First-Principles Interpretations of X-ray Absorption Spectra Indicate the Appearance of Polysulfide Radicals in a Partially Discharged Lithium-Sulfur Battery

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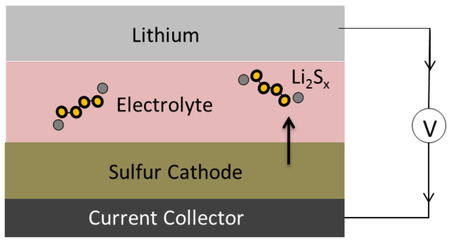
Background



Series of redox reactions

$S_{8(s)} + 2Li^+ + 2e^- \rightarrow Li_2S_8$

$\frac{1}{2}Li_2S_8 + Li^+ + e^- \leftrightarrow Li_2S_4$

$\frac{1}{2}Li_2S_4 + Li^+ + e^- \leftrightarrow Li_2S_2$

$\frac{1}{2}Li_2S_2 + Li^+ + e^- \leftrightarrow Li_2S_{(s)}$

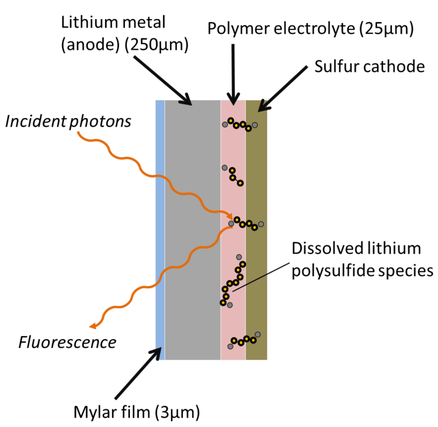
- Lithium-sulfur reaction intermediates diffuse from cathode during charge/discharge, lowering battery capacity and lifetime
- Li-S battery charge/discharge reaction mechanisms taking place in polymer electrolyte environments still being studied
- A fundamental understanding of polysulfide diffusion into polymer electrolytes has not been established.

Objectives

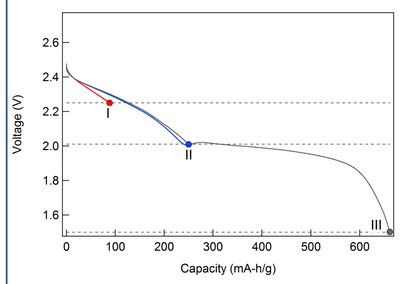
- Perform X-ray absorption spectroscopy on partially-discharge Li-S cells to determine cathode reaction mechanisms
- Consumers stop battery charge/discharge as they please. What polysulfide species can be expected in the electrolyte after charge/discharge is stopped?
- Use theoretical molecular dynamics and XAS simulations to explain experimental XAS findings

Experimental

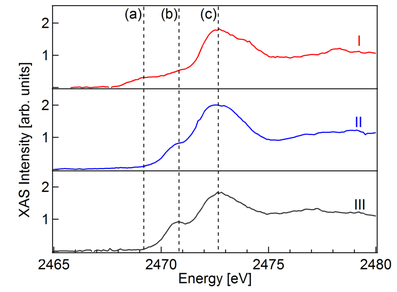
- Li-S cell discharged to three voltages (2.25 V, 2.02 V, and 1.50 V)
- Discharging stopped, cells allowed to sit for three days at 90C to allow for polysulfide dissolution
- Sulfur K-edge XAS performed on cell electrolytes
- Molecular dynamic simulation of polysulfide solvation in TEGDME
- Theoretically calculated XAS for isolated lithium polysulfide species used to interpret experimental spectra



Li-S Cell Cycling and XAS

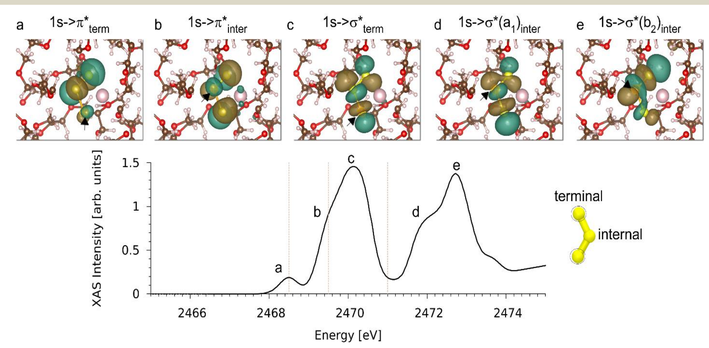


- Voltage vs. current profiles for the three pouch cells tested.
- The cells were stopped at three different points: I,II and III, corresponding to 2.25V, 2.02V, and 1.5V, respectively.

