

Supporting information

Aqueous Solution Synthesis for Lithium-Ion Conductive Tin-Based Sulphide Electrolytes

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Experimental

Preparation. Solid electrolytes with Li_4SnS_4 compositions were prepared via the liquid-phase synthesis. Starting materials Li_2S (99.9%, Mitsuwa Chemical), Sn metal (99.999%, Nilaco), SnS (99%, Nihon Seiko), SnS_2 (99.5%, Mitsuwa Chemical), and S (99.98%, Sigma-Aldrich) were weighed in stoichiometric compositions. Deionized water was added to the mixture of starting materials under atmospheric conditions and stirred at 80 °C for 24 h. The concentrations of the starting materials in the aqueous solution were approximately 4.8 wt%. The aqueous solution was dried at 150 °C in vacuum for 3 h to obtain a sample powder. For comparing the effect of changing the lithium source, the liquid-phase synthesis of Li_4SnS_4 was performed using $\text{LiOH}\cdot\text{H}_2\text{O}$ (98.0%, FUJIFILM Wako Pure Chemical), Sn metal, and sulphur. The experimental results are shown in Figs. S1 and S2.

In the mechanochemical synthesis, Li_2S and SnS_2 were used as starting materials for comparison. The mixture of starting materials (0.5 g) was placed in a 45 mL zirconia pot with 500 zirconia balls (4 mm diameter) in a dry Ar atmosphere, followed by milling at 510 rpm for 40 h using a planetary ball mill (Pulverisette 7, Fritsch).

For the liquid-phase synthesis of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ electrolytes with stoichiometric and excess 10 mol% P composition, Li_2S , Sn, S, and P_2S_5 (99%, Sigma-Aldrich) were used as starting materials. THF (99.5%, FUJIFILM Wako Pure Chemical) was poured into a mixture of Li_2S and P_2S_5 and stirred at 25 °C for 24 h. The weight ratio of Li_3PS_4 in the Li_3PS_4 -THF suspension was approximately 5.7 wt%. The Li_3PS_4 -THF suspension was added to the Li_4SnS_4 - H_2O solution prepared from Li_2S , Sn, and S via the abovementioned process and subsequently stirred at 25 °C for 1 h. The mixed solution was dried at 150 °C in vacuum for 3 h to obtain a precursor powder of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$. The obtained powder was heated at 600 °C for 2 h in a dry Ar atmosphere to enhance its crystallinity. The green compact was prepared via uniaxial pressing at 360 MPa and 25 °C, whereas the sintered body was prepared by heating the green compact at 600 °C for 2 h in a dry Ar atmosphere.

Characterization. For qualitative analysis, X-ray diffraction (XRD) of the obtained powders was performed using an X-ray diffractometer (SmartLab; Rigaku) with Cu K α radiation. Diffraction patterns were collected in the 2θ range of 10°–60° at a scan rate of 5° min⁻¹. The powder samples were placed in a dry Ar atmosphere in an airtight measuring container with a Be metal window or non-air-permeable plastic film window to avoid side reactions with air and moisture.

XRD data were collected to analyse the crystal structure and degrees of crystallinity of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$. The crystal structure of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ was refined via the Rietveld method using the RIETAN-FP software.¹ The peak shapes, background coefficients, and lattice constants were refined using Rietveld refinement. The crystal and local structures were drawn using the VESTA software.²

The Raman spectra of the prepared samples and precursor aqueous solution were collected using a Raman spectrophotometer (LabRAM HR-800, HORIBA) with a 532 nm diode laser. The powder samples were placed in a dry Ar atmosphere in an airtight container with a quartz window to avoid side reactions with air and moisture. The solution was poured into a closed container with a glass window in the atmosphere to prevent spillage during measurement.

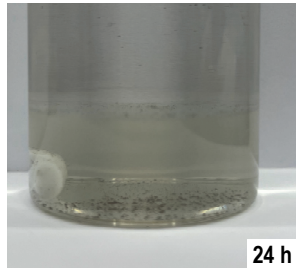
To measure the ionic conductivity, both sides of the green compacts and sintered bodies were covered with gold as ion-blocking electrodes. The ionic conductivity of the pellets was determined through electrochemical impedance spectroscopy (EIS) with an impedance analyser (SI-1260; Ametek Scientific Instruments). The temperature dependence of ionic conductivity was measured in the 25–80 °C temperature range using an oil bath and in the –30–25 °C range using an isopropanol bath. The activation energies of ionic conduction were calculated using the Arrhenius equation: $\sigma = A\exp(-E_a/RT)$, where σ , A , E_a , R , and T represent the ionic conductivity, pre-exponential factor, activation energy, gas constant, and absolute temperature, respectively.

