A paint layer for high-rate and high-capacity solid-state lithium-

metal batteries

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Figure S1. Nyquist plot of garnet ceramic electrolyte at room temperature (garnet wafer: diameter 15mm, thickness 2mm)

The two sides of garnet wafer were covered by uniform silver slurry and polished before using. Agilent E4980A was used to get the Nyquist plot at room temperature. Based on the ohm law, we can get the ionic conductivity of the garnet ceramic electrolyte at room temperature.

$$\sigma = d/S \cdot R$$

 σ is the ionic conductivity, d (2 mm), S (1.76 cm²) and R (523 Ω) are the thickness, surface area and resistance of garnet wafer, respectively. So, we can get the σ =2.17×10⁻⁴ S cm⁻².



Figure S2. The XRD pattern of the graphite coating layer

The graphite paint powder is firstly sprayed on a piece of clean stainless steel and then scraped off after the solvent volatilization. Before the XRD pattern measurement, there is no drying process for the graphite powder. As shown below, the XRD result of the graphite coating layer is matched with the standard graphite XRD peaks (PDF#41-1487).



Figure S3. The optical photograph of the GCL-garnet solid electrolyte after stickup and the two torn tapes. There is only a little graphite torn off from the coating in the first time and barely for the second tape.



Figure S4. The top-view SEM image of the graphite layer



Figure S5. The cross-section SEM images of SSE with graphite coating

A thicker graphite coating layer is achieved by increasing the operation time in figureS4, which still shows the uniform thickness and compact structure without any desquamation. In the magnified image, the intimate contact between the coating layer and the SSE can be found.



Figure S6. XRD of the Li-rich lithium-graphite alloy layer.



Figure S7. Nyquist plot of Li | Garnet SSE | Li cell at room temperature.



Figure S8. The voltage profile of Li | Garnet | Li cell operated at 0.05 mA cm⁻².

The voltage curve shows severe noise in each cycle and a huge polarization in less than 5h, indicating a bad interface evolution during Li plating/stripping processes.



Figure S9. the magnified typical voltage-time profile of the symmetric cell at the different current density



Figure S10. The e;ectrochemical behavior of the Li-S full batteries. (a, b) electrochemical impedance spectroscopy plots and (c) typical voltage-capacity profile ; (d) The discharge capacity of the first ten cycles of a Li-S battery with modified SSE.

Obviously, the Li-S device without GCL on the garnet SSE shows a large ASR (area specific resistance). By contrast, the one with GCL on the garnet SSE reveals a significant ASR decrease. In the galvanostatic discharge/charge test, the typical voltage-capacity profiles of the first cycle at 0.1 mA cm⁻² are performed in figure 2c. due to the tremendous ASR, the Li-S device without GCL shows almost no discharge/charge capacity. While, the Li-S full battery with the garnet SSE modified by GCL exhibits the typical discharge/charge curves. The multiple voltage plateaus in the discharge/charge process also indicate polysulfides formation.



Figure S11. Schematic of the graphite coating layer preparing process by spray; time is 2 second.

Experimental section

Materials synthesis

 $Li_{6.5}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) garnet ceramic electrolyte was synthesized by a conventional solid state reaction of stoichiometric amounts of Li_2CO_3 , La_2O_3 , ZrO_2 and Ta_2O_5 at 1140 °C for 16 h in air atmosphere. The thickness ~ 300µm of the garnet sheet was prepared and all the garnet ceramic sheet used are the same batch. Graphite spraying paint was bought from KONTAKT-SuZhou YongKang Technology co., LTD.

Materials measurement

SEM images were got from a high-resolution SEM (Zeiss). X-ray diffraction (Bruker AXS, using a Cu K α radiation source operated at 40 kV and 40 mA) performed the phase measurement. Raman curves were carried out by WITec with $\lambda = 633$ nm laser. Square resistances were tested by four-point probe method with five random points. The Li⁺ conductivity of LLZTO was measured by Agilent E4980A at room temperature. Typically, the two sides of the LLZTO pellet were polished by using polishing papers with a grit number of 400. Then, uniform silver slurry was covered to the two sides of it before examine.

Electrochemical characterization

The flake-graphite coating layer on garnet solid electrolyte was prepared by a spraying method. Typically, a hole with the area of $\sim 1 \text{ cm}^2$ was made on a common transparent adhesive tape by a punch. Then, to make a refined coating, this adhesive tape was adhered carefully on one side of the garnet electrolyte. The graphite paint can be easily

achieved after the organic solvent volatilizing on the garnet electrolyte. The thickness of the coating also can be controlled by adjusting the distance and the time, as shown in figure S11. The graphite coating layer displays no further treatment before alloy process. The symmetric Li | garnet (garnet-graphite) | Li cells were assembled in a glovebox filled argon (99.999%) with moisture and oxygen levels below 0.1 and 0.1 ppm. Two sides of garnet SSE pellet with flake-graphite layer coated was sandwiched by two lithium foil (240 µm for thickness,) and heated at 230 °C for 3h. The two lithium foil were affixed to two stainless-steel pellet ($\sim 1.8 \text{ cm}^2$) treated as the current collectors. A certain pressure was used to reinforce the lithium contacting to the electrolyte. Here, four stainless-steel wafers were used and the mass of each one is 1.5 g. Here, the electrochemical performances are tested in the glovebox where wires are spread out to connect the test systems. EIS (electrochemical impedance spectrum) measurement was tested by Autolab working station in a frequency range of 1 MHz to 0.1 Hz with a 50 mV perturbation amplitude. The electrochemical performance was obtained at room temperature with a LAND batteries test system.

Li-S full batteries assembling and test

The sulfur cathode is prepared in a traditional method: sulfur powder, carbon black and polyvinylidene fluoride (PVDF) binder with a mass ratio of 8:1:1 are dissolved in N-methyl-2-pyrrolidone (NMP) solvent to obtain the composite slurry. The electrode is dried in vacuum at 80 °C for 12h with aluminum sheet as the current collector. The sulfur element loading is about 1.6 mg/cm². Trace ionic liquid (AMIMTFSI, 6 μ L/cm²) is used to wet the sulfur cathode. The alloy anode in situ formed on the modified SSE

is developed through a heating process as same as fabricating the symmetric cell in which only one side of the garnet SSE is modified by the graphite coating layer. The assembled Li-S battery is sealed in a glass bottle and this glass bottle is also placed in the glove-box. To test the electrochemical behavior, two conductive lines are used to connect the Li-S battery device. The EIS was performed in a frequency range of 1 MHz to 100 mHz with a 50 mV perturbation amplitude. The galvanostatic discharge and charge test is measured using a cutoff voltage window of 1.3 to 3.2 V. Autolab working station (Metrohm AG) and LAND batteries test system (wuhan) are adopted.