Fundamental Studies of Lithium-Sulfur Cell Chemistry

PI: Nitash Balsara

LBNL

June 9, 2015

Project ID # ES224

Overview

Timeline

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

Budget

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

Barriers

- Barriers addressed
  - Energy density
  - Cycle life

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.

FY14 Objectives: Compare computer simulation results of polysulfides XAS with experiments and use them to determine sulfur redox mechanism.

- ❑ Simulated X-ray Absorption Spectroscopy (XAS): Complete the first first-principles simulations of XAS spectra of polysulfide radicals and dianions based on molecular dynamics simulations.
- ❑ In situ Cell for Measurement of XAS Spectra: Complete first 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.
- ❑ Begin Cathode Design: Begin design of sulfur cathodes that exhibit long cycle life.

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	completed
Sept, 2014	milestone	Synthesize binder and other components for *in situ* XAS experiments on sulfur cathode	completed

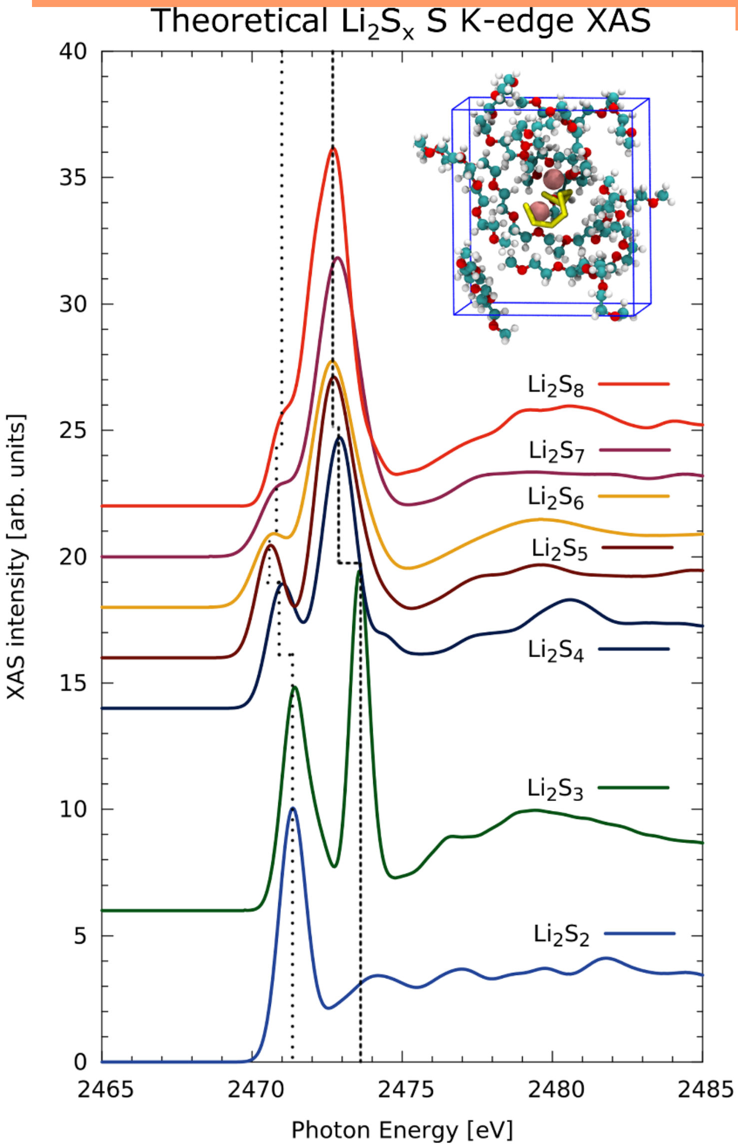
Milestones

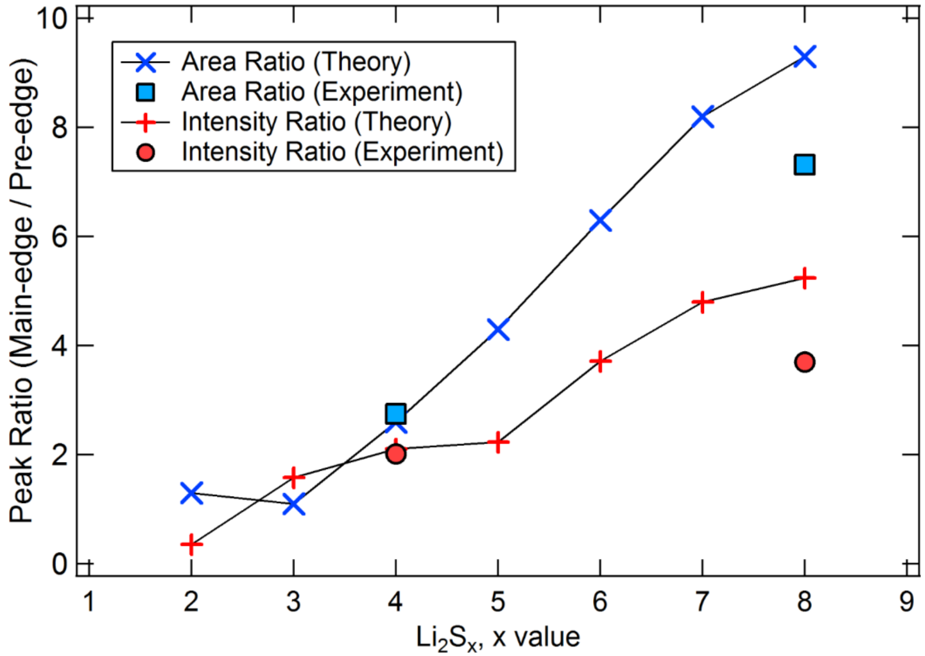
Month/Year	Milestone or Go/No-Go	Description	Status
Dec, 1, 2014	milestone	Extend theoretical calculations of XAS to finite polysulfide concentrations	completed
Jan, 15, 2015	milestone	Experimental study if the effect of polysulfide concentration on XAS spectra	completed
May 20, 2015	milestone	Quantitative comparison of experimental and theoretical XAS spectra	on track
Aug 23, 2015	go/no-go	Build and test cell for in situ XAS analysis	go

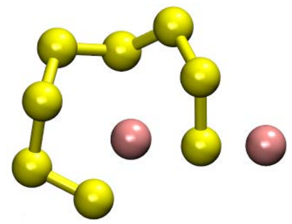
Approach

- 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 with PEO electrolytes 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: XAS Simulations and Experiments

