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Supporting Information
$Li_{10}GeP_2S_{12}$ Solid Electrolytes Synthesised via Liquid-Phase Methods

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Experimental

Synthesis

For the liquid-phase shaking method, a suspension of the solid electrolyte precursor was synthesised using the liquid-phase shaking method described in our previous reports.[21, 22] The raw materials, namely, Li_2S (Mitsuwa Chemicals Co., Ltd., 99.9% purity), P_2S_5 (Merck Co., Ltd., 99% purity), and GeS_2 (FUJIFILM Wako Pure Chemical Corp., 99.9% purity), were mixed in a molar ratio of 5:1:1 (0.5743, 0.5556, and 0.2615 g, respectively) with 4-mm zirconia balls (approximately 32 g) and 1,2-dimethoxyethane (DME) (10 mL; FUJIFILM Wako Pure Chemical Corp., 99.5% purity) or tetrahydrofuran (THF) (10 mL; Fujifilm Wako Chemicals Co., Ltd., 99.5% purity) in a 45-mL polypropylene centrifugation tube (Labcon North America). The suspension was obtained by shaking the mixture at 1500 rpm for 6 h and then stirring for 72 h at 30 °C, or shaking at 1500 rpm for 6 h at 45 °C. Subsequently, the suspension was evacuated at 90 °C and held for 24 h under vacuum using a rotary vacuum pump (GHD-031A, ULVAC, Inc.). The precursor powder was pelletised (diameter = 10 mm, approximately 100 mg) by uniaxial pressing at 120 MPa and 25 °C. The pellet was placed in a SiO_2 tube; Ar gas was supplied to the tube through the inlet and allowed to pass through the outlet. The precursor pellet was heated at 550 °C for 12 h in a tube furnace, which was developed in previous study.[22] The pellet was thoroughly ground using an agate mortar, and a $Li_{10}GeP_2S_{12}$ solid electrolyte powder was obtained.

For the solution processing method, raw materials such as Li_2S, P_2S_5, GeS_2 and elemental sulfur (Sigma-Aldrich, 99.98%) were initially mixed in a molar ratio of 5:1:1:x (where x= 5-15). The mixed powder (2 g) was added into a mixed solvent (20 mL) consisting of ACN (FUJIFILM Wako Pure Chemical Corp., 99.5% purity), THF, and EtOH (Konishi Chemical Ind. Co. Ltd., 99.5% purity) in a volume ratio of 1:1:0.05, respectively. The solvent mixture was stirred and dissolved for 30 min. The obtained solution was vacuum-

dried at 130 °C for 1 h, and then subjected to heat treatment in a tube furnace at 350, 450, or 550 °C for 6 or 12 h to obtain $Li_{10}GeP_2S_{12}$ solid electrolyte powder; the equipment was the same as that used for the liquid-phase shaking method. Excess sulfur evaporated through the heat treatment. All solvents were used after water removal treatment with molecular sieves.

Characterization

The chemical species in the precursor solution were examined by UV–Vis spectrophotometry (Jasco V-670). The crystal structures were characterised using X-ray diffraction (XRD, Smartlab SE, Rigaku). The samples were sealed in holders (Rigaku) in an Ar-filled glove box. The particle size and morphology were evaluated using scanning electron microscopy (SEM; S-4800, Hitachi High-Tech). The ionic conductivity of the solid electrolytes was investigated using electrochemical impedance spectroscopy (EIS) (SI 1260A, Solartron Analytical or HZ-Pro, Hokuto) in the frequency range of 1 MHz to 10 Hz under a dry Ar flow. The EIS samples were prepared by uniaxially pressing the samples (100 mg) into pellets at a pressure of 254 MPa. The electronic conductivity of the solid electrolytes was measured using a direct-current polarisation technique (Hz-Pro; Hokuto Denko).

