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Electronic Supplementary Information

Optimizing milling and sintering parameters for mild synthesis of highly conductive $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ solid electrolyte

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Experiment Section

Solid Electrolyte Synthesis: The starting materials, LiCl (99%, Macklin), P₂S₅ (99%, Macklin) and Li₂S (99.98%, Sigma-Aldrich) were accurately weighed in a predetermined ratio to synthesize Li_{5.5}PS_{4.5}Cl_{1.5} SEs. Initially, a precursor was ball milled using a planetary ball milling apparatus (Retsch, PM 200) with a WC-coated stainless-steel pot and WC balls at various speeds (350, 400, 450, 500, 550 rpm) for 16 hours, with a 10-minute break every 30 minutes. These conditions were denoted as 350 rpm-BA, 400 rpm-BA, 450 rpm-BA, 500 rpm-BA, and 550 rpm-BA. The total weight of the starting materials in each pot was 2.0 g with the ball-to-precursor weight ratio 40:1. The as-milled material was then pressed into pellets at 360 MPa and sealed in vacuum quartz ampoules. Subsequently, the ball-milled mixtures were annealed at 350, 400, 450, and 500 °C for 5 hours with the heating rate of 2 °C min⁻¹, resulting in AA-Li_{5.5}PS_{4.5}Cl_{1.5} electrolytes labeled as 350 °C-5 h, 400 °C-5 h, 450 °C-5 h, 500 °C-5 h, and 550 °C-5 h, respectively. After optimizing the annealing temperature, the condition was fixed at 400 °C-5 h. The samples were naturally cooled to room temperature in the furnace.

Characterization: X-ray diffraction (XRD) patterns were obtained using a diffractometer (Rigaku MiniFlex600/600-c) equipped with a Cu K α radiation source to identify the SE phases. The XRD data were collected within the 2 θ range of 10° to 70° at a scan rate of 5° per minute. To prevent side reactions with moisture and oxygen, the samples were shielded with a polyimide film. Raman spectra were acquired using a Raman spectrometer (LabRAM HR800) with a 532 nm excitation source, covering the range from 100 to 800 cm⁻¹. The samples were sealed in a custom-made chamber covered with a quartz glass capillary tube within a glovebox.

Electrochemical Measurements: For ionic conductivity determination, 100 mg of SE powder was pressed into pellets with a diameter of 10 mm and a thickness of 0.75mm under a pressure of 380 MPa. Stainless steel rods were attached to the pellets to act as current collectors. Alternating current (AC) impedance measurements were conducted using an impedance analyzer (Bio-Logic SP-300) over a frequency range of

7 MHz to 0.1 Hz, with an amplitude of 10 mV at room temperature. Activation energy tests involved collecting impedance data over a temperature range of 30 to 70 °C. The ionic conductivities of the prepared samples at different temperatures were characterized using the AC impedance method. The activation energy was calculated using Nyquist plots, as shown in Fig. S1, Fig. S2 and Fig. S3, based on the Arrhenius equation $\sigma_{\text{ion}T} = \sigma_0 \exp(E_a/k_B T)$, where σ_{ion} stands for the ionic conductivity of $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$, σ_0 is a pre-exponential factor, T is the absolute temperature, and k_B is the Boltzmann constant.

Cell Assembly and Test: For the preparation of composite cathodes, LTO, SE, and CNF powders were thoroughly mixed in specific weight ratios by hand in an agate mortar for 15 minutes. Subsequently, the mixture was ball-milled at a rotation speed of 110 rpm for 1 hour. The resulting composite electrode powders were utilized as working electrodes in all-solid-state batteries (ASSBs). In/InLi| $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ |LTO- $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ -CNT5 ASSB cells were fabricated for galvanostatic cycling tests. The assembly process involved pressing 80 mg of $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ powder into a poly(ether-ether-ketone) model with a diameter of 10 mm. Subsequently, 2 mg of the composite cathode was evenly spread on one side of the solid electrolyte layer under 380 MPa. An indium foil ($\phi 10$, thickness: 50 μm) and a lithium foil ($\phi 5$, thickness: 50 μm) were attached to the other side of the solid electrolyte layer, and the assembly was pressed under 150 MPa. Galvanostatic charge-discharge cycling tests were performed using a multi-channel battery test system (LAND CT2001A) and (Neware CT-ZWj-4s-T-1U) in a voltage range of 0.4-1.9 V (vs. In/InLi), corresponding to 1-2.5 V (vs. Li^+/Li) at 25 °C (RT), and 60 °C (HT). The entire assembly and test procedures were conducted under Ar atmosphere in a glovebox ($\text{O}_2 < 0.1$ ppm, $\text{H}_2\text{O} < 0.1$ ppm).