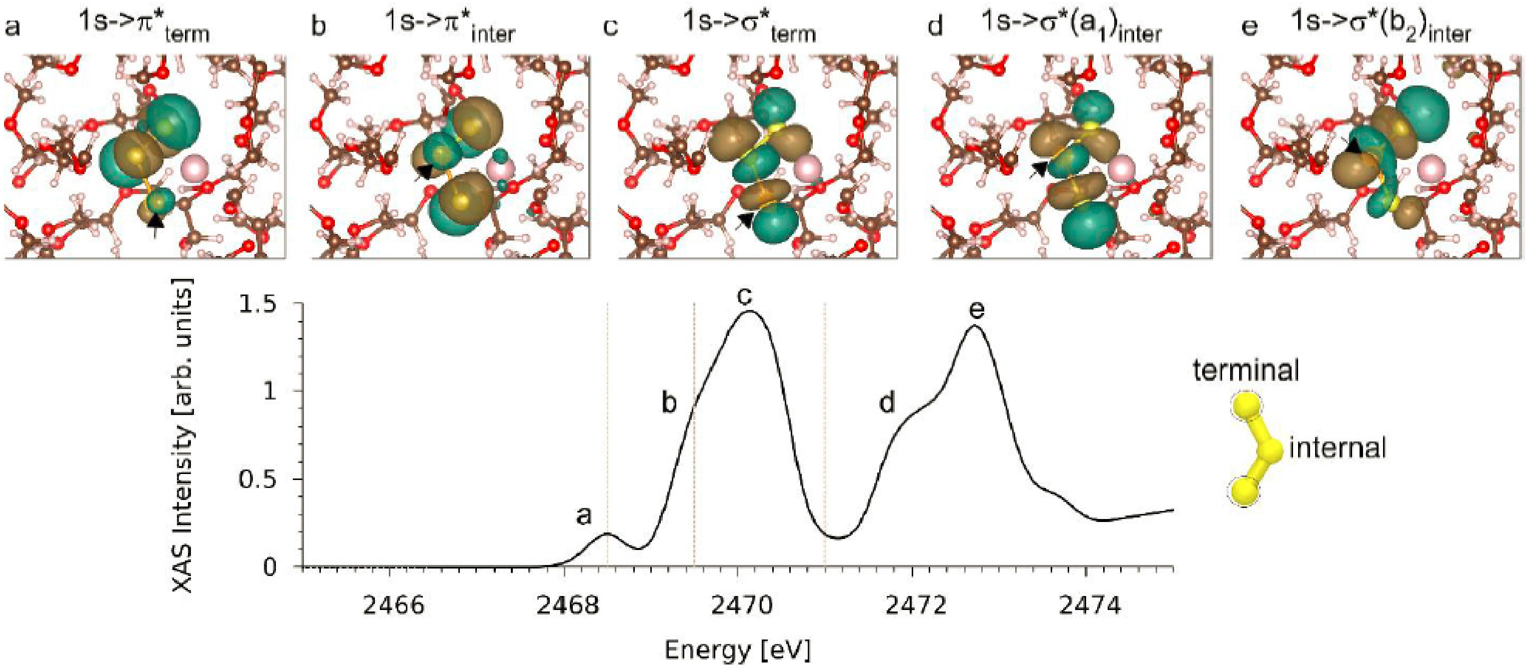






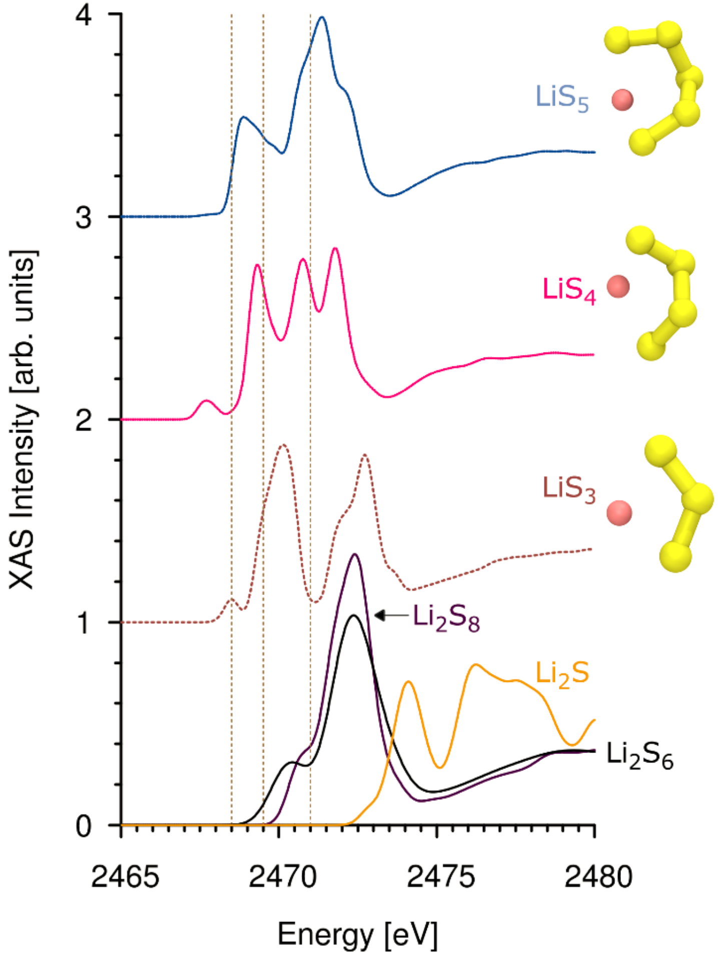
Take-home: Simulated XAS spectra of Li_2S_4 and Li_2S_8 in PEO in agreement with measurements.

