

Understanding the Electrochemical Processes in Li-S Batteries by Operando Methods

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Scope

Amongst the most challenging issues in electrochemical energy storage is developing insightful in situ probes of redox processes for a working cell. This is particularly true for cells that operate on the basis of chemical transformations such as Li-S and Li-O₂, where the factors that govern capacity and cycling stability are difficult to access owing to the amorphous nature of the intermediate species. Here, we investigate cathodes for the Li-S cell comprised of sulfur-imbibed robust spherical carbon shells with tailored porosity that exhibit excellent cycling stability. Their highly regular nanoscale dimensions and thin carbon shells allow highly uniform electrochemical response and further enable direct monitoring of sulfur speciation within the cell over the entire redox range by operando X-ray absorption spectroscopy (XANES) on the S K-edge, coupled with solid state NMR investigations.

Major results

Extremely uniform porous carbon nanospheres controlled to 220 nm in dimension were fabricated using a novel one-step method to create a hollow sphere with a porous casing (Figure 1). The TEM image in the insert of Figure 1 illustrates the relative dimensions of the sphere as well as the completeness of its shell after melt-diffusion at 155°C. The energy dispersive X-ray (EDX) line-scan (insert in Figure 1) also shows a homogeneous sulfur signal throughout the shell of the sphere and inner lining where the sulfur is primarily confined, and no sulfur contribution from the exterior.

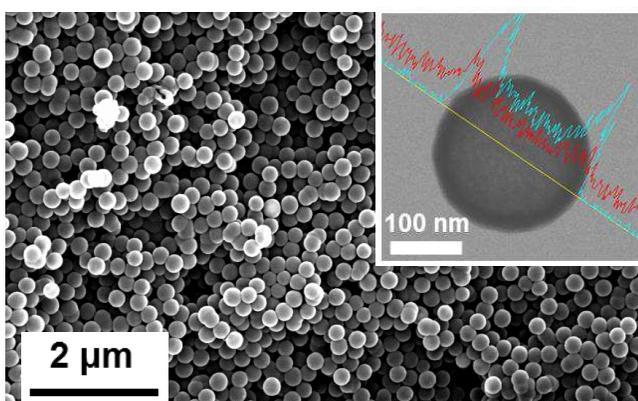


Figure 1. Scanning electron micrograph of the PCNS host for sulfur. Insert: transmission electron microscope and elemental line scans for carbon (red) and sulfur (blue) across the PCNS/S composite material.

The electrochemical properties of the PCNS/S (60 wt% S) were examined in a coin cell configuration using 1M LiTFSI in a mixed solvent of 1,2-dimethoxyethane and 1,3-dioxolane with 2 wt% LiNO₃ as additive for protection of the lithium foil anode. The cells were cycled between 1.5 and 3.0 V at a high

discharge/charge rate of 1C (1672 mA g⁻¹_{sulfur}). After the first few activation cycles, the capacity stabilizes at an average value of 730 mAh g⁻¹_{sulfur} over 100 cycles (Figure 2). The capacity retention with respect to the first cycle remains above 100% after activation and for the duration of at least 100 cycles.

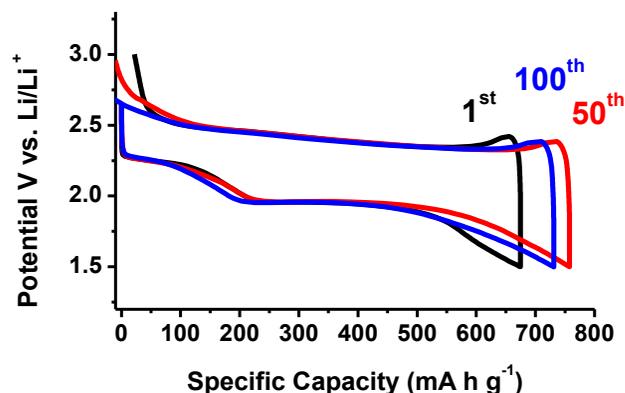


Figure 2. 1st, 50th and 100th galvanostatic cycles at 1C of a Li cell comprised of a nanosphere carbon-sulfur cathode.

Redox reactions in a cell comprised of this cathode were monitored in real time using synchrotron-based operando XANES. Reference spectra of a wide range of standards were measured ex situ but under strictly similar conditions. The results confirm the reversible scission and formation of S₈ rings as shown by a comparison of the pristine electrode and after one cycle (Figure 3a). A similarly high degree of reversibility was exhibited in the spectra acquired at full discharge after the 1st and 2nd cycles (≈ 1200 mAh g⁻¹_{sulfur}, Figure 3b), whereas spectral differences were noted vis a vis stoichiometric Li₂S. Operando spectra acquired at intervals of 50 mAh g⁻¹_{sulfur} – corresponding to intermediate states in the discharge and charge – were fit with a linear combination based on the references to achieve sulfur speciation in the electrode. The results reveal the first detailed evidence on the mechanisms of sulfur redox chemistry on cycling, showing how sulfur fraction and sulfide precipitation impact capacity. Such information is critical for promoting improvements in Li-S batteries.

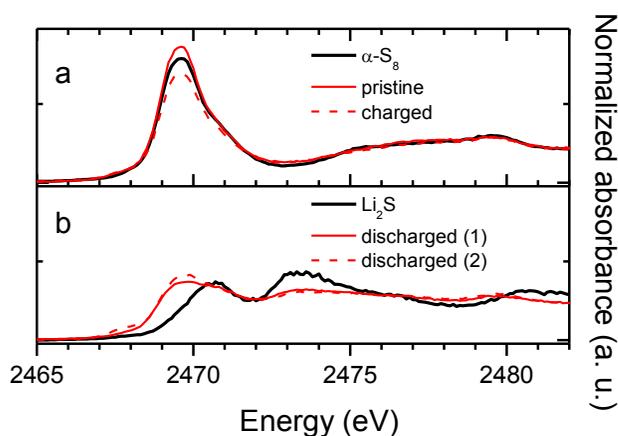


Figure 3. Reference S K-edge XANES spectra for elemental sulfur (a) and lithium sulfide (b). The initial, charged states (a) and discharged states (b) shown in red were obtained operando.

References

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