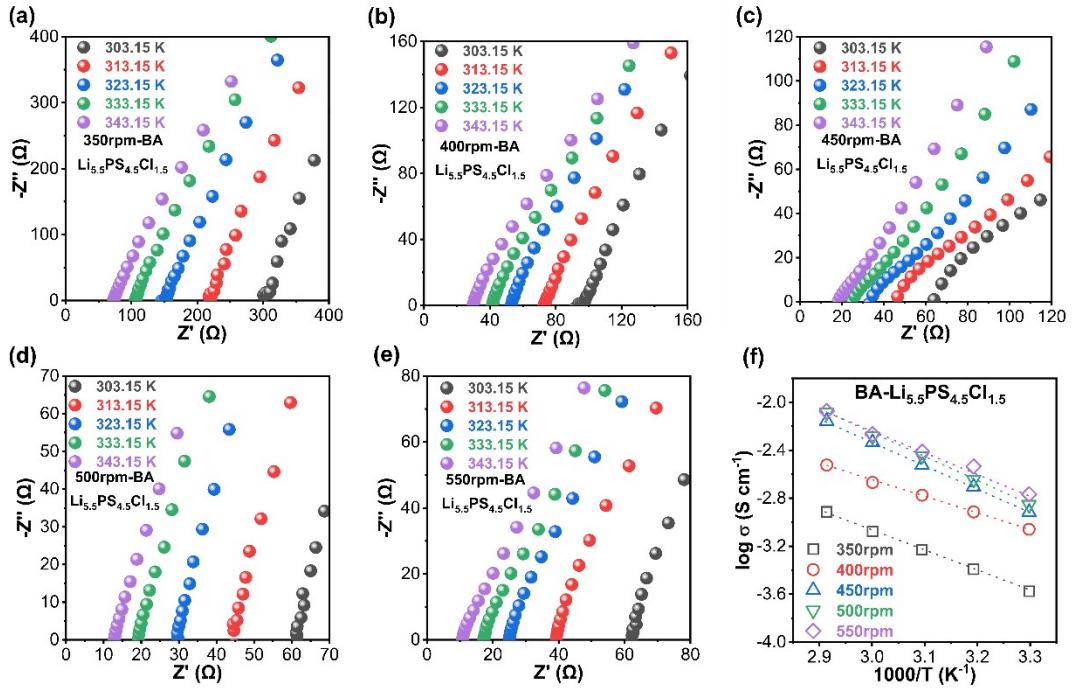


Fig. S1. Li-ion conductivity of the BA-Li_{5.5}PS_{4.5}Cl_{1.5} obtained from different rotation speeds (a) 350 rpm (b) 400 rpm (c) 450 rpm (d) 500 rpm (e) 550 rpm and (f) the corresponding Arrhenius plots.

