

***Operando* X-ray Spectromicroscopy of Sulfur Evolution in Lithium-Sulfur Batteries**

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Lithium-sulfur (Li-S) batteries are a “beyond Li-ion” technology that offers large capacity while also being low cost, earth-abundant, and lightweight. Li-S achieves high capacity via chemical transformation rather than Li intercalation. Elemental sulfur S₈ is reduced through a series of soluble Li polysulfides (Li PS; Li₂S_x, 2 ≤ x ≤ 8) to a final solid discharge product Li₂S, and the process is reversed upon charging. However, Li-S suffers from unrealized theoretical capacity and rapid capacity fade due to loss processes that are not well-understood. Deciphering S speciation and distribution of dissolved PS in the anode, cathode, and electrolyte during cycling is critical for realizing the potential of Li-S. Synchrotron radiation provides high energy resolution and a micron-scale beam size for distinguishing complicated PS spectral features in the tender X-ray regime. From this information, we can observe a spatially and chemically heterogeneous system to see how S speciation and distribution contribute to capacity fade.

Here we present *operando* S K-edge X-ray spectromicroscopy of a Li-S battery performed at the Stanford Synchrotron Radiation Lightsource, BL 14-3. A cross-sectional battery cell was developed to collect spatially-resolved chemical maps that correlate changes in S species with electrochemistry. Significant changes in the electrode were observed including rearrangement of the S₈ matrix and PEO₁₀LiTFSI binder between cycles. PS concentration and spatial extent increased with cycling, indicating that some PS dissolution is irreversible, leading to PS shuttle. Fitting of maps with S standards indicated that upon subsequent charging, the initial S₈ concentration was not fully recovered; PS and Li₂S remained at the cathode with higher order PS as the primary species. Quantification of the PS concentration across the electrolyte and electrode interfaces shows that the concentration begins and ends as constant within the electrolyte, but while cycling, a significant increase in PS with a gradient toward the Li anode forms. To better understand the electrochemical processes in the cross-sectional cell, cyclic voltammetry measurements were performed. Varying chemistries and cell configurations resulted in current responses of different magnitudes, but the trends in peak shifts upon cycling remained consistent. This X-ray and electrochemical analysis provides a foundation for further *operando* spectromicroscopy of Li-S batteries and optimization of the cross-sectional cell design.