Electronic Supporting information

A solid lithium superionic conductor $Li_{11}AlP_2S_{12}$ with thio-LISICON analogous structure

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Experimental

Powder X-ray diffraction (XRD) patterns of the obtained samples were collected in the 2θ range of 10–80° (Rigaku MiniFlex600 using Cu Kα radiation). Raman scattering spectra were obtained by using an argon-ion laser of 532 nm (DXR, Thermo Fisher Scientific). Samples were protected to avoid contamination of moisture and air during measurements. The obtained powders were pressed into dense pellets (diameter=16 mm, thickness≈1 mm) by a conventional coaxial cold press at a pressure of 150 MPa for the evaluation of electrochemical performance. The cross-section microstructures of pellets were observed by scanning electron microscope (SEM, JEOL JSM7500F) with an energy dispersive X-ray detector (EDS). The alternating-current (a.c.) impedance was conducted by electrochemical impedance spectroscopy (EIS) using stainless steel (SUS) served as blocking electrodes. Symmetric SUS/LAlPS/SUS cells were measured on a Parstat 2273A potentiostat/galvanostat workstation with 200 mV constant voltage in the frequency range of 0.1 Hz to 2 MHz. The temperature was changed from 0 to 100 °C, and the samples were kept at each temperature for at least 30 minutes before measurement. Cyclic voltammetry (CV) was carried out on the Li/LAlPS/SUS cells at a scan rate of

5 mV s^{-1} between -0.5 and 5.0 V (vs. Li^+/Li) at 25 °C, in which the SUS served as the current collector and the lithium foil worked as the reference and counter electrode. Direct-current (dc) polarization was measured on the two symmetric cells: non-blocking Li/LAlPS/Li and blocking SUS/LAlPS/SUS with an applied 0.5 V for 1500 s for determination of lithium ion transport number of the synthesized LAlPS electrolytes. The symmetric non-blocking Li/LAlPS/Li cell was continuously discharged and charged at 0.1 mA for evaluation of the compatibility between lithium foils and LAlPS solid electrolyte.

An all-solid-state cell with the configuration of $LiCoO_2$-$LAlPS_{500}$/$LAlPS_{500}$/In was employed to evaluate the feasibility of the $LAlPS_{500}$ solid electrolyte in Li-ion batteries.[1-3] The cathode composite was prepared by mixing the commercial $LiCoO_2$ (Alfa, 99.5%) and $LAlPS_{500}$ with a ratio of 70:30 (wt%) in an airtight powder homogenizer for 20 min at 3500 rotation per minute. 10 mg of the composite was prepressed onto a carbon cloth as current collector, then 150 mg of $LAlPS_{500}$ was added as a Li-ion conducting membrane on the top of the composite cathode. Finally, the bilayer pellet with a diameter of 16 mm was coaxially cold pressed under 150 MPa. An indium foil (Alfa, 99.997%; 0.1 mm thickness) was pressed onto another side of $LAlPS_{500}$, and used as the anode. The assembled cell was tested between 2.3 and 3.7 V at a current density of 0.13 mA cm^{-2} on a LAND-CT2001A testing instrument and 25 °C. All the experiments were conducted under protection to avoid contamination of moisture and air.