Technical Accomplishment: Polysulfide Radical Anion Simulations



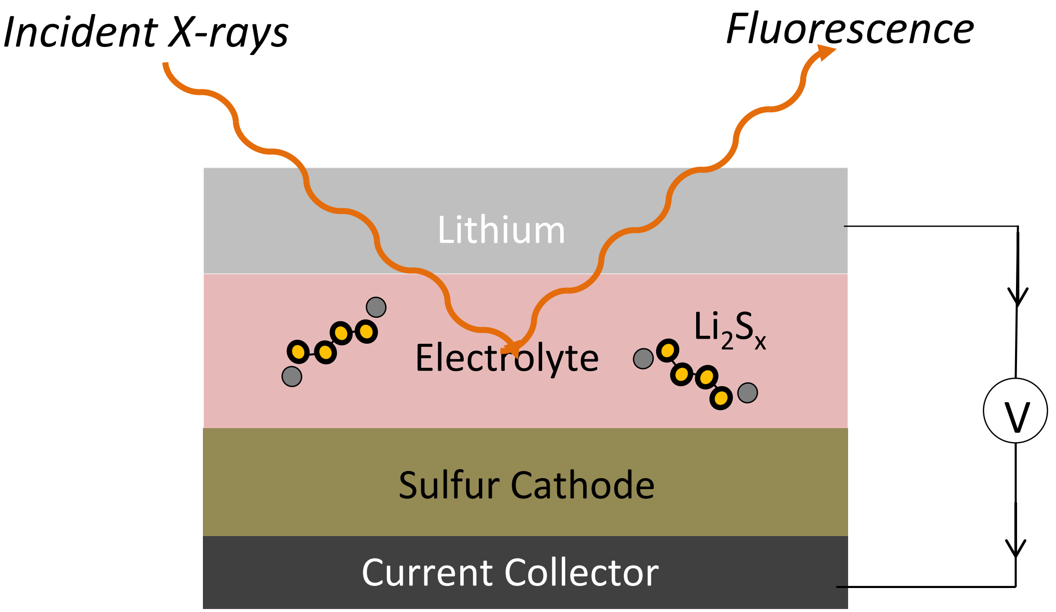
Take-home: LiS_3 radical anions show a unique fingerprint at 2468.5 eV due to π^* orbital of the S_3 radical.

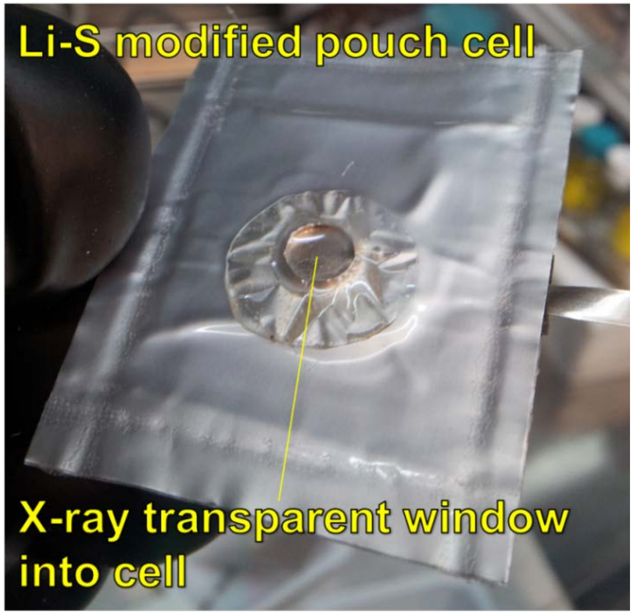
Technical Accomplishment: Polysulfide Radical Anion Simulations



<u>Take-home</u>: All radical anions show a unique fingerprint at 2468.5 eV that is not present in dianions.

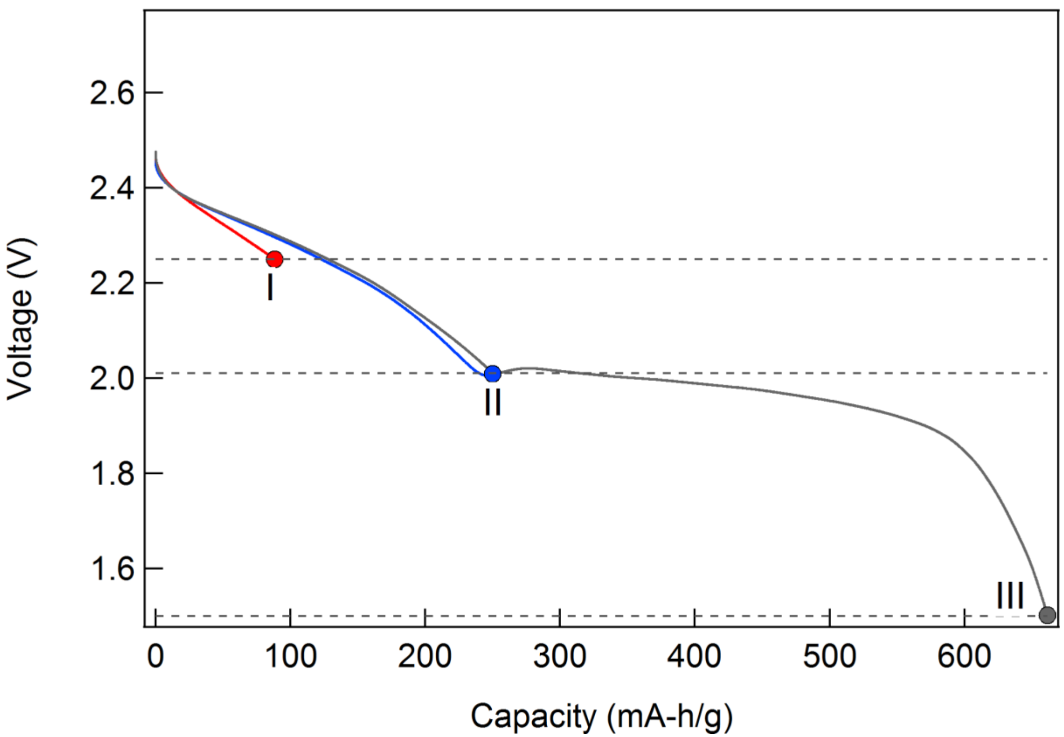
Technical Accomplishment: In situ Li-S cell for XAS was built