Supporting Figure

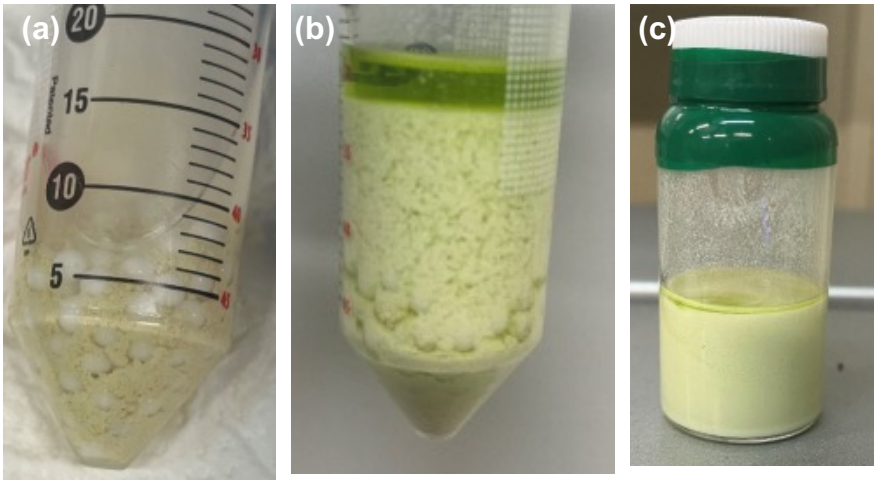

Figure S1. Photographs of $Li_{10}GeP_2S_{12}$ solid electrolyte precursors synthesised using 1,2-dimethoxyethane as solvent (a) before shaking, (b) after shaking for 6 h, and (c) after stirring for 72 h.

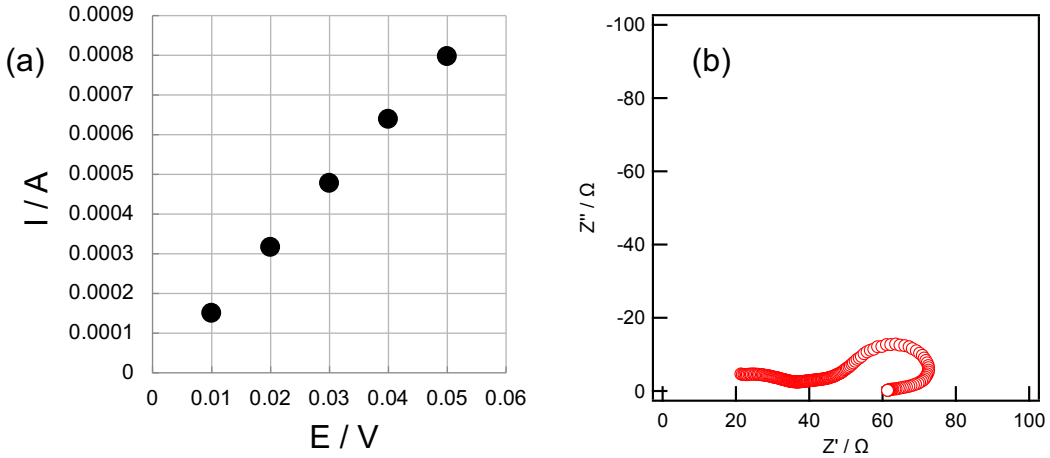

Figure S2. (a) DC polarization test results and (b) Nyquist plot of $Li_{10}GeP_2S_{12}$ solid electrolyte at 25 °C. The sample was synthesised using 1,2-dimethoxyethane (DME) as solvent by shaking at 30 °C.

