Supporting information for

Lithium Dendrite-free Plating/Stripping: A New Synergistic Lithium Solvation Structure Effect for Reliable Lithium Sulfur Full Battery

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Experimental section

Chemicals and Materials Preparation. The chemicals of LiTFSI, LiNO₃, DME and DOL were analytical grade and all purchased from Aladdin, which was used without further purification. The electrolytes of 1.0M LiTFSI/0.4M LiNO₃ (1.0M/0.4M) and 2.5M LiTFSI/0.4M LiNO₃ (2.5M/0.4M) in DOL/DME (v/v, 1:1) were prepared based on the stoichiometric ratio in the Ar-filled glovebox, respectively. The C-S powders and C-S was prepared accordingly.¹ The sulfur (Sigma-Aldrich) and Super P (i.e., carbon, C) with the mass ratio of 7:3 were mixed and thermal-melted at 200 °C to form a sulfur-containing composite. As-prepared S-C composite was mixed with poly(vinylidene difluoride) (PVDF) with mass ratio of 9:1 in NMP to form a slurry and then casted on the aluminum foil. After the electrode was dried at 40 °C in vacuum oven overnight, the electrode was punched into Ø13 mm circular discs for assembling the battery.

Electrochemical Measurements and Materials Characterizations. The lithium was plated on the copper foil using the 2032-type coin cell, in which the cell has the configuration of copper foil|separator (polypropylene)|lithium metal and the current density was set at 0.25 mA cm⁻² for 4, 8, 16, and 32 h, respectively. The linear sweep voltammetry (LSV) curves were measured using the Pt|Pt symmetric cell by VMP3 galvanostat (Bio-Logic) within voltage window of 0-5 V at a constant rate of 0.05 mV., in which the 1.0M/0.4M and 2.5M/0.4M electrolyte was used, respectively. The lithium plating/stripping process was carried using the Li|Li symmetric cell, in which the current density and the (dis-)discharge time was set at 0.5 mA cm⁻² and 4 h, respectively. To obtain the Li⁺ transference number of electrolyte, AC electrochemical impedance
spectroscopy (EIS) and DC polarization were used to test in symmetric cells with Li | electrolyte | Li, and then calculated by using the following formula: \[ t_{Li} = \frac{I_s (\Delta V - R_0 I_0)}{I_0 (\Delta V - R_s I_s)} \], where \( I_0 \) is the initial current when the DC voltage (\( \Delta V \)) was applied, \( I_s \) is the steady-state current, \( R_0 \) and \( R_s \) are resistances before and after DC polarization. The DC polarization was measured by applying \( \Delta V \) voltage of 10 mV, and the AC impedance was performed at a frequency of 200 kHz-10 mHz with 10 mV(AC) signal amplitude.

The lithium-sulfur full battery was assembled using the configuration of C-S cathode|separator (glass fiber) |Cu/Li, in which the Cu/Li was prepared first by lithium plating. An intercalated layer of carbon paper was inserted between the C-S cathode and the separator. The amount of plated lithium (i.e., total capacity) is controlled about three times higher than the total capacity of sulfur electrode. The mass loading of sulfur in electrode is about 1 mg cm\(^{-2}\), wherein the diameter of electrode and theoretical capacity of sulfur is 13 mm and 1675 mAh g\(^{-1}\), respectively. Then, the total capacity of plated lithium is 6.666 mAh (i.e., \( 1675 \times 1 \times 3.14 \times 0.65 \times 0.65 \times 3 = 6.666 \) mAh). The Galvanostatic cycling was conducted within the voltage window of 1.8-2.8 V using the programmable battery testing system (LAND CT2001A). The EIS was acquired over a frequency range of 200 kHz to 100 mHz using a BioLogic VMP3 Electrochemical Workstation. All cells were assembled in the Ar-filled glovebox, in which the content of oxygen and moisture was strictly < 0.5 ppm. Then, the Cu/Li electrode was dis-assembled from the coin cell in the glovebox and washed by DOL for the following experiments. The surface and cross-sectional morphology of Cu/Li electrode was
characterized by Hitachi S-4800 field emission scanning electron microscopy.

**Molecular Dynamics (MD) Simulations.** The classical MD simulations were performed using the similar strategy as we performed in previous work. The empirical force fields were obtained from the existing works, and the combination rule used in this simulation follows the OPLS style, namely, $\sigma_{ij} = (\sigma_{ii} \sigma_{jj})^{1/2}$ and $\varepsilon_{ij} = (\varepsilon_{ii} \varepsilon_{jj})^{1/2}$. To fully equilibrate the systems, the following procedures were performed: firstly, the systems were heated to 500 K at 1 atm in the NPT ensemble, employing the Nose-Hoover thermostat and barostat, and quenched to 300 K during a 5 ns simulation for three times; secondly, each system was equilibrated in the NPT ensemble at 300 K and 1 atm for another 5 ns, and the volume of the system were averaged from the last 3 ns simulation trajectory; thirdly, another 5 ns NVT simulation using the Nose-Hoover thermostat was performed for each system. Thereafter, the electrolyte was put onto the Cu (100) surface, and the partial charge of the surface Cu was assigned to be -0.05 to mimic the negative electrode. Additional 5ns NVT MD simulations were performed for each system, and the last configuration was used as snapshot.
Figure S1. Characterizations of plated Li. SEM of plated lithium in the (a) 1.0M/0.4M and (b) 2.5M/0.4M electrolytes for 16 h, respectively. The scale label is 20 μm.
Figure S2. Characterizations of plated Li. SEM of plated lithium in the (a-d) 1.0M, (e-h) 2.5M and (i-l) 5.0M electrolytes for (a, e, i) 4 h, (b, f, j) 8 h, (c, g, k) 16 h and (d, h, l) 32 h, respectively. Insets are the cross-sectional views. The scale label is 20 μm.
Figure S3. Characterizations of plated Li. SEM of lithium plated in the electrolyte of (a) 2.5M/0.4M and (b) 2.5M for 4 h, respectively. The scale label is 50 μm.
REFERENCES