- *Sulfur Cathode:* Carbon black, elemental sulfur, $LiClO_4$, polystyrene-poly(ethylene oxide) (SEO) solid polymer electrolyte
- *Electrolyte:* SEO, $LiClO_4$
- *Anode:* Lithium metal

Technical Accomplishment: XAS spectra gathered as a function of discharge voltage

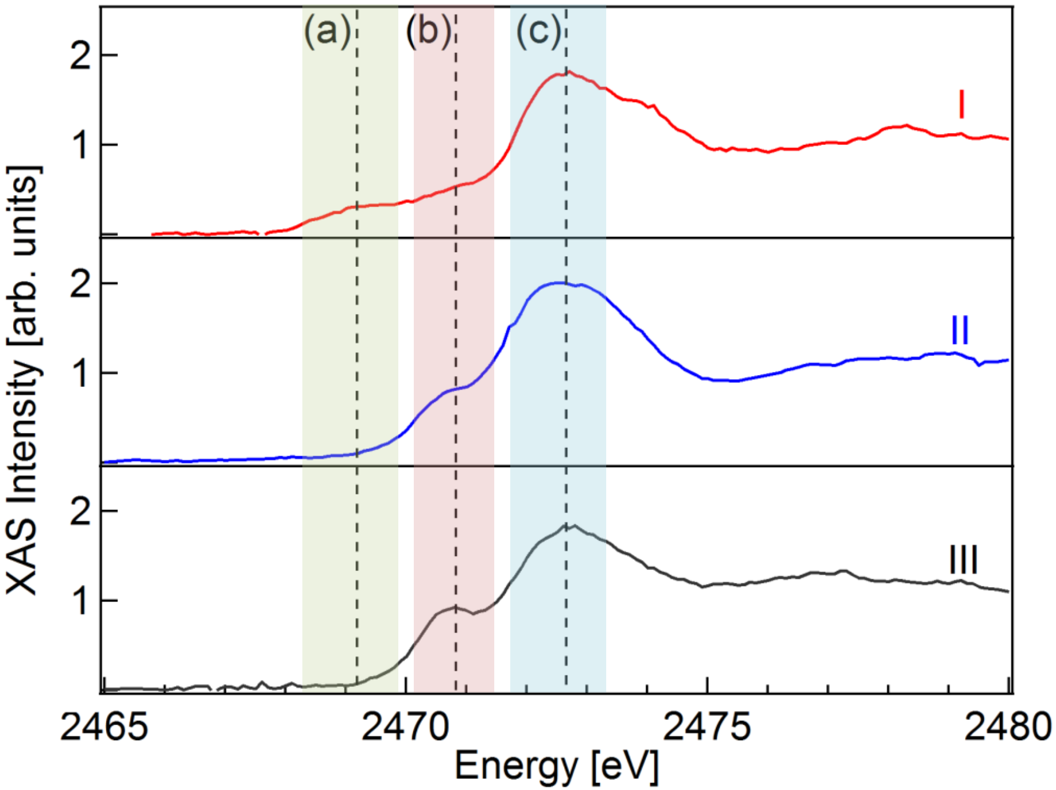


Cell	Cutoff voltage
I	2.25 V
II	2.02 V
III	1.50 V

- Battery cells operated at 90°C and then kept at 90°C for three days

- Discharged at C/40 rate

Technical Accomplishment: XAS spectra measured during discharge