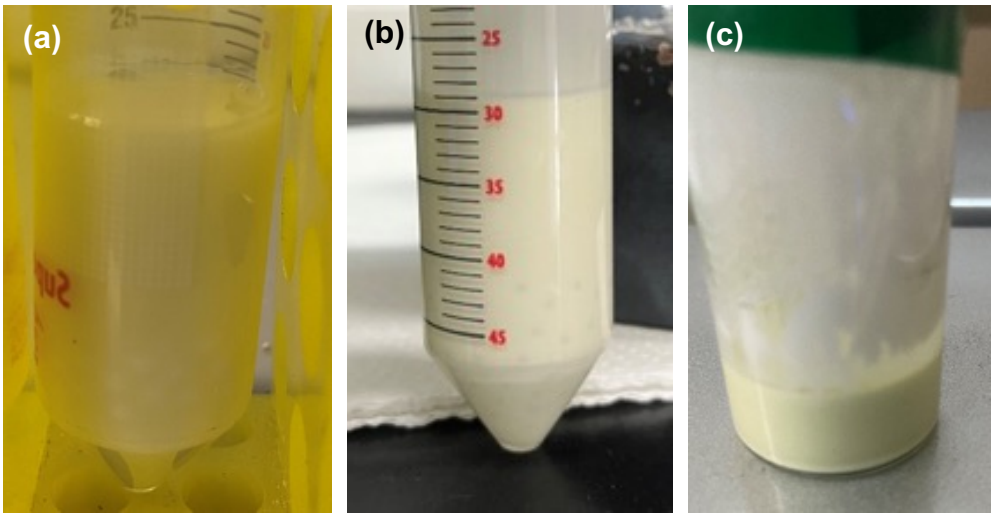

Figure S3. Photographs of $Li_{10}GeP_2S_{12}$ solid electrolyte precursors synthesised with tetrahydrofuran as solvent (a) before shaking, (b) after shaking for 6 h, and (c) after stirring for 72 h.

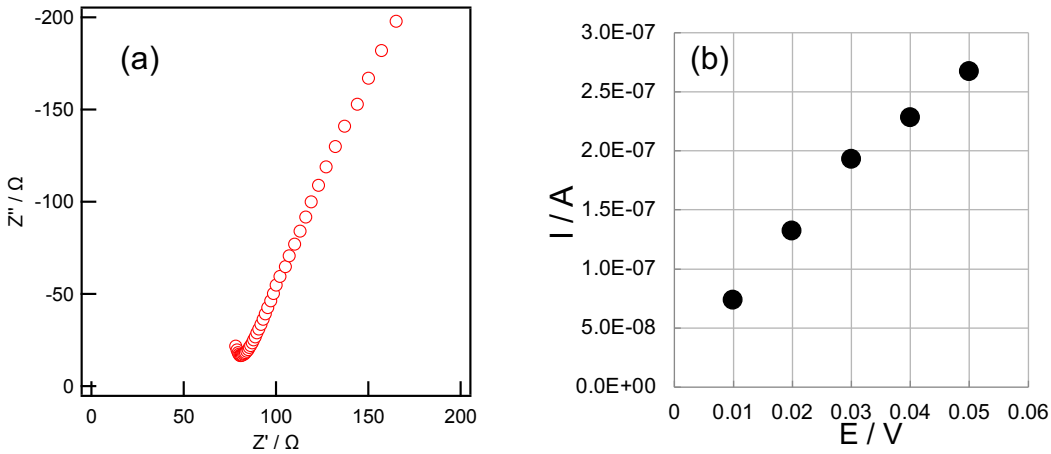

Figure S4. Nyquist plot and (b) DC polarization test results of $Li_{10}GeP_2S_{12}$ solid electrolyte at 25 °C. The sample was synthesised using tetrahydrofuran (THF) as solvent by shaking at 30 °C.

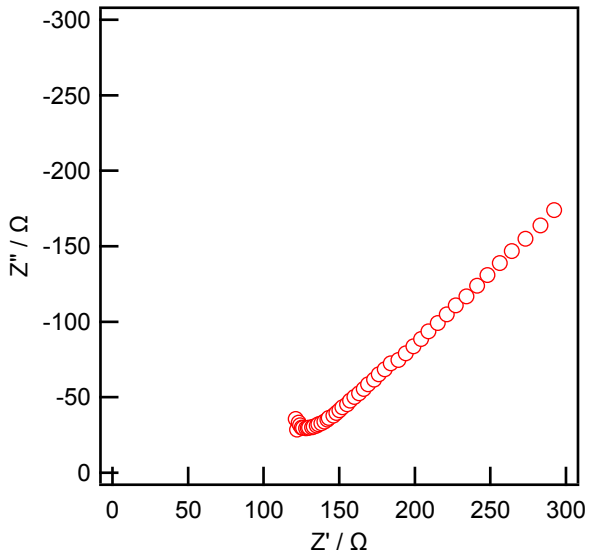

Figure S5. Nyquist plot of $Li_{10}GeP_2S_{12}$ solid electrolyte at 25 °C. $Li_{10}GeP_2S_{12}$ solid electrolyte was synthesised using tetrahydrofuran (THF) as solvent by shaking at 45 °C.