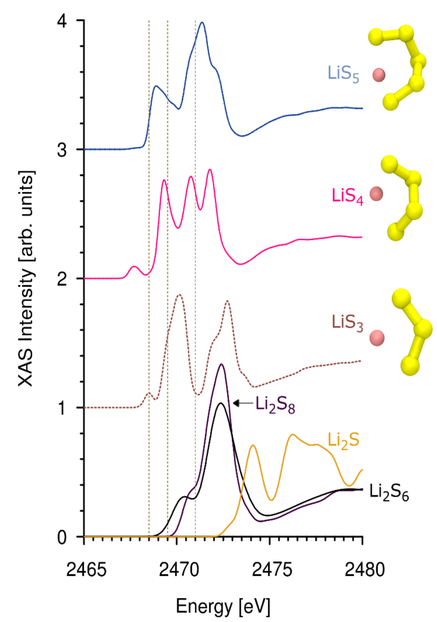


- Sulfur K-edge XAS measurements obtained for three cells after discharge and after holding cells for three days at 90°C
- Dashed vertical lines are included as a guide to highlight several low energy features below the white line near 2472.6 eV.

Theoretical simulations & XAS

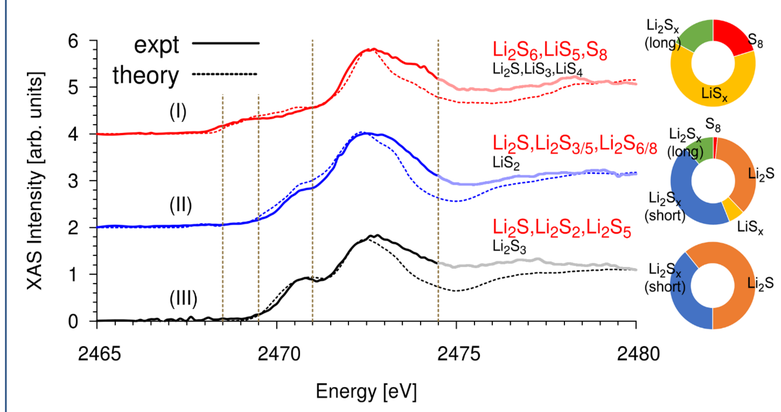


- First principles XANES spectra of the trisulfur LiS_3 molecule dissolved in tetraethylene glycol dimethyl ether (TEGDME) obtained from sampling an *ab-initio* molecular dynamics (AIMD) simulation at 298K.
- Each of the five major transitions that inform the spectra are indicated



- Calculated XAS spectra of the solvated radical LiS_5 (blue), LiS_4 (pink) and LiS_3 (brown) molecules. The XANES spectra of the Li_2S_6 (black) and Li_2S_8 (purple) dianions, as well as crystalline Li_2S (gold) are also included.
- *Right outsets:* Thermodynamically favored state of lithium polysulfide dissolved in TEGDME from AIMD simulations.

Analysis of Li-S Cell Chemistry



- Comparison of the best fit spectra from theory (dashed lines) to experiments (solid lines)
- Isolated species used to obtain the best fit are also indicated: the major components are in red, while the minor components are in black.
- *Right outsets:* Relative molecular composition ratios types of sulfur species (S_8 (red), Li_2S (orange), radicals (yellow) and dianions) from our LSF

	Voltage (V)	S_8	Li_2S	S_3	radicals	Li_2S_x (2≤ x ≤5)	Li_2S_x (6 ≤ x≤ 8)
I	2.25	26%	0%	4%	41%	0%	29%
II	2.02	4%	7%	0%	10%	63%	16%
III	1.5	0%	8%	0%	0%	92%	0%

- Distribution of species at different voltages, described by more general families of species

Conclusions

- Li-S cells discharged to three voltages, XAS performed on cell electrolyte
- Theoretical XAS fingerprints of polysulfide species used to determine electrolyte composition
- Polysulfide radical anions detected after early stages of discharge and are thermodynamically stable in electrolyte
- Experiments designed to probe cell electrolyte rather than cathode – data highlights the composition of soluble polysulfide species

Acknowledgements

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