X-ray Characterization of Lithium-Sulfur Batteries in Action

With the ever-increasing demand to move away from fossil fuels and toward clean, renewable energy, dramatic improvements in energy storage devices are essential. Rechargeable lithium-sulfur (Li-S) batteries hold great potential for high-performance energy storage systems because they have a high theoretical specific energy, low cost, and are eco-friendly.[1,2] However, a detailed understanding of the Li-S battery operating mechanism is vital to designing improvements for higher efficiency and capacity.

Until now, X-ray studies of Li-S electrodes have been done on batteries that were brought to a particular state of charge, allowed to relax, and then disassembled before measurement (an *ex situ* process). But further changes can occur within the battery during relaxation and disassembly, and such measurements may not necessarily give a true picture of battery chemistry and morphology. Additionally, the same region of a single battery cannot be followed throughout the charging and discharging cycle.

In this LDRD-supported project, scientists from SLAC and Stanford University have used a two-pronged approach to characterize Li-S batteries during normal battery operation. *In operando* X-ray Diffraction (XRD) (SSRL BL11-3) was used to characterize real-time changes in the active battery material's crystal structure (Figure 1); while *in operando* X-ray imaging (SSRL BL6-2C) tracked nanometer-sized changes in the material's morphology at 30 nm resolution. By using two complementary techniques during normal battery operation, a more complete picture of the battery mechanism was constructed. The results have provided new information different from previous *ex situ* studies. This highlights the importance of *in operando* studies and suggests possible strategies for improving cycle life.

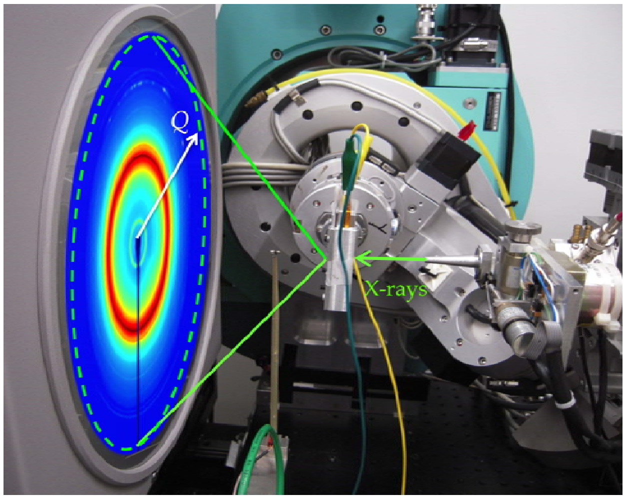

Figure 1. Side view of *in operando* X-ray diffraction setup (SSRL BL11-3) with X-rays coming from the right, traveling through the battery cell at the center of the figure, and scattering to form diffraction rings on the detector. An example of diffraction rings is overlaid on the detector. is the image is integrated, resulting in a diffraction pattern with characteristic peaks. These peaks are fingerprints of a particular crystal structure. By observing these peaks during battery operation, changes in crystal structure can be tracked. (Figure adapted from Nelson *et al*. 2012)

The *in operando* X-ray diffraction studies showed that during the discharge cycle crystalline sulfur interacted with lithium to form amorphous polysulfides. At the end of the discharge cycle crystalline Li_2S did not form (Figure 2), which contradicts most published *ex situ* XRD studies (see for example Yuan *et al*.[3]). In fact, crystalline Li_2S was only detected in a Li-S battery which was rested and disassembled. *In operando* X-ray imaging showed that polysulfides dissolved in the electrolyte, but they remained largely trapped within the electrode's carbon matrix (Figure 2). This trapping will decrease fading of battery capacity due to loss of polysulfides to the electrolyte, which would dramatically reduce the lifetime of the battery.[2] However, *ex situ* imaging of similar electrodes showed a complete absence of sulfur species on a partially discharged electrode. It is believed that during the disassembly of the battery, which includes thoroughly washing the electrolyte off the electrode, the dissolved polysulfides are freed. Thus, *ex situ* studies cannot accurately determine mechanisms for battery electrode failure.

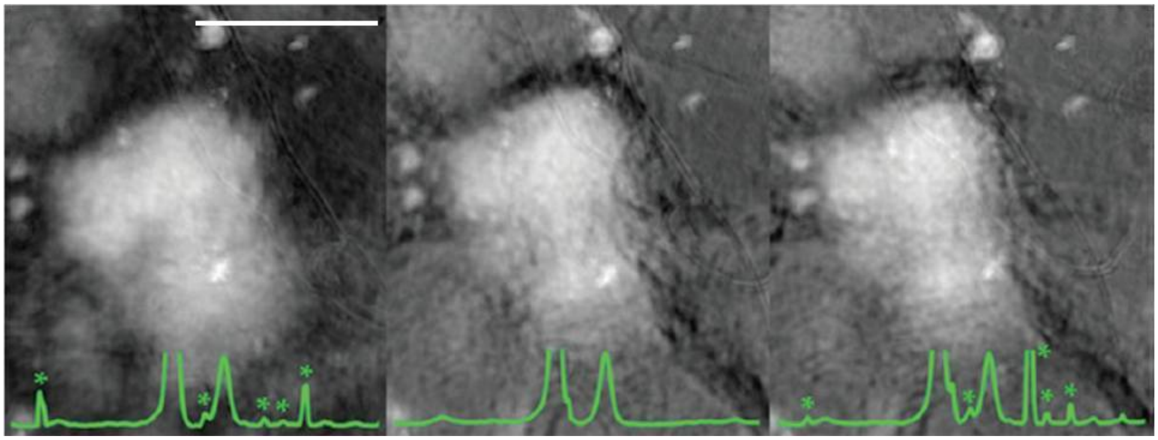

Figure 2. *In operando* X-ray images (SSRL BL 6-2C) of a sulfur particle with the X-ray diffraction results overlaid in green at three key points: before cycling (left), after discharge (center), and after recharging (right). The asterisks indicate the sulfur diffraction peaks. During discharge these peaks disappear and no new peaks form. The sulfur peaks reappear during charging. Although the background absorption in the images increases over time, indicating some polysulfide loss to the electrolyte, the bulk of the polysulfides remains confined. Scale bar is 10 microns. (Figure adapted from Nelson *et al.* 2012)

In operando X-ray studies are essential to avoid misleading results and to understand more completely the changes occurring in active battery material during operation. Such studies not only characterize strengths and flaws of current battery technologies, but also can guide future electrode designs to either avoid or promote certain crystal structures and morphologies, in order to increase capacity in subsequent cycles and to prolong battery life. The *in operando* XRD and X-ray imaging work on Li-S has been published in the Journal of the American Chemical Society.

Primary Citation

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