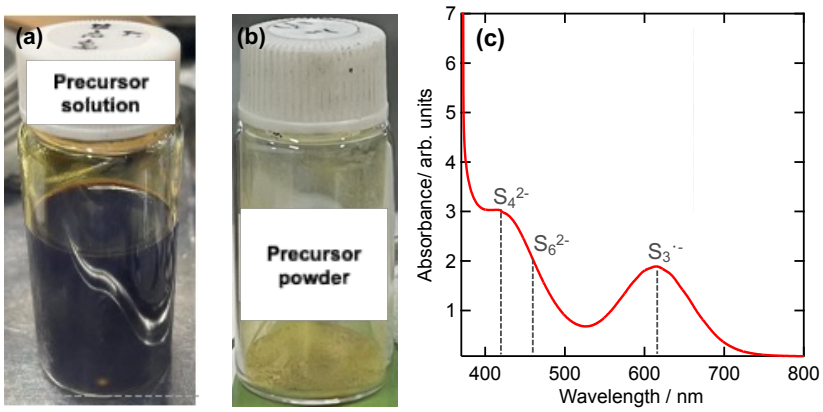

Figure S6. Photographs of $Li_{10}GeP_2S_{12}$ solid electrolyte precursors synthesised via solution processing involving dynamic sulfide radical anions (a) after stirring for 30 min and (b) after drying, and (c) UV-Vis spectra of $Li_{10}GeP_2S_{12}$ solutions at 0.5 mmol L^{-1} in the mixed solvent containing ACN and THF a trace amount of EtOH.