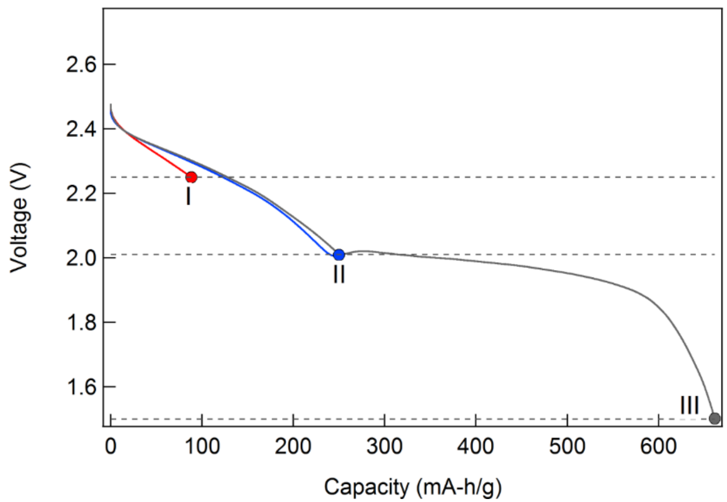


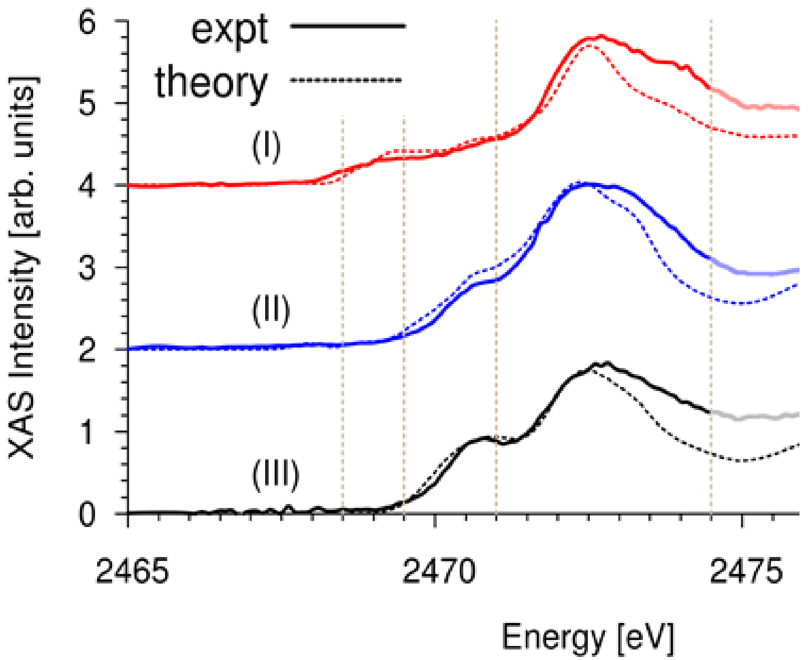
Cell	Cutoff voltage
I	2.25 V
II	2.02 V
III	1.50 V

Label	Energy
(a)	~ 2469 eV
(b)	~ 2471 eV
(c)	~ 2472.5 eV

Take-home: Species determined by comparing simulations and experiments.

Technical Accomplishment: Comparing in situ XAS with simulations





Spectra	S_8 (%)	Li_2S (%)	S_3 (%)	radicals (%)	dianions(short) (%)	dianions(long) (%)
I	26	0	4	41	0	29
II	4	7	0	10	63	16
III	0	8	0	0	92	0

