

## Supporting information

### **Liquid-phase synthesis of $\text{Li}_4\text{GeS}_4$ and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ electrolytes using water as the main solvent**

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## Experimental

### Synthesis

The samples of  $\text{Li}_4\text{GeS}_4$  electrolytes were prepared via liquid-phase synthesis. The starting materials,  $\text{Li}_2\text{S}$  (99.9%, Mitsuwa Chemical),  $\text{GeS}_2$  (99.99%, Kojundo Chemical), Ge metal (99.99%, Kojundo Chemical), and S (99.98%, Sigma-Aldrich), were weighed to obtain stoichiometric compositions. Deionized water was added to the mixture of the starting materials under atmospheric conditions and stirred at 80 °C for 6 h. The starting material concentration in the aqueous solution was approximately 5.0 wt%. The aqueous solution was dried under vacuum at 200 °C for 3 h to obtain the powdered  $\text{Li}_4\text{GeS}_4$  sample.

For the liquid-phase synthesis of the LGPS electrolyte,  $\text{Li}_2\text{S}$ ,  $\text{GeS}_2$ , and  $\text{P}_2\text{S}_5$  (99%, Sigma-Aldrich) were used as starting materials. The preparation scheme is shown in Fig. 2. A THF (99.5%, FUJIFILM Wako Pure Chemical) mixture of  $\text{Li}_2\text{S}$  and  $\text{P}_2\text{S}_5$  was stirred at 25 °C for 24 h. The weight ratio of  $\text{Li}_3\text{PS}_4$  in the  $\text{Li}_3\text{PS}_4$ -THF suspension was approximately 5.7 wt%. The  $\text{Li}_3\text{PS}_4$ -THF suspension was added to the 5.0 wt%  $\text{Li}_4\text{GeS}_4$  aqueous solution, followed by being shaken in a few seconds in a separating funnel. The mixture was separated into two liquid layers, a yellow aqueous solution and a colourless THF layer, in the funnel, and the aqueous layer was removed to obtain the LGPS precursor solution. Note that THF can be easily separated and reused as a separation solvent, making the process environmentally friendly despite using an organic solvent. The aqueous solution was dried under vacuum at 200 °C for 3 h to obtain the LGPS precursor powder. The obtained powder was heated at 600 °C for 2 h in a dry Ar atmosphere.

### Characterization

For qualitative analysis, XRD of the obtained powders was performed using an X-ray diffractometer (SmartLab; Rigaku) with Cu K $\alpha$  radiation in the  $2\theta$  range of 10°–60° at a scan rate of 5° min<sup>-1</sup>. The powder samples were placed in an airtight container with a non-air-permeable plastic film window under a dry Ar atmosphere to avoid side reactions with air and moisture.

The Raman spectra of the prepared samples were collected using a Raman spectrophotometer (LabRAM HR-800, HORIBA) with a 532 nm diode laser. The prepared powder samples were pressed in an Al pan to flatten the surface, and then sealed in an airtight container with dry Ar atmosphere and a quartz window.

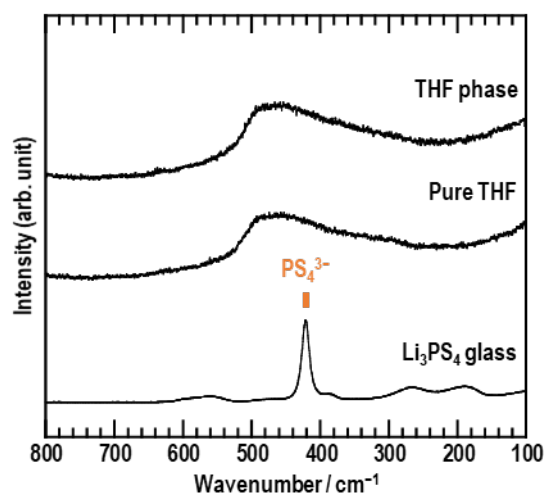
Thermogravimetry differential thermal analysis (TG-DTA) were performed using a thermal analyser (Thermo PlusTG8110; Rigaku). The powder samples were sealed in an Al pan under the dry Ar atmosphere, and then heated to 500 °C at a rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere.

