Supporting Information

## Synthesis of AlI<sub>3</sub>-doped Li<sub>2</sub>S Positive Electrode with Superior Preformance in All-Solid-State Battery

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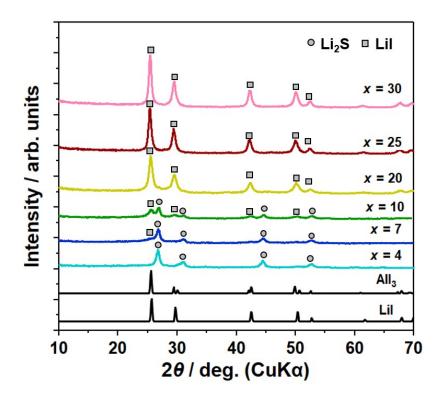


Fig. S1. X-ray diffraction patterns of  $(100 - x)Li_2S \cdot xAlI_3$  samples.

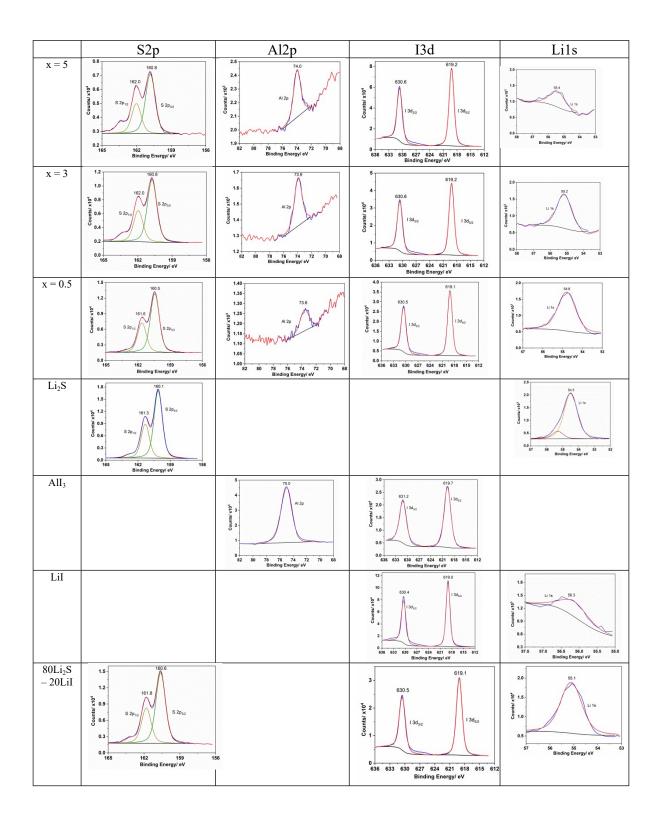


Fig. S2. X-ray photoelectron spectroscopy spectra of the prepared samples and standard materials.

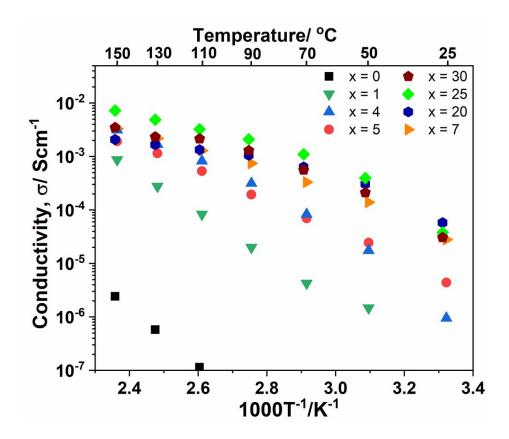


Fig. S3. Temperature dependence of ionic conductivity of  $(100 - x)Li_2S \cdot xAII_3$ .

