Supporting Information

Realizing compatibility of Li metal anode in all-solid-state Li-S battery by chemical iodine-vapor deposition

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Experimental Section

The preparation of the LiI layer on Li metal surface: Li foil was polished and punched into 10 mm-diameter discs. Iodine particles (99.99%, Aladdin) were ground into powder by hand milling. The five treated Li pieces and 0.5 g of iodine power were sealed in a strain bottle in an argon-filled glovebox with oxygen and water (<0.1 ppm). Then, the strain bottle was heated to 120 °C for 12 h before cooling down to room temperature to obtain the final LiI layer on Li metal.

Preparation of fluorine-containing SEI: The LiTFSI–LiNO₃ electrolyte comprised 1 mol LiTFSI with DME/DOL (volume ratio = 1:1) and 3 wt% LiNO₃. Adding LiFSI to the LiTFSI–LiNO₃ electrolyte until LiFSI:LiTFSI = 2:1 (molar ratio) produced the LiTFSI–LiNO₃–LiFSI electrolyte. This electrolyte was used to assemble a Li-Cu battery. This battery was cycled 10 times at a current density of 0.5 mA cm² and subsequently disassembled. The Li film with fluorine-containing SEI was washed with DME several times and dried at 60 °C in a glove box overnight. **Preparation of LGPS and S cathode with a KB (S@KB):** LGPS was purchased from MTI. To evaluate the ionic conductivity of LGPS. About 150 mg of powder was placed in a homemade mold cell (10 mm in diameter) and pressed at 280 MPa for 5 min. The LGPS thickness was about 1 mm. The EIS, SEM, and XRD of pristine LGPS are shown in **Figure S18**. The calculated ionic conductivity was about 2×10^{-3} S cm⁻¹. As for S@KB cathode, a typical melt-diffusion method was used to prepare the S@KB composite material. First, 150 mg of KB and 350 mg of sulfur were mixed and ground for 1 h. The powders were then placed in a sealed autoclave accompanied by sintering at 155 °C for 5 h under Ar atmosphere. Finally, the mixture was reground and heated at 200 °C for 2 h to obtain the final product.

Cell Assembly: (i) Symmetric cell: 150 mg of power was placed in a mold cell (10 mm in diameter) and pressed under 280 Mpa for 5 min. Then, the pristine Li or LiI-coated Li anode electrode was laid on both side of LGPS and pressed under 80 Mpa. (ii) All-solid-state Li-sulfur battery: the cathode materials were obtained by mixing the S@KB, LGPS, and acetylene black with a weight ratio of 3:4:1 and balling together for 10 h at 500 rpm using high-energy ball milling. In a homemade mold cell, 150 mg of LGPS was pelletized under 280 MPa. After spreading a certain amount of cathode materials on one side of the LGPS pellet, it was pressed under 190 MPa for 5 min. A Li or LiI-coated Li electrode was placed on another side of the LGPS pellet, and the whole cell was pressed under 80 Mpa. A steel frame was used to keep the cell under pressure.

Electrochemical Tests: All-solid-state Li-sulfur batteries and symmetric cells were tested by the LAND system from 1.2 V to 3.0 V at room temperature. The battery specific capacity was calculated based on the mass of sulfur in the cathode. Alternating-current impedance tests were performed on an impedance analyzer (Solartron 1287 coupled with Solartron 1260). A perturbation voltage of 5 mV in the frequency range of 1 MHz to 0.1 Hz was applied. ZPlot software was used to analyze the experiment data.

Materials Characterization: LGPS and LiI (1:1 in wt.) were mixed thoroughly by ball milling for 6 h on 400 rpm. X-ray spectroscopy test was performed using PHI 5000 VersaProbe (Ulvac-Phi Co.). XRD measurements were performed with a Rigaku Ultima III. SEM characterization was conducted on a Hitachi SU8010 scanning electron microscope. Solid-state NMR measurement was performed on a Bruker AVANCE III 400 MHz NMR spectrometer using a 4 mm DVT MAS NMR probe at room temperature, with a ⁷Li Larmor frequency of 155.5 MHz. The samples were packed into the center of the rotors, and the spinning rate was set to 8–10 kHz. AFM (Asylum Research Cypher S AFM) and AC160TS-R3 tip (Olympus) were used to analyze the surface smoothness and Young's modulus. Sneddon model was used to fit the force curves. Over 100 spots were randomly chosen on the selected region and, the number of Young's modulus in the specific range was counted. AFM force curves were obtained in a glove box to avoid sample oxidation.



Figure S1 | The inner structure of human leg bone (a) Optical image of cross-section of actual human bone. Reproduced with permission, copyright science source image, 2021. (b) Sectional model diagram.



Figure S2 | Rietveld refinements of XRD patterns of (a) commercial LiI powder and (b)Nano-LiI crystal prepared by CIVD. (c) Schematic diagram of the corresponding crystal structure. The LiI layer prepared by CIVD showed increased lattice parameters in the b-axis and c-axis directions, especially in b-axis direction.



Figure S3 | SEM image of LiI layer. (a) Top-view SEM image. (b) Cross-sectional SEM image. (c-d) back-scattered electron image and its corresponding EDS energy spectrum.



Figure S4 | Surface roughness of (a) LiI layer and (b) Fluorine-containing SEI. The surface of the prepared LiI layer was continuous and relatively flat, while the fluorine-containing SEI showed an uneven surface with abundant randomly distributed particles.