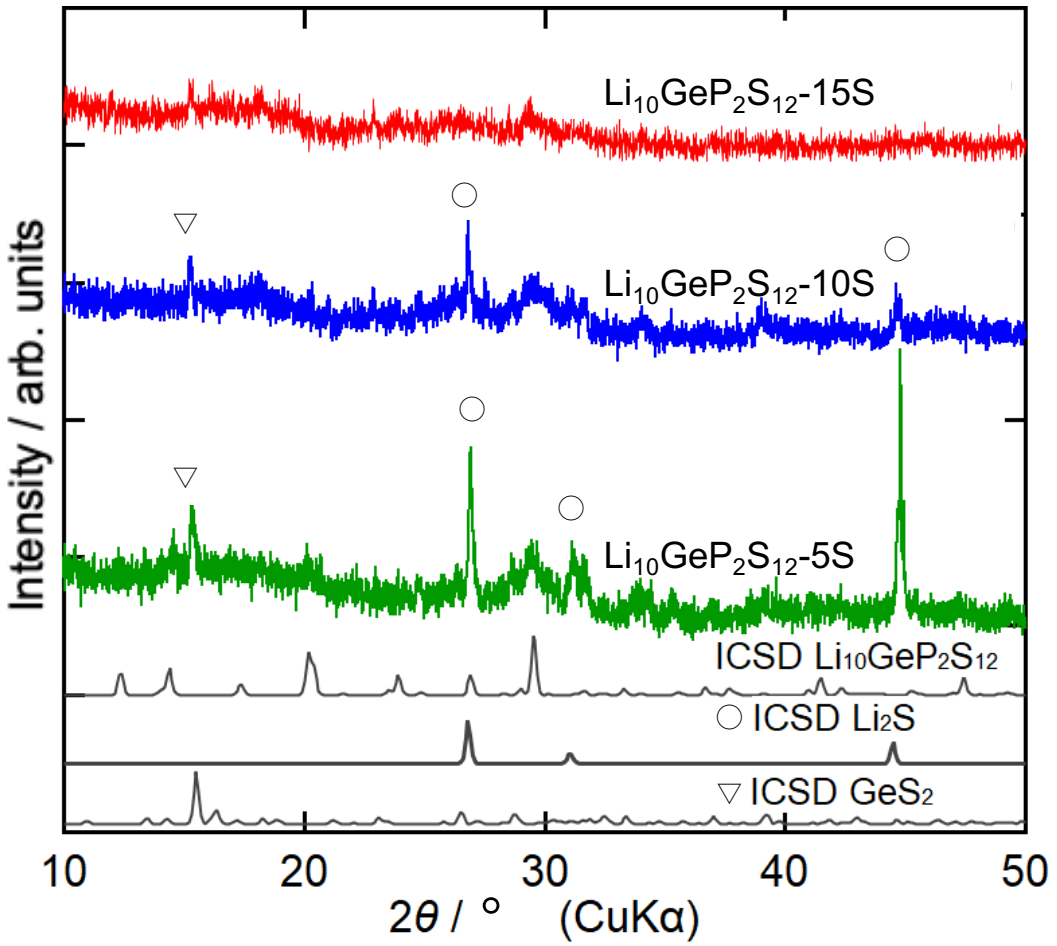

Figure S7. Powder X-ray diffraction (XRD) patterns of $Li_{10}GeP_2S_{12}$–xS precursors with x = 5–15.

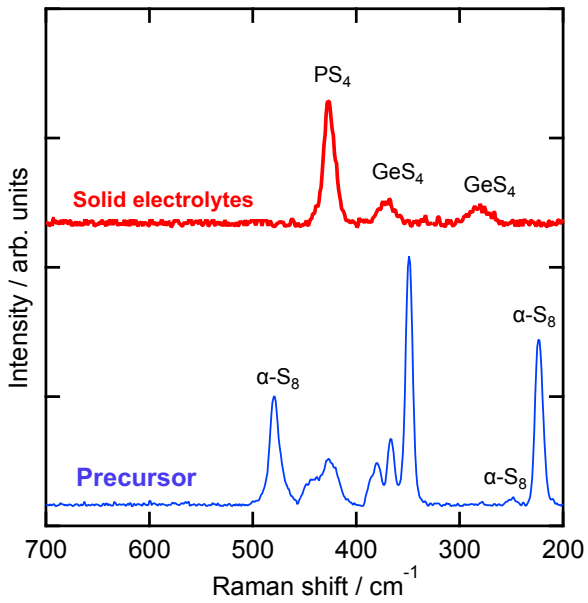

Figure S8. Raman spectrum of $Li_{10}GeP_2S_{12}$–10S precursor and solid electrolyte.

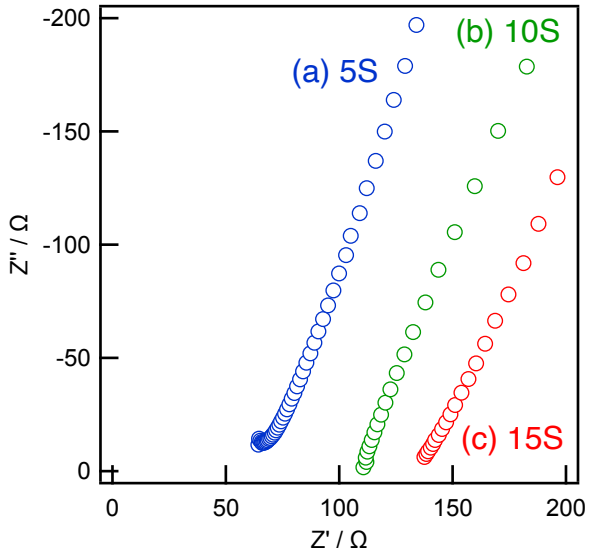

Figure S9. Nyquist plot of $Li_{10}GeP_2S_{12}$–xS solid electrolytes ((a) x=5, (b) x=10, (c) x=15) synthesised via solution processing with dynamic sulfide radical anions at 25 °C. The samples were heat-treated at 550 °C for 12 h. It is noted that the absolute resistance value depends on the sample thickness.

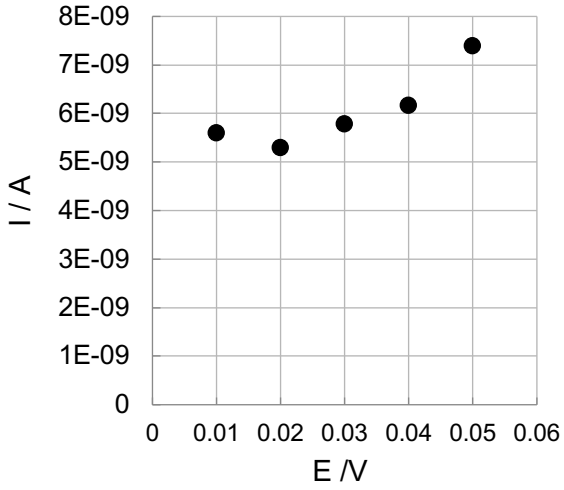

Figure S10. DC polarization test results of $Li_{10}GeP_2S_{12}$–10S solid electrolyte synthesised via solution processing with dynamic sulfide radical anions at 25 °C. The samples were heat-treated at 550 °C for 12 h.