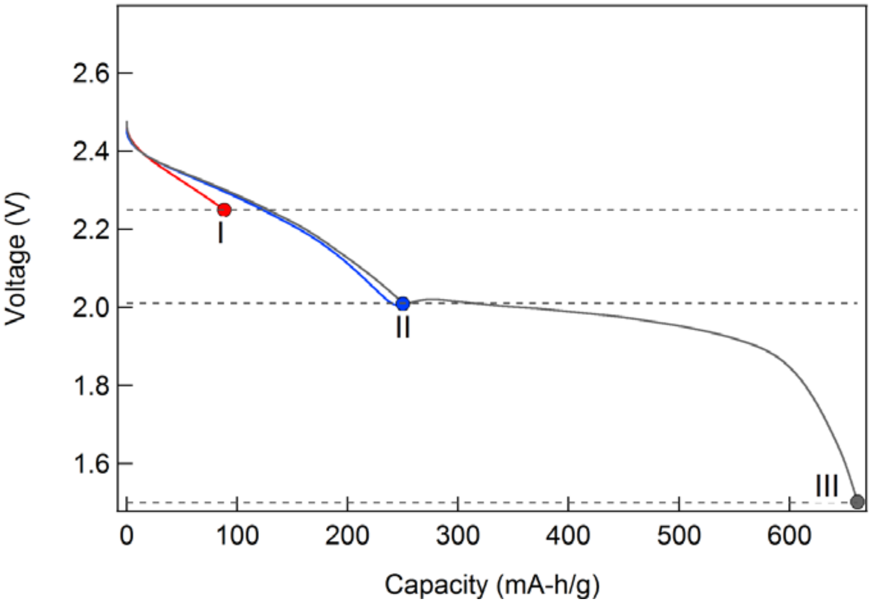
Technical Accomplishment: Proposed Reaction Mechanism

Step I

$S_8 + 2e^- + 2\ Li^+ \rightarrow Li_2S_8$ (1)

$Li_2S_8 \rightarrow LiS_3 + LiS_5$ (2a)

$Li_2S_8 \rightarrow 2LiS_4$ (2b)



Step II

$LiS_3 + 1e + 1Li^+ \rightarrow Li_2S_3$ (4a)

$LiS_5 + 1e + 1Li^+ \rightarrow Li_2S_5$ (4b)

$LiS_4 + 1e + 1Li^+ \rightarrow Li_2S_4$ (4c)

$Li_2S_x + 2e + 2Li^+ \rightarrow Li_2S + Li_2S_{(x-1)}$; $8 \leq x \leq 5$ (5)

Step III

$Li_2S_x + 2e + 2Li^+ \rightarrow Li_2S + Li_2S_{(x-1)}$; $5 \leq x \leq 2$ (6)

<u>Take-home</u>: Radical anions dominate early discharge.

Technical Accomplishment: Approach enables elimination of reactions

Electrochemistry

Li_2S_8 reactions with 1 electron

$Li_2S_8 + 1e- + 1Li+ \rightarrow Li_2S_7 + LiS$

$Li_2S_8 + 1e- + 1Li+ \rightarrow Li_2S_6 + LiS_2$

$Li_2S_8 + 1e- + 1Li+ \rightarrow Li_2S_5 + LiS_3$

$Li_2S_8 + 1e- + 1Li+ \rightarrow Li_2S_4 + LiS_4$

$Li_2S_8 + 1e- + 1Li+ \rightarrow Li_2S_3 + LiS_5$

$Li_2S_8 + 1e- + 1Li+ \rightarrow Li_2S_2 + LiS_6$

Li_2S_8 reactions with 2 electrons

$Li_2S_8 + 2e- + 2Li+ \rightarrow Li_2S_6 + 2LiS$

$Li_2S_8 + 2e- + 2Li+ \rightarrow Li_2S_5 + LiS + LiS_2$

$Li_2S_8 + 2e- + 2Li+ \rightarrow Li_2S_4 + 2LiS_2$

$Li_2S_8 + 2e- + 2Li+ \rightarrow Li_2S_4 + LiS_3 + LiS$

$Li_2S_8 + 2e- + 2Li+ \rightarrow Li_2S_3 + LiS_3 + LiS_2$

$Li_2S_8 + 2e- + 2Li+ \rightarrow Li_2S_3 + LiS_4 + LiS$

Take-home: These reactions cannot occur due to the absence of highlighted species.