The particle size and shape of prepared solid electrolytes were observed by using scanning electron microscope (JSM-6610A; JEOL). The samples were placed in an air-tight sample holder in a dry Ar atmosphere and introduced into the SEM chamber to avoid exposure to the ambient air. The SEM images are shown in Fig. S3. Primary particles of Li_4SnS_4 have a sub-micron diameter and form secondary particles of a few microns; secondary particles of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ consist of primary particles of a few microns.

References

1. F. Izumi, K. Momma, *Solid State Phenom.*, 2007, **130**, 15–20.
2. K. Momma, F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272–1276.

(a) Lithium source: Li_2S



(b) Lithium source: LiOH

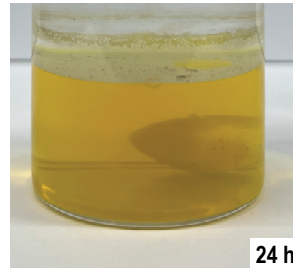


Figure S1 Photographic images of aqueous precursor liquid prepared from tin metal, sulphur, and two difference lithium sources: (a) Li_2S and (b) LiOH . Each number at the bottom right is the elapsed time from the start of stirring.

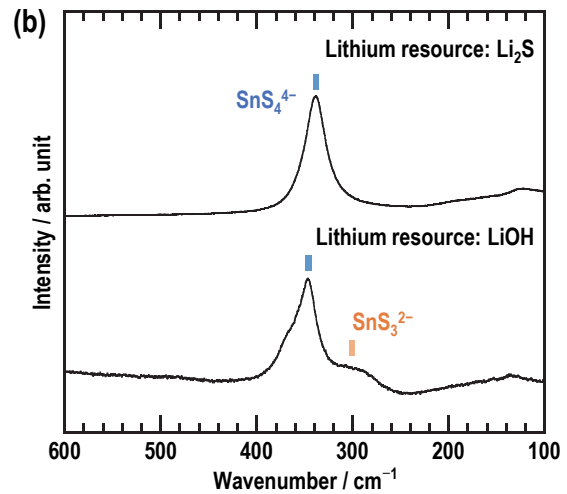
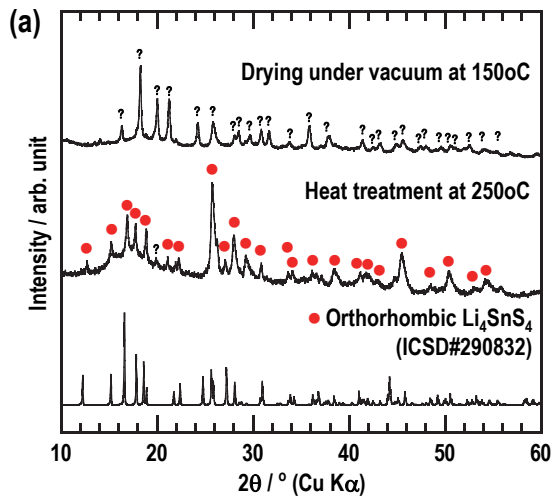
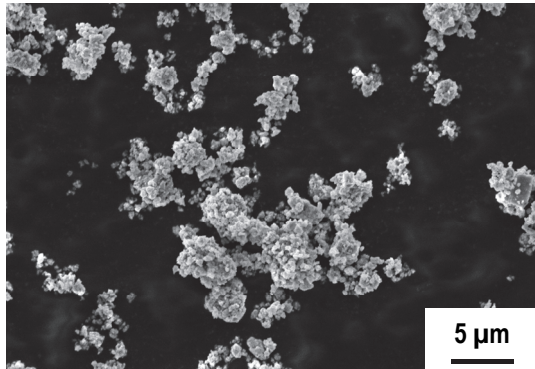


Figure S2 (a) XRD patterns of dried powder of the solution under vacuum at 150 °C and heated sample under Ar at 250 °C in synthesis of Li_4SnS_4 from LiOH , tin metal, and sulphur. (b) Raman spectra of Li_4SnS_4 prepared by liquid phase synthesis from various lithium sources.

