Supporting Information

Exploring Reaction Dynamics in Lithium-sulfur Batteries by Time-resolved *Operando* Sulfur K-edge X-ray Absorption Spectroscopy

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Experimental section

Sulfur cathode preparation

The sulfur/carbon composite was prepared by dissolving the sulfur active materials into the carbon disulfide (CS₂) forming a 10 wt% solution. Then the carbon nanotube (CNT) was added into sulfur-CS₂ solution, followed by sonication for 25 min to form homogeneous slurry. A stirred process and ambient temperature were used to evaporate the CS₂ in the slurry. In order to improve the sulfur distribution inside the carbon framework via capillary action, finally, the obtained powder (90 wt% sulfur) in the last step was ground and heated at 155 °C for one night in Teflon-lined stainless-steel autoclave. The sulfur electrode was prepared by grinding a mixture containing the S-CNT composite, super P and polyvinylidenefluoride (PVDF) with a weight ratio of 90:5:5 in N-methyl pyrrolidone (NMP) solvent, then coating the mixture onto a carbon paper, and evaporating the solvent at 50 °C inside of a glove box and drying overnight.

Electrochemical measurements

Operando XAS experiments were carried out using a CR2032 coin cell with a 2 × 1 mm² window covered with a thin polyethylene film (8 μ m) to allow X-ray beam to pass through. Coin cell was assembled in an Ar-filled glove box with S/carbon paper electrode as working electrode, lithium foil as counter electrode and glassy fiber as the separator. 1 M LiClO₄ and 1.5 wt% LiNO₃ dissolved in a mixture of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1 in volume) was used as electrolyte. The Li-S cells were cycled at various discharge rate of 1/8 C, 1/2 C, and 2 C to a cutoff voltage of 1.5 V vs. the lithium metal anode (1 C = 1672 mA g⁻¹, based on a theoretical capacity of 1672 mAh g⁻¹ for sulfur).

X-ray absorption spectroscopy measurements

The *operando* sulfur K-edge XAS spectra were measured at beamline X15B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The XAS spectra were performed in fluorescence mode using a Si (111) double-crystal; Energy resolution was optimized and higher-order harmonics were eliminated by using a vertically collimating mirror between the source and monochromator.

Electrochemical kinetics simulation

To simulate the electrochemical kinetic conversation process of α -S₈ to long-chain soluble polysulfides Li₂S_x, a simplified electrochemical reaction model can be expressed as

$$S_8 + 2e^- \xrightarrow{k} S_n^2$$

Here k is reaction rate coefficient, quantifying the rate of the conversion process. Set the initial concentration of α -S₈ as c_0 , then it will be c_0 -c after reaction time t while the concentration of

polysulfides S_n^{2-} is c. Then the reaction rate v can be expressed as:

$$\nu = \frac{dlc}{dlt} = k(c_0 - c)^{\alpha}$$

Here α is defined as the reaction order. It can be assumed that the conversion reaction is a first-order reaction, i.e., $\alpha = 1$,

Rearrange to give:

$$\frac{dlc}{c_0 - c} = kdt$$

Integrate both sides of the equation, the concentration of polysulfides S_n^{2-} at time t is

$$c = c_0 \Big[1 - e^{-k(t - t_0)} \Big]$$

Here t_0 is initial time of Li polysulfides formation, it can be obtained from the discharging curve at different electrochemical rates. The initial concentration of α -S₈ c_0 at different rates can be normalized to 1.

Based on the specific electrochemical experiment data, the formula c(t) can be simulated at the discharging rate of 2 C, 1/2 C, and 1/8 C:



Figure S1. The kinetics simulation of conversion process of α -S₈ to long-chain soluble polysulfide



 Li_2S_x at the rate of 1/8 C, 1/2 C, and 2 C during the first discharging process.

Figure S2. The comparison of previous research rates used by various *in-situ/operando* characterization techniques. ¹⁻¹⁴



Figure S3. S K-edge XAS spectra of the S cathode collected simultaneously with electrochemical cycling at 1/2 C during the first discharging process.



Figure S4. S K-edge XAS spectra of the S cathode collected simultaneously with electrochemical cycling at 2 C during the first discharging process.



Figure S5. S K-edge XAS spectra of different discharged state (a, b, c, and d) at the rate of 1/8 C, 1/2 C, and 2 C during the first discharging process.

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