SEM and EDS

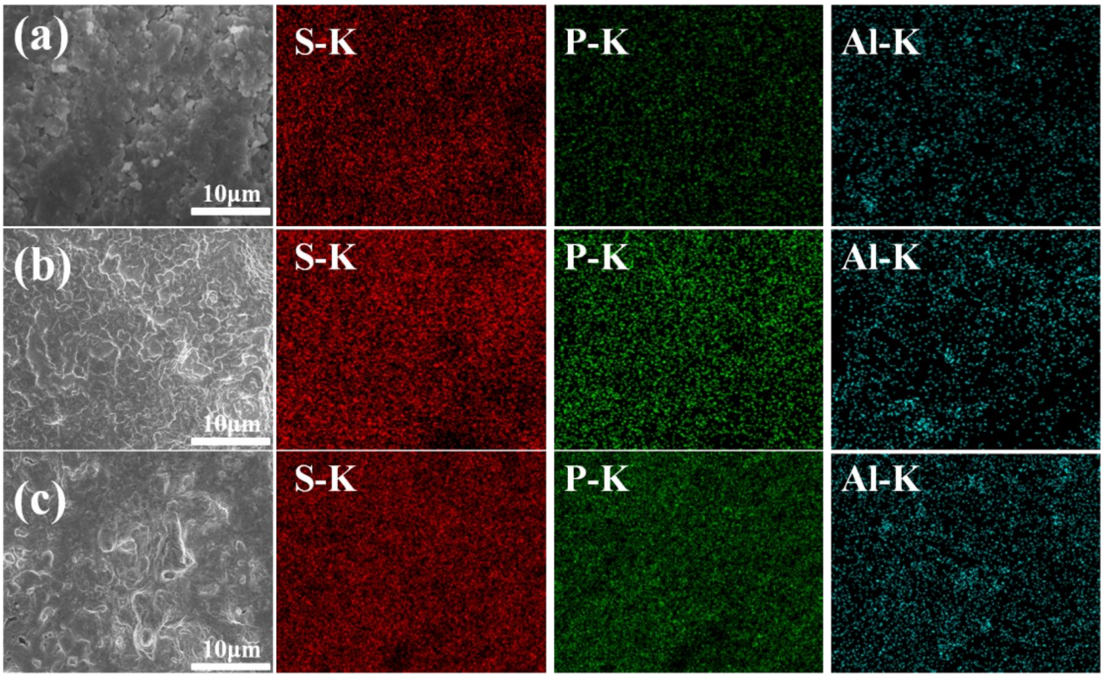

Fig. S1 Cross-section morphologies and EDS elemental mappings of $LAlPS_{400}$ (a), $LAlPS_{500}$, (b) and $LAlPS_{600}$ (c).

Table S1 EDS elemental compositions of $LAlPS_{400}$, $LAlPS_{500}$, and $LAlPS_{600}$.

Composition	Atomic ratio (%)		
	Al-K	P-K	S-K
$LAlPS_{400}$	6.86	14.85	78.29
$LAlPS_{500}$	7.59	14.20	78.21
$LAlPS_{600}$	6.50	13.95	79.55

Table S1summarizes the EDS elemental compositions of $LAlPS_{400}$, $LAlPS_{500}$, and $LAlPS_{600}$. The Al/P/S ratio was determined to be 6.86:15.85:77.29 (1.05:2.27:12), **7**.59:14.20:78.21 (1.16:2.17:12), and 6.50:13.95:79.55 (0.98:2.10:12) for $LAlPS_{400}$, $LAlPS_{500}$, and $LAlPS_{600,}$ respectively. They are approaching to the stoichiometric ratio of Al/P/S=1:2:12.