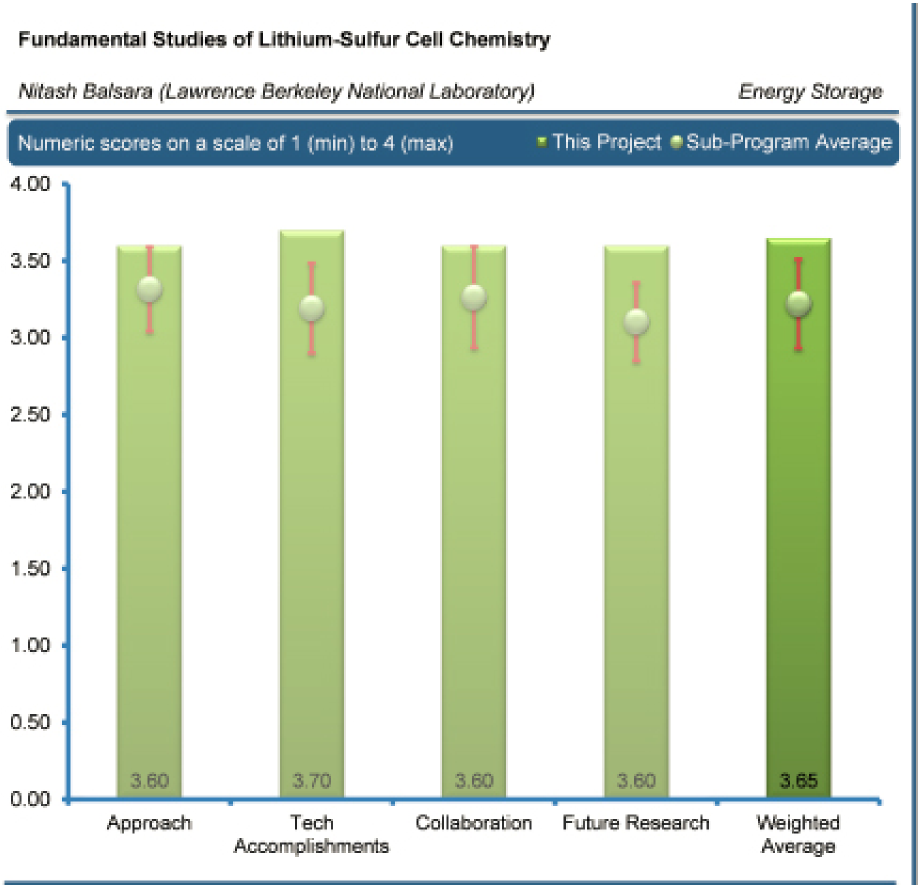
Response to Reviewers' Comments

<u>Comment 1:</u> *Project needs to establish more collaborations with leading research groups.*

All other comments were positive.

<u>Comment 2:</u> *The reviewer observed that an appropriate level of collaboration existed. These include National Energy Research Scientific Computing Center (NERSC), ALS, LBNL, University of Illinois, ONRL and BNL. The reviewer added that many of the investigators were within the Vehicle Technology Office and this was very good.*

<u>Response:</u> We are working on establishing new collaborations. Our work with Dr. Wang of BNL is being written up for a publication.



Generally, 2014 reviews were positive.

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): XAS data analysis using PCA. Outside VT program.
- Wayne C. Stolte (ALS, LBNL) XAS measurements. Outside 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.
- Feng Wang (BNL): Cathode characterization. Within VT program.

Remaining Challenges and Barriers

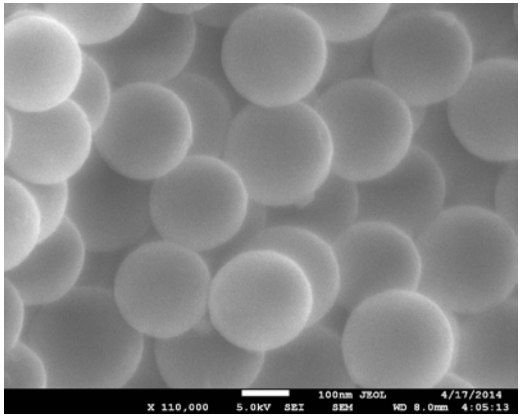
- Determine species formed during cycling at different C-rates.
- Simulations of polysulfides under electrochemical potential.
- Use fundamental knowledge to build a better lithium-sulfur battery.

Summary

- ❑ 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.

Future Work

- Continue *in situ* cell studies to determine reaction products as a function of C-rate.
- Time-resolved *in situ* studies to study kinetics of polysulfide disproportionation.
- Design simulations to study electrochemical reactions in sulfur cathode.
- Use fundamental knowledge to systematically build a lithium-sulfur cell with long cycle life and high energy density. Sulfur impregnated into carbon spheres shown below.



Take-home: Construction of model sulfur cathodes has begun.