

ADVANCED ENERGY MATERIALS

Supporting Information

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In Situ TEM Observation of Electrochemical Lithiation of Sulfur Confined within Inner Cylindrical Pores of Carbon Nanotubes

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Supplementary Information

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Modeling Details

We employ first-principles computational methods to investigate the electronic properties of the polysulfides. Calculations based on Density Functional Theory are performed using the Vienna Ab-initio Simulation Package (VASP). Projector-augmented-wave potentials are used to mimic the ionic cores, while the generalized gradient approximation in the Perdew-Burke-Ernzerh flavor is employed for the exchange and correlation functional. We treat $1s^22s^1$ orbitals as the valence configuration for Li. The atomic structures and system energy are calculated with an energy cutoff of 400 eV. The energy optimization is considered complete when the magnitude of the force on each atom is smaller than 0.02 eV \AA^{-1} .

We study the density of states (DOS) as a measure of the electronic property of the intermediate states of lithiated sulfur. The pristine sulfur has a space group of Fddd and lattice parameters $a = 11.86 \text{ \AA}$, $b = 14.16 \text{ \AA}$, and $c = 26.17 \text{ \AA}$. The intermediate compounds Li_2S_8 and Li_4S_8 are generated by gradually inserting Li into the S lattice. The insertion sites are determined by the Delaunay triangulation analysis that the largest void spaces are regarded as the energetically-favorable positions for Li insertion. LiS and Li_2S are studied on the basis of their crystalline phases, LiS with the space group $\text{Fm}\bar{3}\text{m}$ and lattice parameters $a = b = c = 5.02 \text{ \AA}$, Li_2S with the space group $\text{Fm}\bar{3}\text{m}$ and lattice parameters $a = b = c = 5.72 \text{ \AA}$, respectively.

In-Situ TEM Details

The experiment was carried out inside a FEI Tecnai F30 TEM operating at 300 kV of accelerating potential. A low electron dose rate (electron beam intensity) less than 10 A/m^2 is

typically used under the magnification below 15k. The CNT-S nanostructures were dispersed in ethanol using an ultrasonic treatment, and a tip-flattened aluminum (Al) rod was dipped into the solution for several seconds. Some individual S-filled CNTs found at the edge of the Al rod served as working electrodes. Lithium metal was scratched on the tip of a tungsten wire from a freshly cut surface inside a glove box (with H₂O and O₂ concentration below 1 ppm), serving as the counter/reference electrode and Li source. Both the Al rod with S-filled CNTs and W wire with Li metal were mounted on the two sides of Nanofactory TEM-scanning tunneling microscopy (STM) holder inside the same glove box. A naturally-grown Li₂O layer on the surface of Li metal was formed during transfer of the holder into a FEI Tecnai F30 TEM with a sealed plastic bag, which served as solid-state electrolyte for allowing Li ion transport. Using a piezomanipulator the Li₂O/Li electrode was driven to contact with one of the selected S-in-CNT samples. Lithiation reaction was controlled by applying a constant potential hold to the WE vs. CE/RE. Potentials of -2 V vs. Li/Li⁺ was typically applied to drive the lithiation reaction.

Supplementary Figures

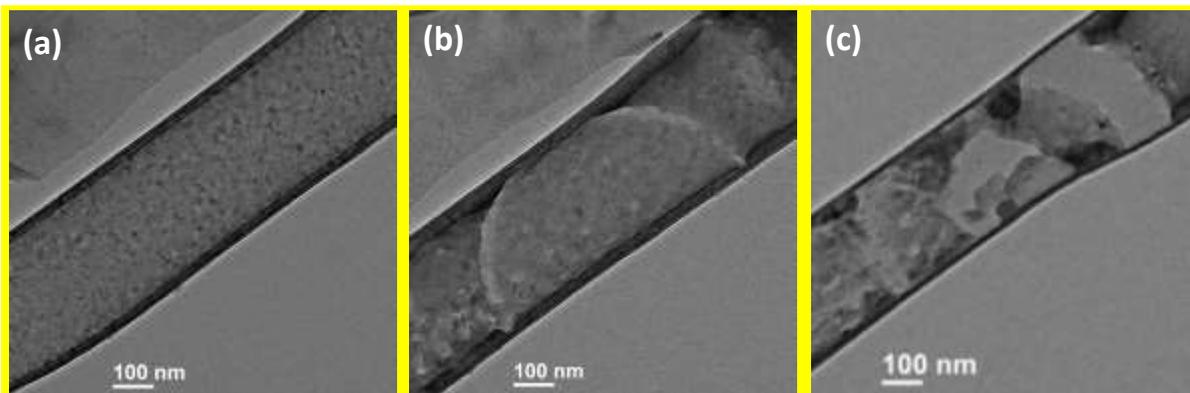


Figure S1: Low resolution TEM micrographs illustrating the damages induced in a sample during HRTEM studies (a) before HRTEM, (b) after HRTEM, (c) a nearby region after similar HRTEM studies.

Supplementary Movies

Movie S1: In-situ TEM lithiation of an individual S-in-CNT sample, showing a flat reaction front propagating along the cylinder length. The movie was recorded at 2 frames/sec and played at 40 frames/sec (i.e. 20x speed).

Movie S2: In-situ electron diffraction study of S-in-CNT sample, showing the phase transformation of pure S into nanocrystalline Li₂S. The movie was recorded at 2 frames/sec and played at 60 frames/sec (i.e. 30x speed).