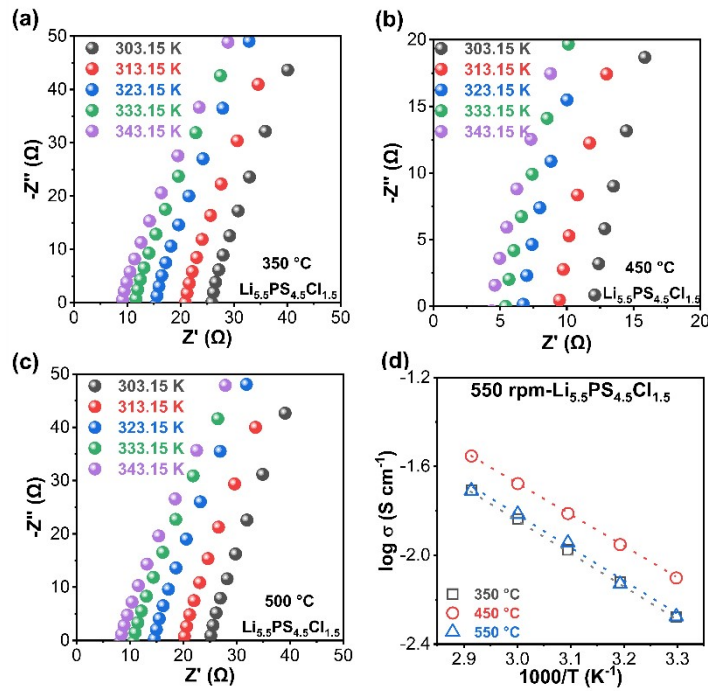


Fig. S2. Li-ion conductivity of the 550 rpm-Li_{5.5}PS_{4.5}Cl_{1.5} obtained at various sintering temperatures (a) 350 °C (b) 450 °C (c) 500 °C and (d) the corresponding Arrhenius plots. (550 rpm-Li_{5.5}PS_{4.5}Cl_{1.5} obtained at 400 °C shown in Fig. S3)

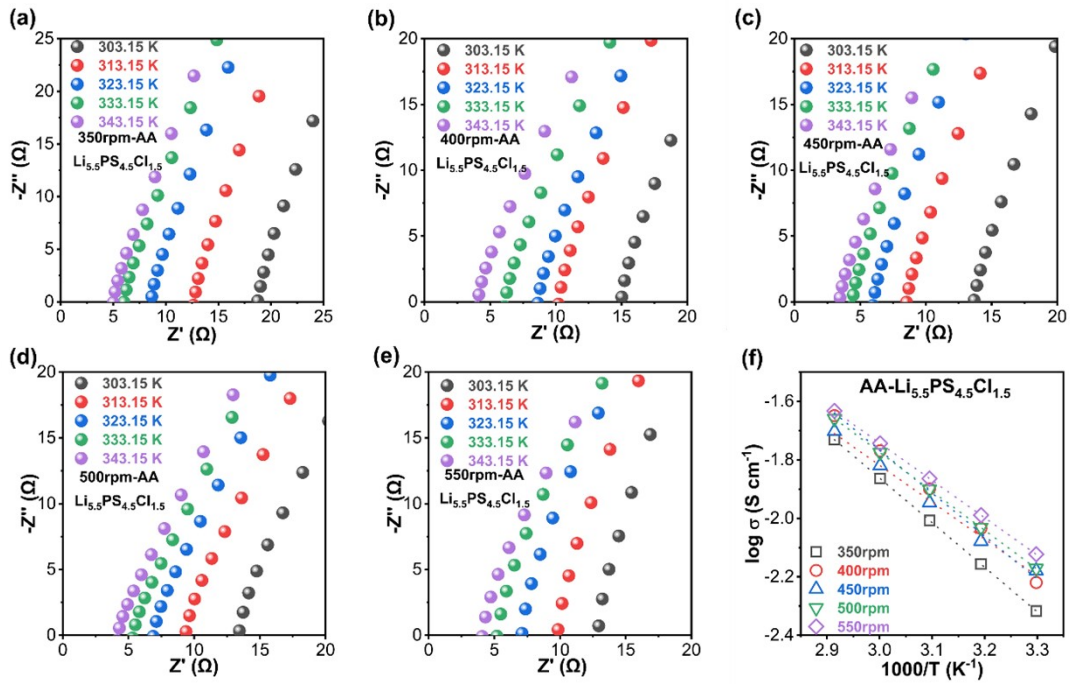


Fig. S3. Li-ion conductivity of the AA- $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ obtained from different rotation speeds (a) 350 rpm (b) 400 rpm (c) 450 rpm (d) 500 rpm (e) 550 rpm and (f) the corresponding Arrhenius plots.