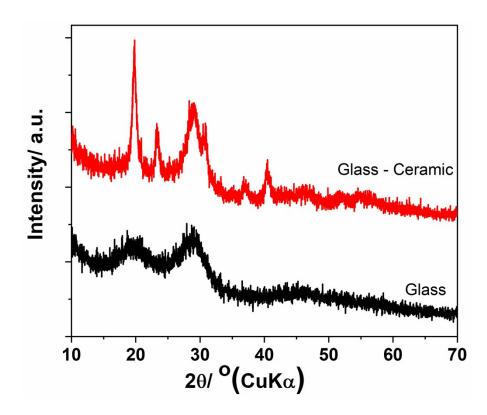


Fig. S4. X-ray diffraction patterns of  $Li_{10}P_3S_{12}I$  solid electrolytes.

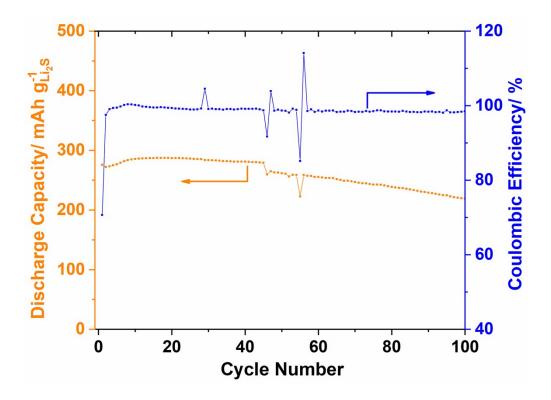


Fig. S5. Cyclic property at room temperature of the all-solid-state Li–S cell employing 80(95Li<sub>2</sub>S·5AlI<sub>3</sub>)–20Ketjen Black (KB) composite as the positive electrode composite (without Li<sub>10</sub>P<sub>3</sub>S<sub>12</sub>I solid electrolyte in the positive electrode).

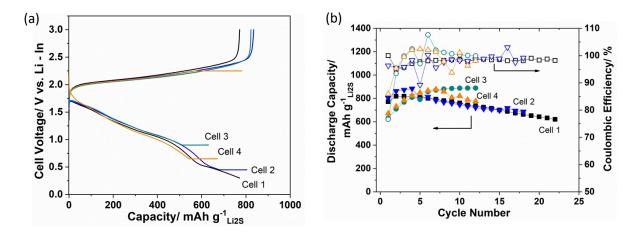


Fig. S6. Performances of four cells with different cut-off voltages. (a) charge–discharge curves at the first cycle; (b) cyclic properties of the cells.

• Cell construction:

Positive electrode:  $50(97\text{Li}_2\text{S}\cdot3\text{AlI}_3)-40\text{Li}_{10}\text{P}_3\text{S}_{12}\text{I}-10\text{Ketjen Black (KB)}$ , ~4 mg Separator:  $\text{Li}_{10}\text{P}_3\text{S}_{12}\text{I}$ , ~80 mg Negative electrode: In–Li alloy

• Charge–discharge conditions:

For the first cycle:

Cell 1: CC mode, 0.1C (about 0.25 mA cm<sup>-2</sup>), cut-off voltage 3.0-0.3 V vs. Li-In

Cell 2: charge with CC mode (0.1C), cut-off voltage 3.0 V vs. Li–In discharge with CC–CV mode: 0.1C with CC mode until 0.45 V vs. Li–In, then change to CV mode at 0.45 V until the current reaches 0.01 mA

Cell 3: charge with CC mode (0.1C), cut-off voltage 3.0 V vs. Li–In discharge with CC–CV mode: 0.1C with CC mode until 0.90 V vs. Li–In, then change to CV mode at 0.90 V until the current reaches 0.01 mA

Cell 4: charge with CC–CV mode: 0.1C with CC mode to 2.25 V vs. Li–In, then change to CV mode at 2.25 V until the current reaches 0.01 mA discharge with CC–CV mode: 0.1C with CC mode until 0.65 V vs. Li–In, then change to CV mode at 0.65 V until the current reaches 0.01 mA

<u>From the second cycle</u>: The discharge modes were maintained as previously described; the charge mode was changed to 0.1C with CC mode to 2.25 V vs. Li–In, then change to CV mode at 2.25 V until the current reaches 0.01 mA