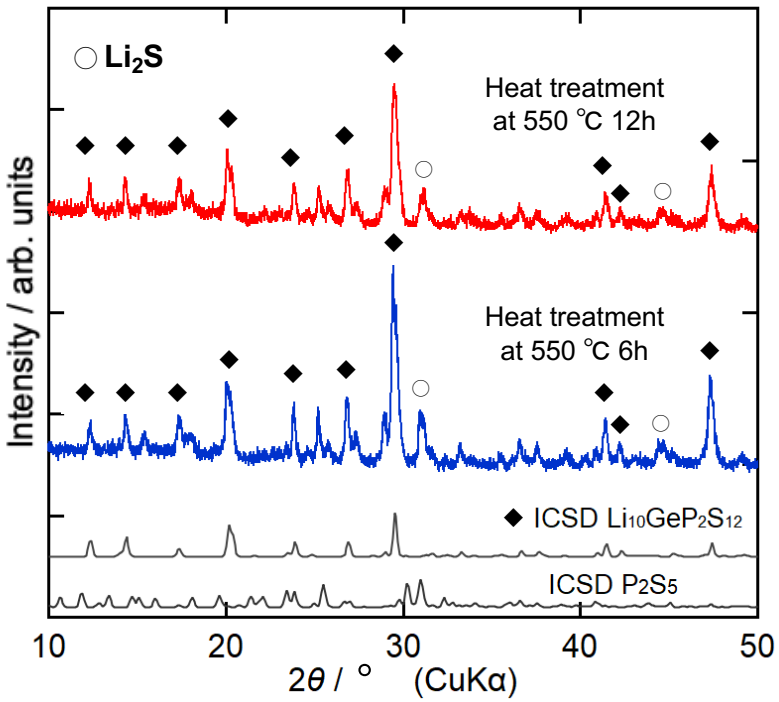

Figure S11. Powder XRD patterns of $Li_{10}GeP_2S_{12}$–10S subjected to heat treatment at 550 °C for 6 and 12 h.

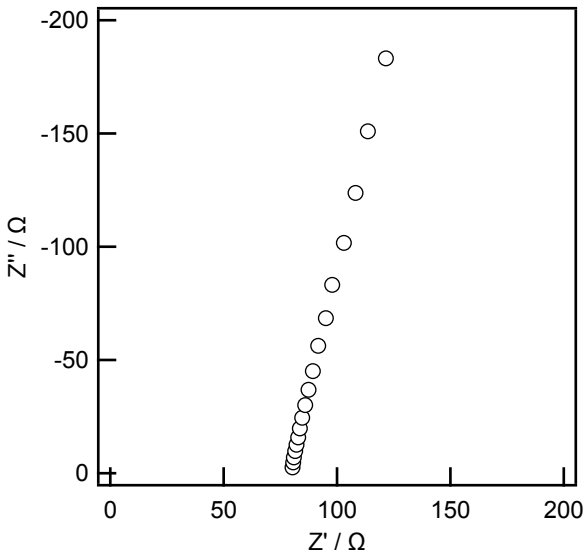

Figure S12. Nyquist plot of $Li_{10}GeP_2S_{12}$–10S solid electrolytes synthesised via solution processing with dynamic sulfide radical anions at 25 °C. The samples were heat-treated at 550 °C for 6 h.