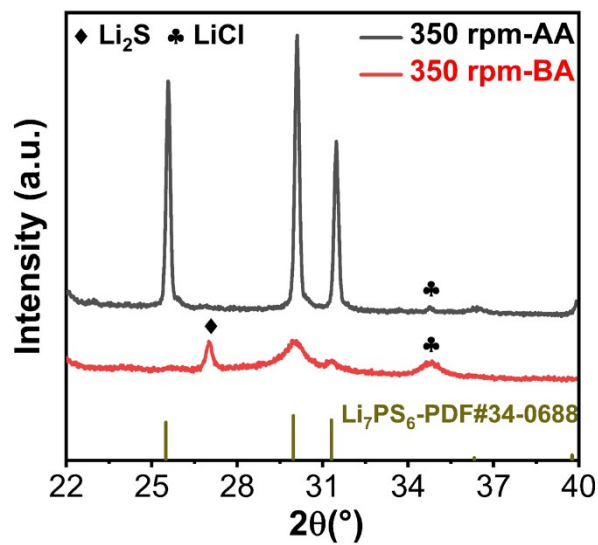


Fig. S4. XRD patterns of $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ obtained before and after sintering under 400 °C in 5 h.

AA-Li_{5.5}PS_{4.5}Cl_{1.5}-400rpm

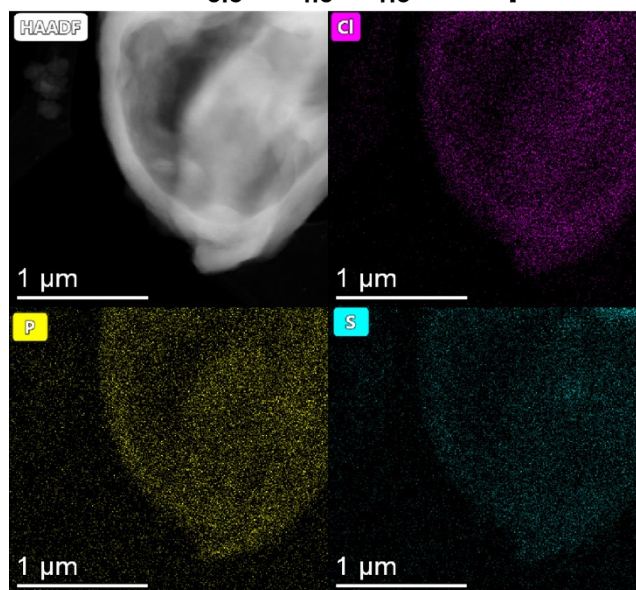


Fig. S5. EDS mapping results of AA-Li_{5.5}PS_{4.5}Cl_{1.5}-400 rpm.

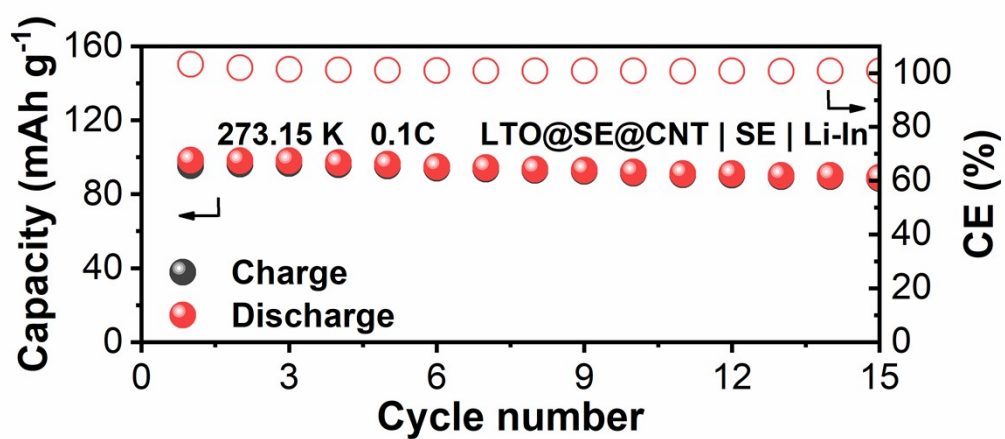


Fig. S6. Cycling performance of ASSBs under 273.15 K at 0.1C.