Raman spectra

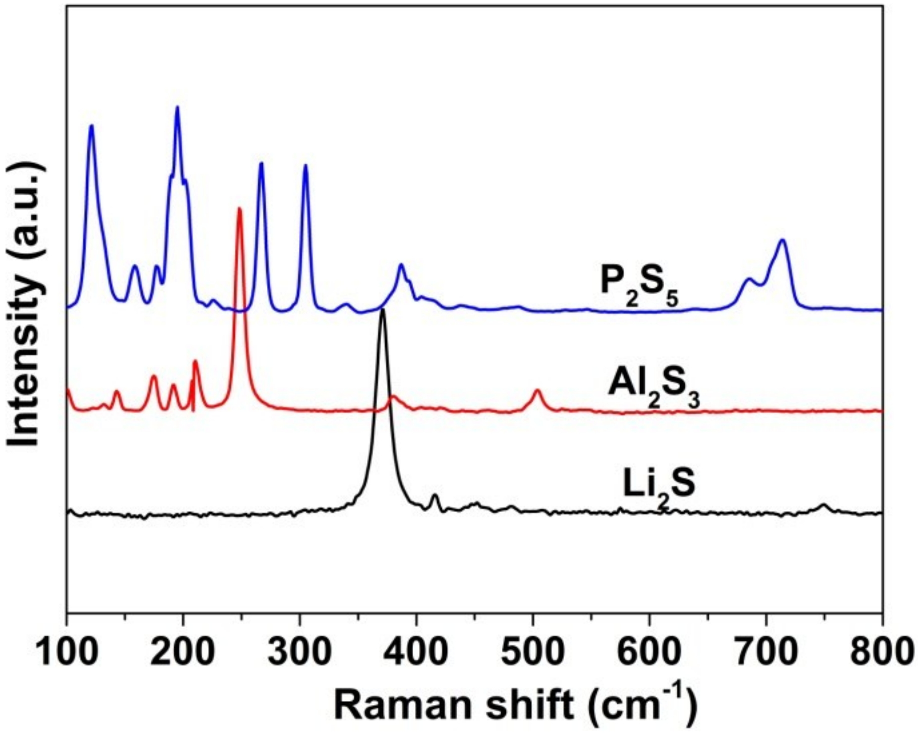

Fig. S2 Raman spectra of the starting materials, Li_2S, P_2S_5, and Al_2S_3.

Crystalline structure

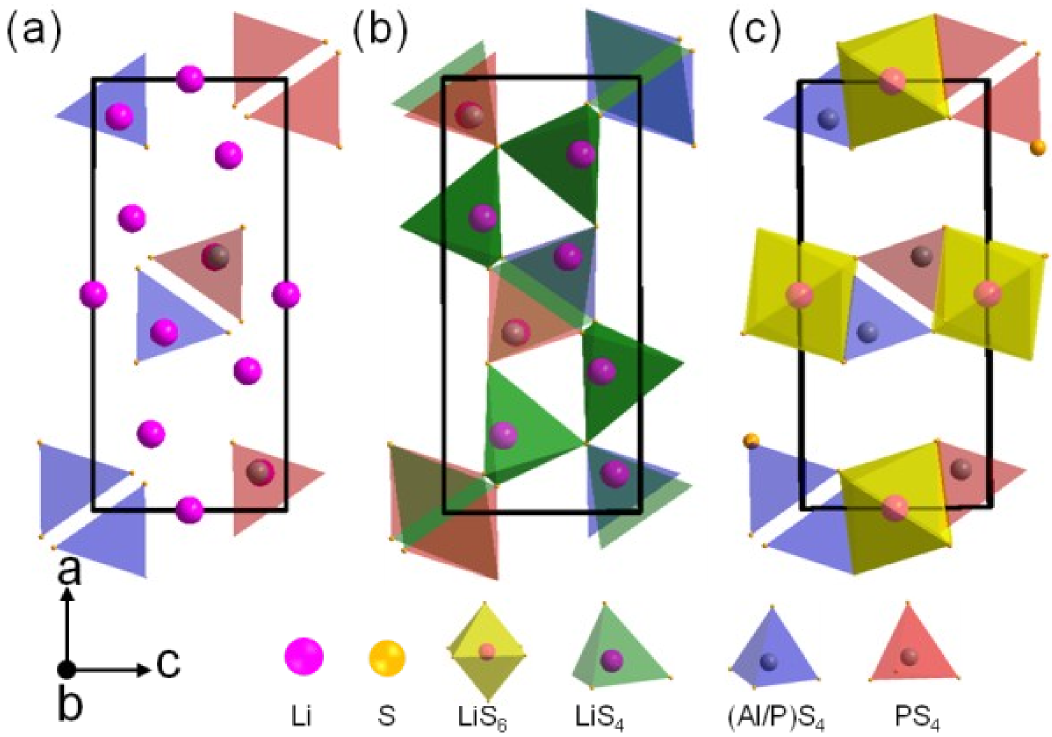

Fig. S3 Schematic structure of $LAlPS_{500}$: (a) only PS_4 tetrahedra are indicated; (b) and (c) show the connection of PS_4 tetrahedra with LiS_4 tetrahedra and LiS_6 octahedra, respectively.