To evaluate the formability of the prepared samples, the relative densities of the green and sintered compacts were determined. Green compacts were prepared by pressurising the powder samples at 360 MPa and room temperature for 5 min. The sintered compacts were prepared by heating the green compacts at 600 °C for 2 h in a dry Ar atmosphere. The relative density was determined by dividing the density of the pellets by the powder density of the sample, which was measured using a gas pycnometer (AccuPyc II 1340; Shimadzu) in a dry Ar atmosphere.

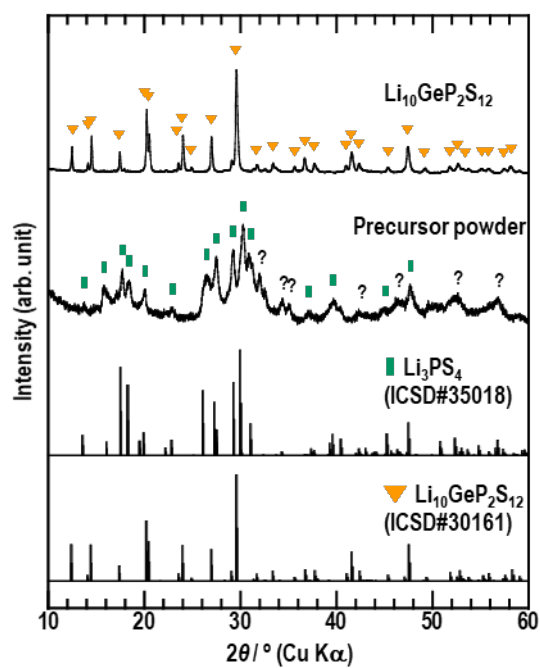
The ionic conductivities of the prepared samples were measured using AC impedance spectroscopy. A thin

gold film was applied to both sides of the green and sintered compacts as ion-blocking electrodes. The ionic conductivities of the pellets were measured using an impedance analyser (SI-1260; Ametek Scientific Instruments) in the temperature range from  $-30$  to  $110$  °C. The activation energy ( $E_a$ ) of ionic conduction was calculated using the Arrhenius equation:  $\sigma = A \exp(-E_a/RT)$ , where  $\sigma$ ,  $A$ ,  $R$ , and  $T$  represent the ionic conductivity, pre-exponential factor, gas constant, and absolute temperature, respectively.

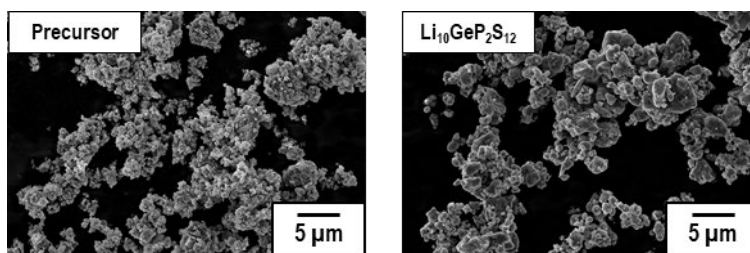
Positive electrodes were prepared by hand mixing  $\text{TiS}_2$  and LGPS in a weight ratio of 50:50 or  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC) and LGPS in a weight ratio of 70:30. The all-solid-state cells were fabricated as follows. LGPS powder (80 mg) was placed in a polycarbonate tube (diameter: 10 mm) and pressed at 72 MPa. One of the prepared positive electrodes ( $\text{TiS}_2$  loading:  $3.89 \text{ mg cm}^{-2}$  or NMC loadings:  $7.58 \text{ mg cm}^{-2}$ ) was placed on the solid electrolyte (SE) layer and pressed at 360 MPa for 5 min. Li (thickness: 0.25 mm, diameter: 7 mm) and In foil (thickness: 0.3 mm, diameter: 8 mm) were placed on either side of the SE layer, and the cells were tightened and then left for 12 h for Li-In alloy formation. Finally, the cells were tightly restrained.