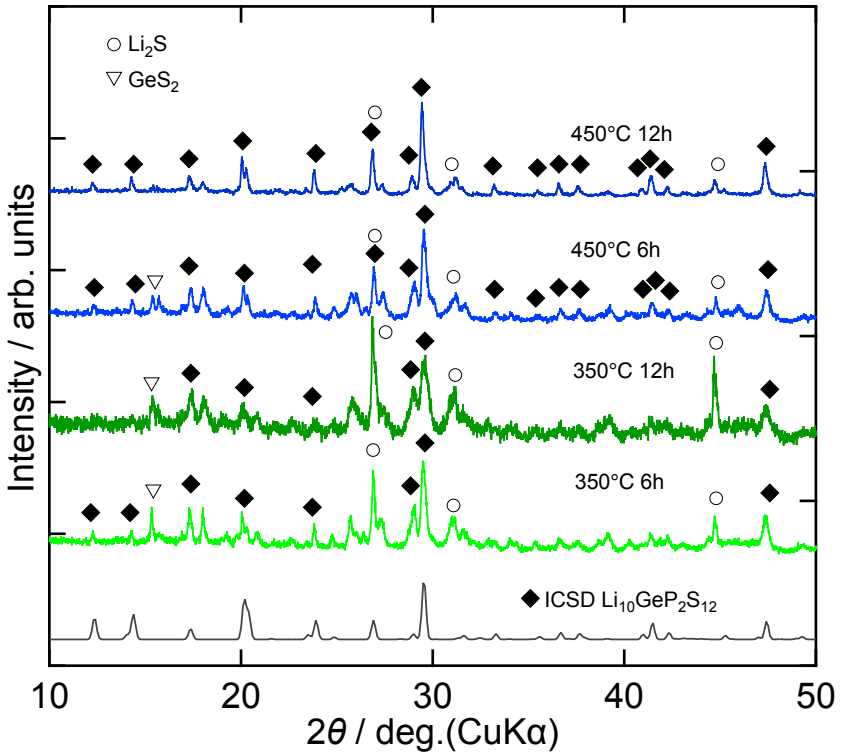

Figure S13. Powder XRD patterns of $Li_{10}GeP_2S_{12}$–10S subjected to heat treatment at 450 and 350 °C for 6h or 12h.

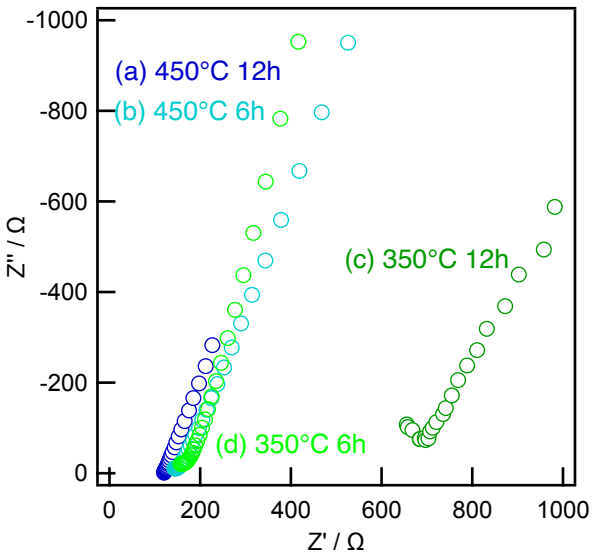

Figure S14. Nyquist plot of $Li_{10}GeP_2S_{12}$–10S solid electrolytes synthesised via solution processing with dynamic sulfide radical anions at 25 °C. The samples were heat-treated at (a) 450 °C 12h, (b) 450 °C 6h, (c) 350 °C 6h and (d) 350 °C 12h. It is noted that the absolute resistance value depends on the sample thickness.

Table S1. Lists of lithium-ion and electronic conductivity of materials obtained under different conditions

Method	Liquid phase shaking		solution processing with dynamic sulfide radical anions (Basically, composition is $Li_{10}GeP_2S_{12}$–10S (denoted as 10S))			
Solvent	DME	THF	ACN+THF+EtOH			
Heat treatment	550℃12h			550℃6h	450 ℃ 12h (6h)	350 ℃ 12h (6h)
Lithium-ion conductivity	-	1.6×10^{-3}	1.0×10^{-3}	1.6×10^{-3}	1.0×10^{-3} (0.3×10^{-3})	0.2×10^{-3} (0.3×10^{-3})
Electron conductivity	0.16×10^{-4}	9.5×10^{-7}	9.8×10^{-9}	-	-	-