Figure S5 | (a) Cross-sectional SEM image of Li/LiI/LGPS three-phase interface. The area within the white dashed line represents the LiI layer (b) EDS spectrum of Li/LiI/LGPS three-phase interface.



Figure S6| (a) The cross-section image of LGPS/Li interface with LiI layer after 400 cycles in Li/LiI/LGPS/LiI/Li cell and (b-f) corresponding EDS spectra. The diffusion of LiI caused by the volume change can be observed.



Figure S7 | the XRD patterns of pristine LiI (green line), pristine LGPS (blue line), and the mixture of LiI and LGPS with the weight ratio of 1:1. (red line). No peak change occurs for the mixture of LGPS and LiI after ball milling, demonstrating that LiI is chemically stable with LGPS.



Figure S8 | EIS results of LiI pellet at 25°C. The thickness of the LiI pellet is 300µm. The ionic conductivity calculated by $\sigma = \frac{L}{R \times A}$ is 2.5×10⁻⁷ S cm⁻¹, corresponds to those mentioned in the previous literature



FigureS9 (a)TGA curve for the S cathode with a Ketjen Black (KB), yielding a sulfur content of \approx 75 wt% at a ramp rate of 10 °C min⁻¹ under Ar flow.



Figure S10 Electrochemical curve of Li/LGPS/S cell in Figure 5a. A huge overpotential was observed for the cell at 20th cycle, which was attributed to the irreversible decomposition of LGPS against Li metal.



Figure S11| the comparison of the electrochemical curve between Li/LGPS/S cell and Li/In /LGPS/S cell under the same test parameters.



Figure S12| The electrochemical curve of (a) Li/LiI/LGPS/S cell and (b) Li/LGPS/S cell tested at different rates at 25°C. the Li/LiI/LGPS/S cell showed specific capacities of 1400, 1271 and 872 mAh g⁻¹ at 0.1C, 0.2C and 0.5C respectively, while significant lower specific capacities for the Li/LGPS/S cell was observed, amounting 1369, 871 and 297 mAh g⁻¹ at 0.1C, 0.2C and 0.5C respectively. This proves a seriously deteriorated Li/LGPS interface at high current densities without the protection of LiI layer.



Figure S13 (a) Galvanostatic cycling performance and (b) corresponding charge/discharge profiles at 25°C at an ultrahigh mass loading of 6.5 mg cm⁻². The cell exhibited the highest reversible capacity up to 8.87 mAh cm⁻² at a current density of 0.2 mA cm⁻² for the first cycle. The corresponding specific capacity is 1364 mAh g⁻¹. This cell displayed a capacity decay, but still delivered a reversible capacity of 5.13 mAh cm⁻² after 8 cycles. The reason for cell failure can be attributed to the interface contact problem caused by the huge volume expansion of the cathode material.



Figure S14| The comparison of the discharge voltage and the areal capacity of the all-solid-state Li-S battery reported recently.



Figure S15| (a) Cycling performance of the Li/LGPS/S cell at 0.5 mA cm⁻² at 60°C. (b) Charge/discharge curves in different cycles at 0.5 mA cm⁻² at 60°C. The cell showed a quick capacity fading from ~1150 mAh g⁻¹ to ~200 mAh g⁻¹ within 50 cycles. A huge overpotential was observed for the cell at 40th cycle.



Figure S16| (a) Cycling performance of Li/LiI/LGPS/S cell at 0.5 mA cm⁻² at 60°C. The cell presents discharge capacity of 1308.6 and 1240 mAh g⁻¹ in first and second cycle. It can maintain a capacity of 881 mAh g⁻¹ after 150 cycles. (b) Cycling performance of Li/LiI/LGPS/S cell at 1 mA cm⁻² at 60°C. The cell presents an initial discharge capacity of 965 mAh g⁻¹ and it increased slowly to 1113.3 mAh·g⁻¹ in the first ten cycles due to the activation process of cathode material. it can maintain a capacity of 875 mAh g⁻¹ after 100 cycles.



Figure S17| Stacked Nyquist plots of Li/LiI/LGPS/S cell during the discharge and charge process. Galvanostatic charge/discharge was carried out at 0.2C. The resistance gradually increases during discharging and back to the beginning after complete the charging process.



Figure S18 (a)The EIS plot (b) SEM image and (c) XRD pattern of LGPS.



Figure S19 Porosity calculation of LiI layer. (Computational support provided by image-pro plus 6.0) we have calculated the porosity of the cross section of the LiI layer, the proportion of voids is about 24%.

NoteS1:

Estimation of the ionic conductivity of the LiI layer:

By comparing the resistance of Li symmetrical cell with Lil@Li layer symmetrical cell, the ionic conductivity of the nano-scale Lil layer can be obtained by the following calculation (Data is obtained from Figure3b-c).

 $R_{Lil} = R_{1.5\mu m * 2} \approx R_{Lil@Li \ symmetrical \ cell} - R_{Li \ symmetrical \ cell} = 182 \ \Omega - 92 \ \Omega = 90 \ \Omega$

Since $R_{Lil} = \frac{L}{\sigma A}$ $\sigma = \frac{L}{AR_{Lil}} = \frac{3 \, \mu m}{0.5 \text{ cm}^2 \times 3.14 \times 90\Omega} = \frac{3 \times 10^{-4} \text{ cm}}{0.5 \text{ cm}^2 \times 3.14 \times 90\Omega} = 4.2 \times 10^{-6} \text{ S cm}^{-1}$

Where R_{LiI} is the resistance of LiI Layer, L is the thickness of LiI layer, A is the area of LiI layer. σ is the ionic conductivity.