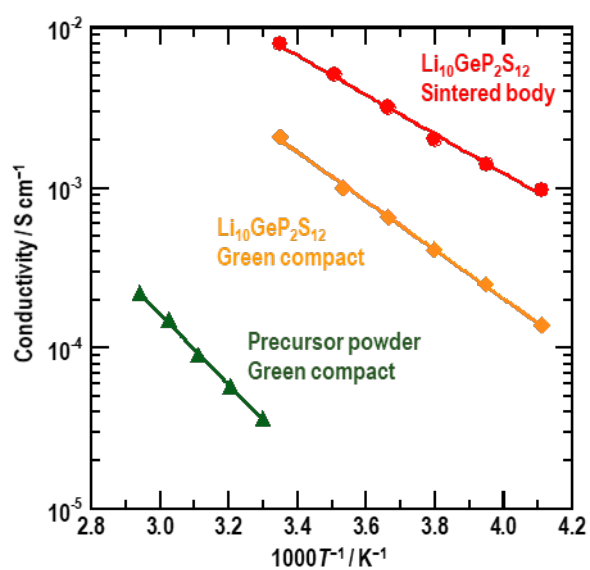
**Fig. S1** Raman spectra of THF phases after mixing.



**Fig. S2** XRD patterns of precursor powder and  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ .



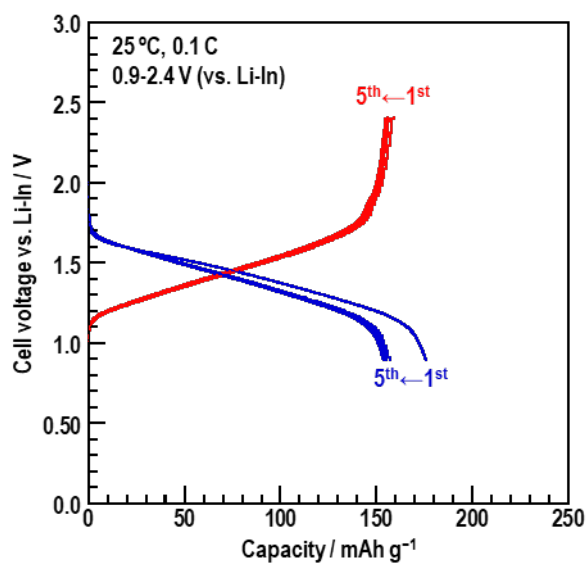
**Fig. S3** SEM images of (a) precursor powder and (b) Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> sample prepared liquid-phase synthesis.



**Fig. S4** Temperature dependence of conductivities of precursor powder and Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> prepared by liquid-phase synthesis using water as solvent.

**Table S1** Ionic conductivities, activation energies, and relative densities of  $\text{Li}_4\text{GeS}_4$ , precursor powder, and  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  samples.

Sample	Pellet	Ionic conductivity $\sigma_{25^\circ\text{C}} / \text{S cm}^{-1}$	Activation energy $E_a / \text{kJ mol}^{-1}$	Relative density / %
$\text{Li}_4\text{GeS}_4$	Green compact	$8.5 \times 10^{-6}$	41	-
Precursor powder	Green compact	$2.7 \times 10^{-5}$	43	-
$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$	Green compact	$2.0 \times 10^{-3}$	29	77
$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$	Sintered body	$7.7 \times 10^{-3}$	26	91



**Fig. S5** Charge–discharge curves of the cells  $\text{Li-In}/\text{Li}_{10}\text{GeP}_2\text{S}_{12}/\text{TiS}_2$  with the conventional mixed electrode prepared by the hand-mixing of  $\text{TiS}_2$  and  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  particles using a mortar.