Supporting Information

Multifunctional self-supporting LLTO/C interlayer for high-

performance lithium-sulfur battery

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S1 Experimental Section

S1.1 Synthesis of LLTO/C nanofibers

First, prepare the spinning solution by dissolving acetic acid (2 mL) and polyacrylonitrile (Mw = 150,000 g/mol, 2.5 g) in dimethylformamide (16 mL), stirring to form a clear, uniform solution. After waiting for the bubbles to disappear, add lithium nitrate, lanthanum nitrate hexahydrate, and titanium butoxide to the solution, turning it yellow. Stir the mixture overnight.

Electro-spun the solution using a high voltage of 20 kV with a feeding rate of 0.9 mL/h. The distance between the needle tip and the aluminum collector should be fixed at 17 cm. The LLTO/C was obtained by heating at 380°C for 1 hour in air, then heating in argon at 800°C for 1 hour with a ramp rate of 1°C/min.

S1.2 Visualized Adsorption of Li₂S₆

A molar ratio of 5:1 of S to Li_2S was dispersed in a 1, 2-dimethoxyethane/1, 3-dioxolane (DME/DOL) solution with a volumetric ratio of 1:1. The resulting mixture was stirred at 60 °C for 24 h, yielding a 0.005 mol L^{-1} Li_2S_6 solution. To perform a visual adsorption test, 10 mg of MWCNTs and LLTO/C were separately added to the Li_2S_6 solution (1 mL). After 12 h, a final digital photograph was taken.

S1.3 Assembly of Symmetric Cells

LLTO/C was dispersed in ethanol, resulting in a uniform suspension after ultrasonic dispersion. This suspension was then dropped onto carbon paper (CP) and allowed to dry naturally at room temperature. The same method was used to prepare MWCNT

electrodes, with both electrodes having a mass loading of approximately 1 mg cm⁻².To assemble a Li_2S_6 symmetric cell, Celgard 2400 was employed as the separator, while two identical electrodes were used in the cell. The electrolyte comprised 40 µL of a DME/DOL solution (v/v = 1:1) containing 0.5 mol L⁻¹ Li₂S₆, 2.0 wt% LiNO₃, and 1.0 mol L⁻¹ lithium bis(trifluoromethanesulfonyl)imide (LiTFSI).

S1.4 Nucleation of Li₂S

Initially, Li₂S and S were dissolved in a DME/DOL (v/v = 1:1) electrolyte containing 1.0 M LiTFSI and 2.0 wt% LiNO₃, with a molar ratio of 1:7. After stirring at 60°C for 24 hours, a Li₂S= electrolyte ([S] = 0.25 M) was successfully prepared. For the experiment, LLTO/C was dispersed in absolute ethanol before dropping the suspension onto carbon paper (CP) with a diameter of 10 mm. The mixture was then dried at 60°C for 12 hours to create the electrodes. MWCNT electrodes were prepared using the same method. The resulting mass loading of both electrodes was approximately 1 mg cm⁻². For the nucleation of Li₂S, a 2032-type coin cell was utilized with Celgard 2400 as the separator. Lithium metal foil was used as the anode, and the prepared electrodes were used as the working electrode. A Li₂S₈ electrolyte (20 μ L) was applied to the anode. The cells were galvanostatically discharged at 0.112 mA until the voltage reached 2.06 V. The voltage was then maintained at 2.05 V to facilitate Li₂S nucleation. The tests were completed using a VMP3 multichannel electrochemical workstation (BioLogic, France).

S1.5 Assembly of the Cells and Electrochemical Measurements

The MWCNT and sulfur powder were ground together for 30 min to ensure thorough mixing. The resulting mixture was heated at 155°C for 12 h in a stainless-steel autoclave to obtain MWCNT/S. The MWCNT/S composite was then mixed with LA133 and Super P in a mass ratio of 8:1:1 in water to form a homogeneous suspension. This suspension was coated onto aluminum foil and dried at 60 °C for 12 hours in an oven. The dried cathodes were then punched into disks with a diameter of 13 mm, achieving a sulfur loading of approximately 1.5 mg cm⁻².

