X-ray Absorption Spectroscopy of Lithium-Sulfur Battery Discharge/Charge Reaction Intermediates

Kevin Wujcik,*[§] Tod Pascal,[§†] Juan Velasco-Velez,[§] Matthew Marcus,[‡] Jordi Cabana,[#] Jinghua Guo,[‡] Miquel Salmeron,[§] David Prendergast,[§†] Nitash Balsara*[§#]

*Department of Chemical and Biomolecular Engineering, University of California, Berkeley
[§]Materials Science Division, [#]Environmental Energy Technology Division, the [†]Molecular Foundry, and the [‡]Advanced Light Source, Lawrence Berkeley National Laboratory
201 Gilman Hall, University of California, Berkeley, CA 94720

Lithium polysulfide reaction intermediates formed during the charge and discharge reactions of a lithium-sulfur battery are known to diffuse out of the cathode during cycling, thereby lowering battery capacity and lifetime. While numerous techniques have been developed to confine intermediates to the battery cathode, little is known about the complex reaction mechanism responsible for their formation. Work to examine the reaction mechanism has been made difficult by the fact that Li_2S_x species are difficult to differentiate experimentally. Because of this, the Li-S battery discharge mechanism has historically been controversial.[1] We report on the use of x-ray absorption spectroscopy (XAS) to distinguish lithium polysulfide molecules in polymer electrolytes.

Lithium polysulfide species (Li_2S_x, x = 2, 4, 6, 8) dissolved in poly(ethylene oxide) and a block copolymer of polystyrene-poly(ethylene oxide) were probed at the sulfur K-edge. Resulting x-ray spectra were found to have absorption features that allow one to distinguish between various polysulfide molecules, as shown in Figure 1. Theoretical spectra were generated using eXcited electron and Core Hole (XCH) methods and resembled spectra obtained experimentally.[2] We conclude that XAS at the sulfur K-edge may allow one to distinguish polysulfide molecules; XAS may be a valuable experimental technique to develop lithium-sulfur battery reaction mechanisms and examine polysulfide solubility in electrolyte systems.

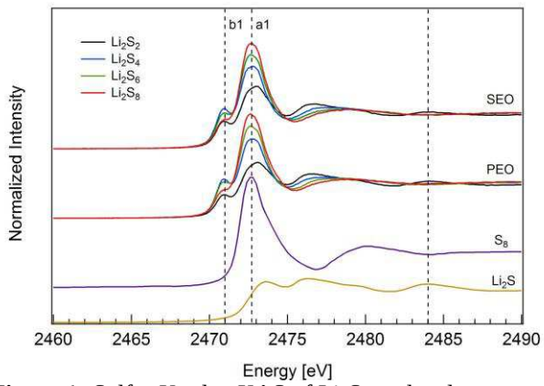

Figure 1: Sulfur K-edge XAS of Li_2S_x molecules dissolved in thin films of polymer electrolytes

References

1. Barchasz, C.; Molton, F.; Duboc, C.; Lepretre, J.; Patoux, S.; Alloin, F.; Anal. Chem. **2012**, 84, 3973-3980
2. Prendergast, D.; Galli, G.; Phys. Rev. Lett. **2006**, 96, 215502