(a) Li_4SnS_4



(b) $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$

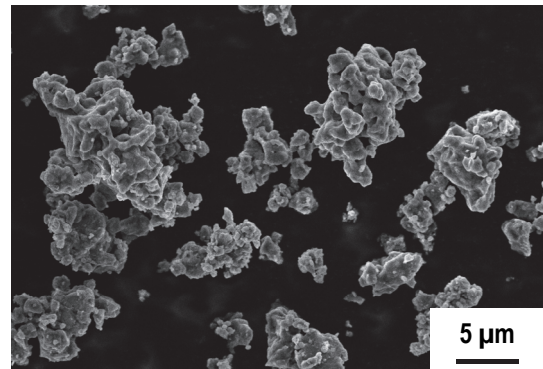
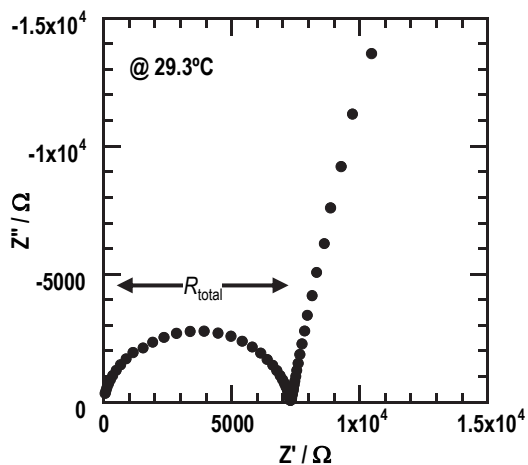


Figure S3 SEM images of particles for (a) Li_4SnS_4 and (b) $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ prepared by liquid phase synthesis.

(a) Li_4SnS_4



(b) $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ at P-rich composition (sintered body)

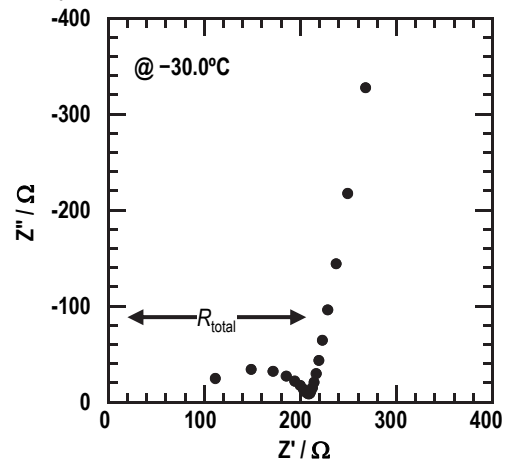


Figure S4 Nyquist plot at specific measuring temperatures for (a) green compact of Li_4SnS_4 and (b) sintered body of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ at P-rich composition prepared by liquid phase synthesis.