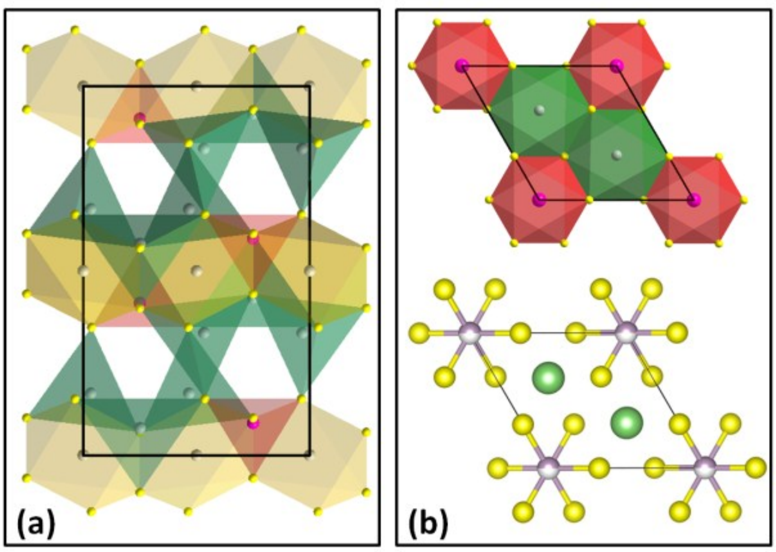

Fig. S4 Schematic structure of the Li_3PS_4 (a) and $Li_4P_2S_6$ (b) phase.[4-6]

Impedance spectroscopy

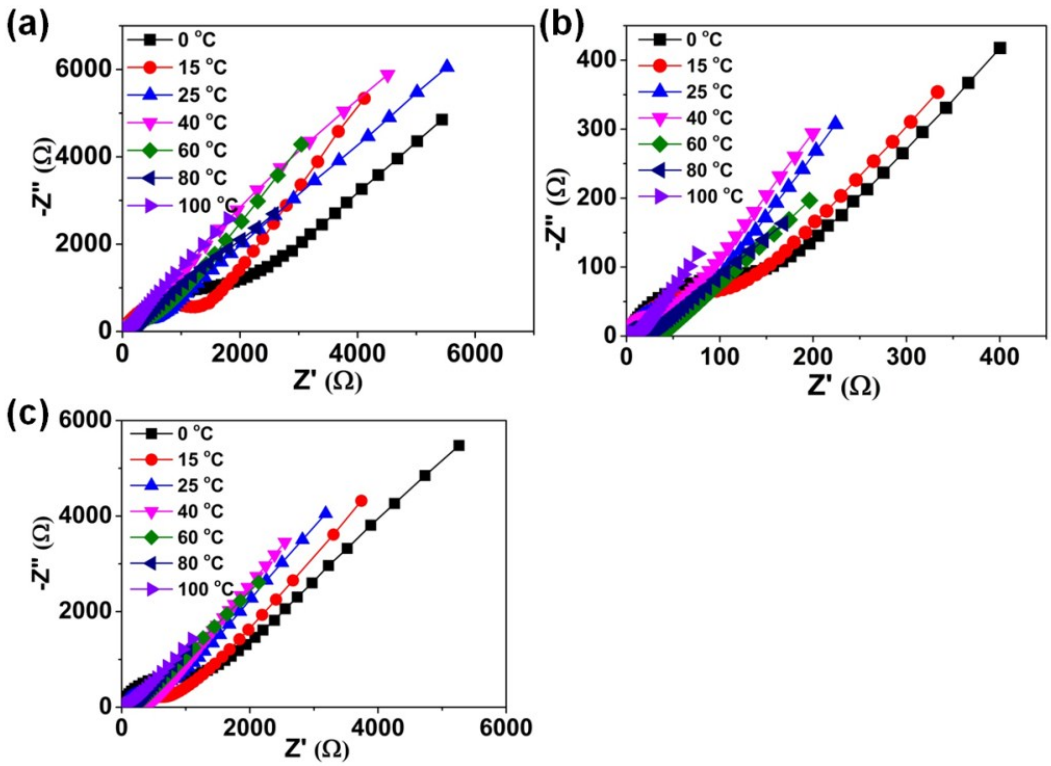

Fig. S5 (a-c) Nyquist plots of $LAlPS_{400}$, $LAlPS_{500}$, and $LAlPS_{600}$ at different temperatures measured in symmetric SUS/LAlPS/SUS cells.

