In-Situ Constructed Polymer Layer Modified Dry-Processable Solid Electrolytes Enables High-Performance All-Solid-State Batteries

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Method

Preparation of LiPSCl SSEs: The preparation of SSEs is conducted entirely under an argon gas environment in a glove box. A precise quantity of PTFE binder (0.1%) and sulfide electrolyte Li_6PS_5Cl (99.9%) is weighed and mixed thoroughly in an agate mortar, then vigorously ground until the materials form a cohesive sheet-like film, and subsequently flattened to the desired thickness using a hot rolling press.

Preparation of LiPSCl@PCSSE: [VBIM][TFSI] IL polymer monomer, PEGDA polymer monomer and LiTFSI lithium salt were combined in a mass ratio of 28:5:12, agitated with magnetic stirrers for 2 h, and then mixed with 1 wt.% AIBN (as the initiator of in-situ polymerization) for 1 h. The slurry was evenly coated onto the surface of SSEs film using a precision coating device. LiPSCl@PCSSE (polymer-sulfide composite solid electrolyte film) was obtained by vacuum drying at 60 °C for 24 h followed by curing.

Preparation of cathode and anode: In a controlled argon atmosphere within a glovebox, NCM811, Li_6PS_5Cl, VGCF conductive agent, and PTFE binder were meticulously combined in a milling jar in a mass ratio of 85:15:1:1. After ball milling and hand grinding, a seamless sheet-like electrode can be obtained. Subsequently, the cathode sheet was thinned to the desired thickness or load using a hot rolling press. The preparation methods for the anode are similar to those for the cathode, with graphite being used to replace NCM811.

Preparation of solid-state battery: The composite cathode sheet, the as-prepared SSEs, and the anode sheet were stacked together in sequence, and then pressed into shape under a pressure of ~450 MPa.

Characterization: The microstructure was characterized by SEM and EDS using Hitachi SU8010 scanning electron microscope. Electrochemistry related tests were carried out at Princeton PMC-1000 electrochemical workstation. The rate and cycle performance were evaluated by the LAND battery test system.

Electrochemical measurement: To measure the ionic conductivity (σ) of electrolytes, the coin cells with the stainless steel (SS)/electrolyte/SS configuration were assembled to perform the electrochemical impedance spectroscopy (EIS) measurement with the frequence from 10^6 Hz to 0.1 Hz and the AC amplitude of 10 mV at 30−70 °C. The calculation formula of ionic conductivity was shown in the Equation S1:

$$\sigma = \frac{L}{RS} \qquad (1)$$

where L represents the thickness of the electrolyte film, R is the electrolyte resistance obtained from the EIS results and S is the area of the SS electrode.

The distribution of relaxation time (DRT) analyses of Li symmetric cells at different temperatures were carried out by the MATLAB GUI tool box developed by Ciucci's research team

The exchange current density of Li plating/stripping processes was determined by Tafel fitting of LSV results from −0.05 V to 0.05 V with a scanning rate of 0.1 mV/s of Li symmetric cells. The electrode reaction kinetics of NCM811 full cells were characterized by CV with a voltage range from 2.5 V to 4.25 V.

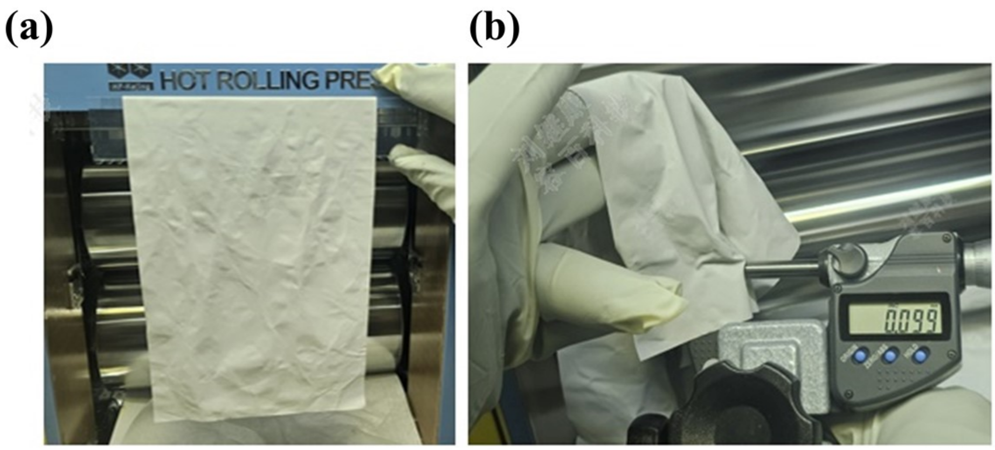

Fig. S1 (a) The digital graph, (b) the thickness of LiPSCl up to about 100 μm.

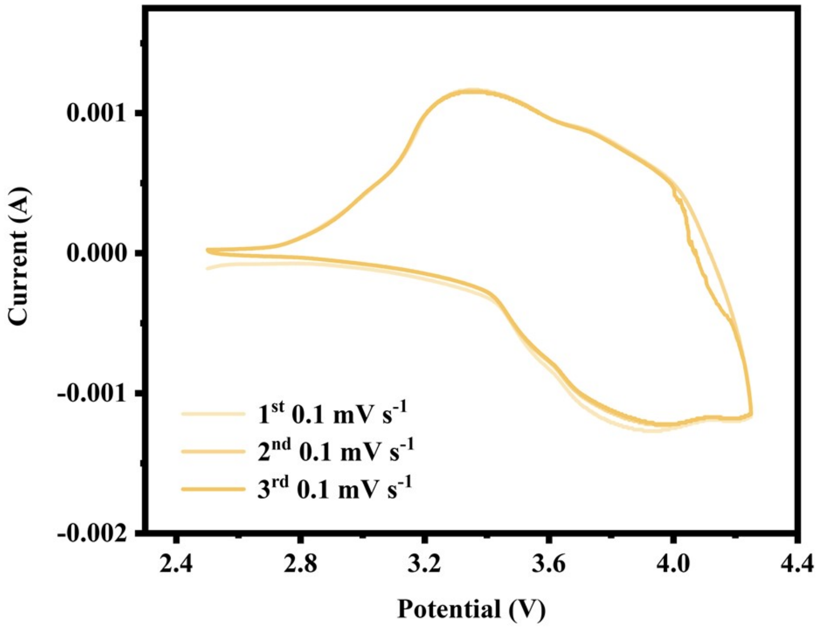

Fig. S2 The first three CV curves at 0.1 mV s^{-1} of the cell with LiPSCl.