Supporting Information for

Electrochemical behaviors of Li-argyrodite-based allsolid-state batteries under deep-freezing conditions

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Experimental

Preparation of Li-argyrodite SE

Li-argyrodite (Li₆PS₅Cl) powder was prepared by 12-h high-energy ball milling [PM 200 planetary milling machine (Retsch) with ZrO₂ balls (diameter = 5 mm, total weight = 60 g)] of a 5:1:2 (w/w/w, total weight = 2 g) mixture of Li₂S (Sigma-Aldrich) : P₂S₅ (Sigma-Aldrich) : LiCl (Sigma-Aldrich) at 650 rpm. The thus obtained glassified powder was annealed at 550 °C for 2 h to afford a crystalline structure. All sample preparation steps were performed in a glovebox filled with high-purity (O₂ and H₂O < 0.1 ppm) Ar, and annealing was performed in a quartz container carefully sealed to avoid contamination.

The crystal structure of as-synthesized Li₆PS₅Cl powder was examined by X-ray diffraction (XRD; D/Max 2500, Rigaku; Cu K_{α} radiation). Scanning was performed from 10 to 70° at a rate of 2.68° min⁻¹ and a step size of 0.027°, and a protective seal was used to minimize air contamination. Surface and cross-sectional imaging of the as-prepared ASSB cell was performed by scanning electron microscopy (SEM) coupled to a focused-ion beam (FIB; Quanta 3D, FEI) employing a vacuum transfer holder. A cell cross-section with a total area of 20 μ m × 25 μ m was prepared by Ga-ion-beam milling. Li-ion conductivities (σ _{Li}) were measured by EIS in a frequency range of 3 MHz to 1 kHz using a frequency response analyzer (1260, Solartron) and an electrochemical interface (1287, Solartron) apparatus. For the above measurement, both sides of the pellet (diameter = 5.63 mm, thickness = 1.97 mm thickness) prepared by uniaxial cold-pressing at 563 MPa followed high-temperature annealing at 550 °C were coated with silver paste as a current collector. The as-prepared specimen was mounted on a home-made gas-tight test zig to exclude exposure to air/moisture, and the zig was placed into an environmental test chamber (TH-KE-025, JEIO Tech) to measure σ _{Li} at various temperatures (-30 to 40 °C).

Figure S1a shows the XRD pattern of as-synthesized solid electrolyte (SE), showing that although the peaks of Li₂S were still present after milling, only Li₆PS₅Cl peaks remained after annealing. The above pattern was well matched with that of the Li₆PS₅Cl standard (PDF #04-

018-1429) and did not indicate the presence of any secondary phases. Figure S1b shows the σ_{Li} of Li₆PS₅Cl as a function of temperature (-30 to 40 °C) and the activation energy (E_a) derived from the slope of the regression line. Li₆PS₅Cl powder synthesized by high-energy ball milling showed an excellent σ_{Li} of 3.67 mS cm⁻¹ at 25 °C and 0.132 mS cm⁻¹ at -30 °C.

Cell fabrication

The composite cathode contained $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM, active material), $\text{Li}_6\text{PS}_5\text{Cl}$ SE, and vapor-grown carbon fiber (VGCF, conductive agent) in a weight ratio of 57.7:38.5:3.8. Stainless steel balls (diameter = 4.76 mm, total weight = 3.05 g) and the above mixture (0.52 g) were fed into a stainless steel bowl, and dry mixing was carried out for 11 min using a vibration mixer mill (MM400, Retsch).

The cell comprised an In metal counter-electrode, SE separator, and the abovementioned composite cathode. For cell preparation, Li₆PS₅Cl powder (0.04 g) was placed into a 10-mm-diameter mold and compressed at 192 MPa for 2 min. One side of the produced pellet was covered with the composite cathode (0.02 g) material, and the pellet was further pressed at a pressure of 317 MPa for 2 min. Subsequently, $100-\mu$ m thick-In metal foil was placed on the other side of the SE pellet, and an additional pressure of 125 MPa was applied. Finally, as-prepared three-layer pellets were fabricated into CR2032-type coin cells.

Electrochemical characterization

Charge/discharge tests of CR2032-type coin cells were carried out in the voltage range of 2.0–3.6 V (vs. In/InLi) at both low (-30 °C) and room temperature (RT; 25 °C) using a multi-

channel potentiostat (1470E, Solartron). The theoretical capacity of NCM was assumed to equal 180 mAh g⁻¹, and the current rate was computed based on the amount of NCM (11.54 mg) in one coin cell. Charging was performed in constant current-constant voltage (CC-CV) mode, while discharging was performed in CC mode. The end condition of the CV mode was set to 20% of the CC-mode current density. Electrochemical performance was characterized at current rates of 0.02, 0.04, and 0.06 C. EIS analyses of as-fabricated half-cells were carried out in the frequency range of $0.01-10^6$ Hz and at a signal amplitude of 50 mV using the abovementioned equipment (1260 and 1287, Solartron). The results were obtained at various C-rates after charge (to 3.6 V vs. In/InLi) and discharge (to 2.0 V vs. In/InLi).



Fig. S1. (a) XRD patterns of as-milled (blue line) and annealed (red line) Li_6PS_5Cl , with the diffraction pattern of the reference (PDF #04-018-1429) provided for comparison (black line). (b) Arrhenius plot of σ_{Li} for Li_6PS_5Cl showing the value of E_a calculated from the slope of the regression line (dashed line)



Fig. S2. Charge/discharge curves of ASSB cells on 2, 6, 11 cycles at (a) −30 °C and (b) 25 °C. All tests were performed at 0.02 C-rate. The dashed line represents the initial cycle performed at 25 °C for validation purposes. Discharge capacities (closed squares) and Coulombic efficiencies (open squares) during 10 cycles at (c) −30 °C and (d) 25 °C.



Fig. S3. Separated resistance values from the fitted results in Fig. 3 after (a) charging and (b) discharging. All resistance components became larger and, in particular, the $R_{\text{SE/cathode}}$ and the $R_{\text{SE/anode}}$ significantly influenced at charged and discharged state, respectively.



Fig. S4 Separated resistance values from the fitted results in Fig. 4 after (a) charging and (b) discharging. All resistance components were linearly increased and the $R_{SE/anode}$ component was the most influential in the entire cycle at discharged state.