Table S2 Lithium ionic conductivity and activation energies of the reported thio-LISICON electrolytes.

Compounds	Conductivity σ_{Li} (S cm^{-1}, 25 °C)	Activation Energies E_a (kJ mol^{-1})	References
Li_2GeS_4	2.0×10^{-7}	-	7
$Li_{4-2x}Zn_xGeS_4$	3.0×10^{-7}	-	7
$Li_{4+x+\delta}(Ge_{1-\delta'-x}-Ga_x)S_4(x=0.25)$	6.5×10^{-7}	-	7
$Li_{3+5x}P_{1-x}S_4(x=0.065)$	1.5×10^{-4}	22.0	8
$Li_{3.25}Ge_{0.25}P_{0.75}S_4$ thin film	1.8×10^{-4}	40.5	9
$Li_{4-x}Ge_{1-x}P_xS_4(x=0.75)$	2.2×10^{-3}	20.0	10
$Li_{11}AlP_2S_{12}$(thio-LISICON)	8.0×10^{-4}	25.4	This work

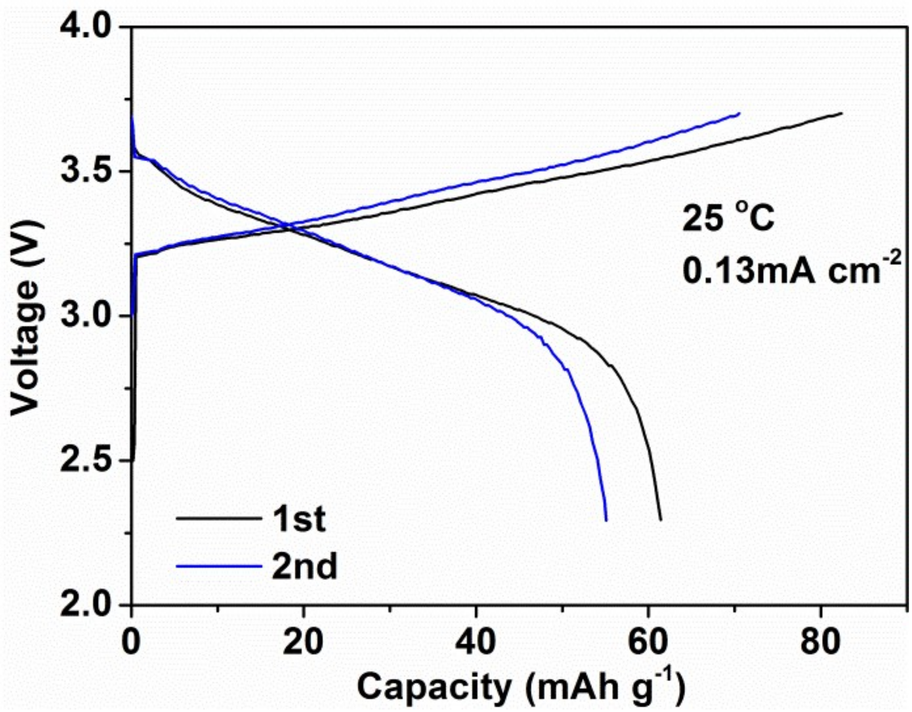

Fig. S6 Charge-discharge curves of the all-solid-state $LiCoO_2$-$LAlPS_{500}$/$LAlPS_{500}$/In cell at 0.13 mA cm^{-2} and 25 °C.

References

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