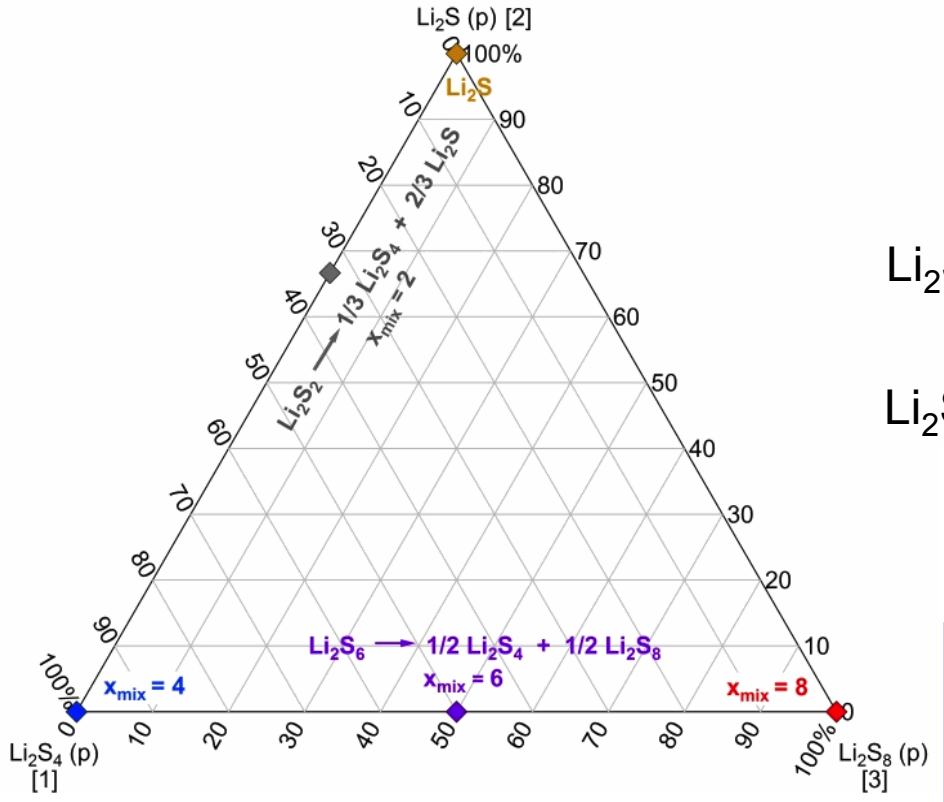


1. Li_2S_4
2. Li_2S
3. Li_2S_8



Take-home: Li_2S_2 and Li_2S_6 do not exist as pure components. Li_2S_4 and Li_2S_8 do exist as pure components.

Technical Accomplishment: PCA-based Determination of Polysulfide Disproportionation Reactions



$Li_2S_2 \rightarrow 1/3\ Li_2S_4 + 2/3\ Li_2S$

$Li_2S_6 \rightarrow 1/2\ Li_2S_4 + 1/2\ Li_2S_8$

Take-home: Only Li_2S_4 and Li_2S_8 species are likely to exist in the sulfur cathode.

- "Ideal" ternary diagram if proposed disproportionation were exact.
- Measured ternary diagram (slide 12) is similar to ideal diagram.

Response to Reviewers' Comments

At last AMR meeting, PI announced completion of solid electrolytes for lithium met al anode project. Most of the reviewer comments were aimed at this project.

The two comments related to Li-S project were:

Comment: *The reviewer mentioned that the plans for work on Li-S system are of interest. However, the reviewer cautioned that there have already been many workers in this area, and asked what was new in this project.*
Response: We feel that both the simulations and experiments presented in this poster are entirely new contributions to the Li-S literature.

Comment: *The reviewer, however, felt that it would be important to set up some collaboration with interested industrial partners in this area (Li-S).*
Response: We feel that it was too early to engage industrial partners during FY14 as the project just was getting off the ground. We will work on this in the coming years.

Collaborators

- David Prendergast (NERSC, 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
- Matthew Marcus (ALS, LBNL): XPS data analysis using PCA. Outside VT program.
- Jordi Cabana (University of Illinois, Chicago Circle): X-ray spectroscopy experiments and data analysis. Within VT program.
- Miquel Salmeron (Materials Sciences Division, LBNL): X-ray spectroscopy experiments. Outside VT program.
- Jinghua Guo (ALS, LBNL): X-ray spectroscopy instrumentation. Outside VT program.
- Nancy Dudney (ONRL): Solid electrolyte characterization. Within VT program.
- Feng Wang (BNL): Cathode characterization. Within VT program.

Remaining Challenges and Barriers

- Establish methodology for fingerprinting electrochemical reaction products.
- Simulations of polysulfides under electrochemical potential.
- Use fundamental knowledge to build a better lithium-sulfur battery.

Summary

- Completed first-principles molecular dynamics simulations to determine charge distribution and X-ray absorption spectra of polysulfide solutions.
- Determined species present in polysulfides created by chemical reactions using principle component analysis on experimentally determined X-ray absorption spectra.
- Used simulations to obtain the molecular underpinnings of X-ray spectral features.
- Obtained a simple hypothesis for sulfur oxidation in ether-based solvents.

Future Work

- Run simulations at high polysulfide concentrations and examine effect of concentration on fingerprints.
- Conduct X-ray spectroscopy experiments as a function of polysulfide concentration and chain length and re-examine proposed fingerprinting strategy.
- Build *in situ* cell to create polysulfides by electrochemical reactions and use fingerprinting strategy to determine reaction products.
- 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.