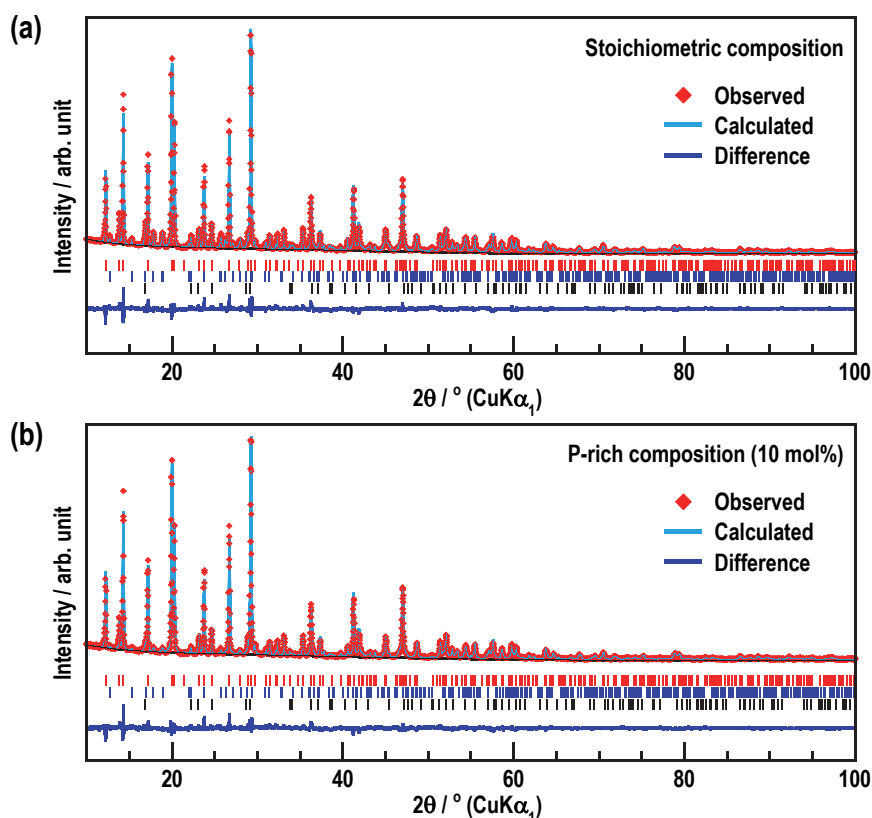


Figure S5 Rietveld refinement of X-ray diffraction data (Cu $K\alpha_1$ radiation) for electrolytes at (a) stoichiometric composition of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ and (b) P-rich composition obtained by liquid phase synthesis. The red rhombi, light blue line, and dark blue line represent the observed intensity, calculated intensity, and intensity difference, respectively. The allowed peak positions are indicated by red, blue, and black vertical lines for the main phase ($\text{Li}_{10}\text{SnP}_2\text{S}_{12}$) and impurity phases (thio-LISICON and Li_3PO_4), respectively.

Table S1 Lattice parameter and weight ratio of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$, thio-LISICON, and Li_3PO_4 obtained by Rietveld refinement of X-ray diffraction data (Cu $K\alpha_1$ radiation) for electrolytes at stoichiometric composition of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$.

	Space group (No.)	Lattice parameter			Weigh ratio / %
		$a / \text{\AA}$	$b / \text{\AA}$	$c / \text{\AA}$	
$\text{Li}_{10}\text{SnP}_2\text{S}_{12}$	$P4_2/nmc$ (137)	8.7387 (2)	8.7387 (2)	12.7786 (4)	84.8
thio-LISICON	$Pnma$ (62)	13.8899 (25)	7.9681 (14)	6.3629 (11)	7.5
Li_3PO_4	$Pmn2_1$ (31)	6.1296 (5)	4.2606 (21)	4.9360 (20)	7.7

※ $R_{wp} = 6.933$, $R_{F(\text{Li}_{10}\text{SnP}_2\text{S}_{12})} = 1.511$, $R_{B(\text{Li}_{10}\text{SnP}_2\text{S}_{12})} = 4.052$, $S = R_{wp}/R_b = 2.2206$.

Table S2 Lattice parameter and weight ratio of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$, thio-LISICON, and Li_3PO_4 obtained by Rietveld refinement of X-ray diffraction data (Cu $K\alpha_1$ radiation) for electrolytes at P-rich composition obtained by liquid phase synthesis.

	Space group (No.)	Lattice parameter			Weigh ratio / %
		$a / \text{\AA}$	$b / \text{\AA}$	$c / \text{\AA}$	
$\text{Li}_{10}\text{SnP}_2\text{S}_{12}$	$P4_2/nmc$ (137)	8.7382 (2)	8.7382 (2)	12.7704 (4)	91.7
thio-LISICON	$Pnma$ (62)	13.8587 (67)	7.9724 (41)	6.3593 (27)	2.9
Li_3PO_4	$Pmn2_1$ (31)	6.1315 (28)	5.2647 (20)	4.9397 (20)	5.4

※ $R_{wp} = 7.057$, $R_{F(\text{Li}_{10}\text{SnP}_2\text{S}_{12})} = 1.439$, $R_{B(\text{Li}_{10}\text{SnP}_2\text{S}_{12})} = 3.787$, $S = R_{wp}/R_b = 1.5214$.