The LLTO/C interlayer was prepared by punching LLTO/C nanofibers into disks with a diameter of 15 mm. The MWCNT separator was prepared by dissolving MWCNT and polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidinone (NMP), followed by filtering the solution over a separator. The masses of LLTO/C and MWCNT for the interlayer and separator were controlled to be around 3.5 mg. The thickness of the LLTO/C interlayer is around 30 μ m and the MWCNT separator is around 10 μ m as shown in Fig.S11.

Electrochemical measurements were carried out using 2032-type coin cells. The setup included a Li foil as the anode, Celgard 2400 as the separator, and an LLTO/C interlayer with an MWCNT/S cathode. A control experiment used a similar setup but directly incorporated the MWCNT separator. The electrolyte consisted of 1.0 M LiTFSI and 2.0 wt% LiNO₃ in a DME/DOL (v/v = 1:1) solution. Galvanostatic discharge/charge (GCD) tests were conducted within a voltage range of 1.7 to 2.8 V using a LANCT battery test system (Wuhan, China). Cyclic voltammetry (CV) measurements were

performed using a VMP3 multichannel electrochemical workstation (Biologic, France), within a voltage range of 1.7–2.8 V and at a scan rate of 0.1 mV s⁻¹.

S1.6 Assembly of Symmetric Cells

LLTO/C was dispersed in ethanol, resulting in a uniform suspension after ultrasonic dispersion. This suspension was then dropped onto carbon paper (CP) and allowed to dry naturally at room temperature. The same method was used to prepare MWCNT electrodes, with both electrodes having a mass loading of approximately 1 mg cm⁻². To assemble a Li_2S_6 symmetric cell, Celgard 2400 was employed as the separator, while two identical electrodes were used in the cell. The electrolyte comprised 40 µL of a DME/DOL solution (v/v = 1:1) containing 0.5 mol L⁻¹ Li₂S₆, 2.0 wt% LiNO₃, and 1.0 mol L⁻¹ lithium bis(trifluoromethanesulfonyl)imide (LiTFSI).

S1.7 Characterization of the Materials

The morphology and microstructure of all samples were characterized using scanning electron microscopy (SEM, SU70, Hitachi, Japan) and transmission electron microscopy (TEM, FEI, Tecnai TF20), respectively. X-ray diffraction (XRD, Rigaku D/max2600 with Cu K α) was carried out in the range of 10–80° to detect the crystalline structure. The nitrogen adsorption/desorption isotherms were obtained on an ASAP 2010 accelerated surface area and porosimetry instrument (Micromeritics). X-ray photoelectron spectroscopy (XPS, Kratos AXIS SUPRA+ with a monochromatic Al K α source) was used to evaluate the surface chemical states of samples.

1.8 Calculation of the Li⁺ ion diffusion properties

$$Ip = 2.69 \times 10^5 \times n^{1.5} \times A \cdot D_{Li}^{+0.5} \times C_{Li}^{+} \times v^{0.5}$$

In this equation, Ip represents the peak current, n is the number of electrons involved in the reaction, A is the cathode area, C_{Li}^+ denotes the Li⁺ concentration in the electrolyte (mol mL⁻¹), and v is the CV scanning rate (V s⁻¹).

Supplementary figures



Figure S1. GCD profiles of a MWCNT cell.



Figure S2. Polarization voltage of the LLTO/C cell and MWCNT cell at different rates

from 0.1 to 7 C.



Figure S3. GCD profiles of the LLTO/C cell at various cycle numbers at 0.1C.



Figure S4. Radar chart comparing the performances of the cathodes with previously reported LLTO-based cathode or interlayer including VN@NG⁴⁰, NC/G⁴¹,

TiO₂@MoS₂⁴², SC-Co⁴³.



Figure S5. GCD profiles of the LLTO/C cell at various cycle numbers at 5 C.



Figure S6. High-resolution XPS spectra of La 3d before and after adsorption.



Figure S7. High-resolution XPS spectra of O 1s before and after adsorption.



Figure S8. Tafel plots corresponding to oxidation of Li₂S.



Reaction coordinate

Figure S9. Relative activation energy of Li_2S to Li_2S_n .



Figure S10. CV curves of the MWCNT cell at different scan rates.



Figure S11. Lithium-ion diffusion rate corresponds to the reductions and oxidations

of (a) R1, (b) R2, (c) O1, and (d) O2.



Figure S12. Cross-sectional SEM images of the LLTO/C interlayer and MWCNT

interlayer.