

***Operando* X-Ray Spectromicroscopy of Lithium-Sulfur Batteries**

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Li-S batteries are an attractive “beyond Li-ion” technology due to their large theoretical capacity, low cost, and earth abundance. The high capacity of Li-S results from operation via chemical transformation rather than Li intercalation as in Li-ion. Elemental sulfur S₈ is reduced to a final solid discharge product Li₂S through a series of soluble Li polysulfides (Li₂S_x, 2 ≤ x ≤ 8). However, Li-S batteries suffer from unrealized theoretical capacity and rapid capacity fade due to loss processes that are not well-understood. Deciphering speciation and the distribution of dissolved polysulfides in the electrolyte during cycling is imperative for realizing the potential of Li-S. Here we present *operando* characterization using sulfur K-edge X-ray absorption spectromicroscopy performed at SSRL. Cells consisting of a S₈/Super P carbon cathode, Li anode, and 1 M LiClO₄ + 0.5 LiNO₃ in 1,3-dioxolane/1,2-dimethoxyethane were discharged, and maps were collected at energies sensitive to the expected S and Li polysulfide species. Tuning the energies used to map during cycling allows for targeted observation of species such as polysulfides, sulfates, elemental sulfur, and lithium sulfide. Typically, *operando* X-ray characterization is conducted perpendicular to battery electrodes, providing an average of the chemistry through the entire stack. The cross-sectional geometry demonstrated here provides a spatially resolved picture of sulfur diffusion between the cathode and anode, which cannot be achieved by typical characterization methods. Synchrotron radiation provides high energy resolution for distinguishing the complicated polysulfide spectral features. From this information, we can observe a spatially heterogeneous and chemically diverse system to gain insight into how sulfur speciation contributes to capacity fade.