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SUPPORTING INFORMATION

An argyrodite sulfide-based superionic conductor synthesized by a liquid-phase technique with tetrahydrofuran and ethanol

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For comparison, Li_6PS_5Br SEs were also synthesized *via* three other processes (Schematic illustrations are presented in Figure S1); Li_6PS_5Br was synthesized from Li_2S, P_2S_5, and LiBr (a) with EtOH and (b) with THF only. (c) Li_6PS_5Br was synthesized *via* the LP technique with EtOH only using $75Li_2S{\cdot}25P_2S_5$ glass instead of the Li_3PS_4-THF precursor as the staring material. $75Li_2S{\cdot}25P_2S_5$ glass was prepared using the mechanochemical (MC) technique presented in our previous report. The concentration of Li_6PS_5Br in the precursor solution was 10 wt.%. The precursor solutions were dried at 150 °C under vacuum for 3 h to prepare the solid powder. The synthesis conditions are summarized in Supplementary Table S1.

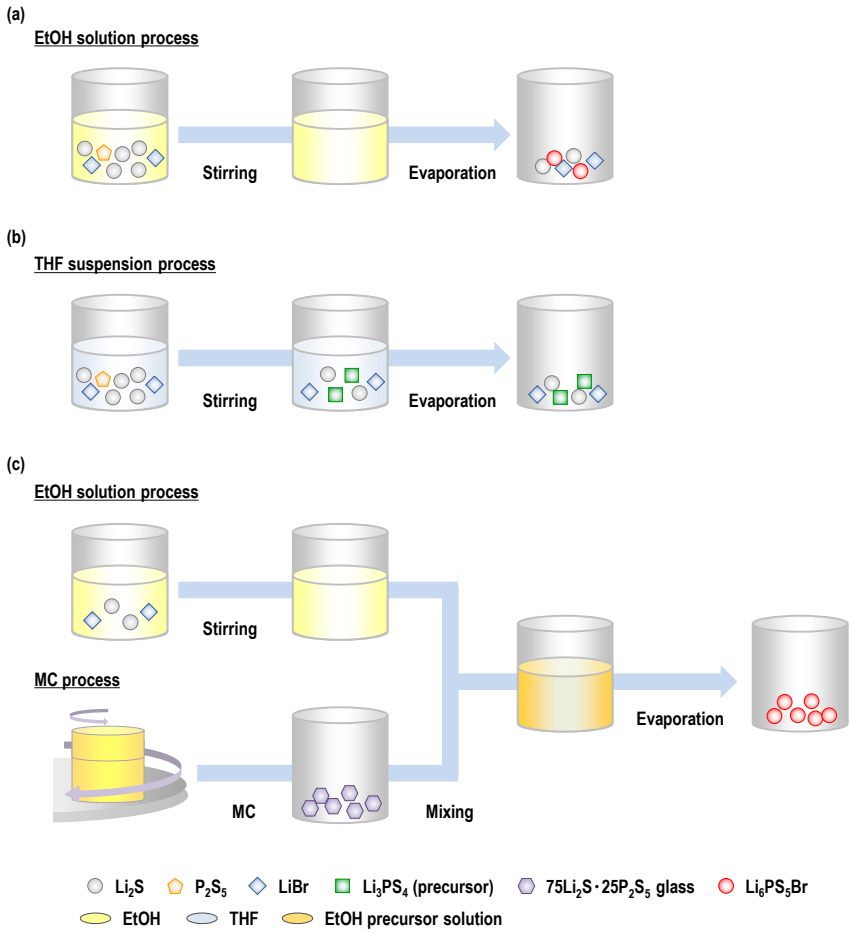

Figure S1. Schematic illustrations of the LP techniques for synthesis of Li_6PS_5Br with (a) EtOH only, (b) THF only, and (c) *via* EtOH solution and MC processes.

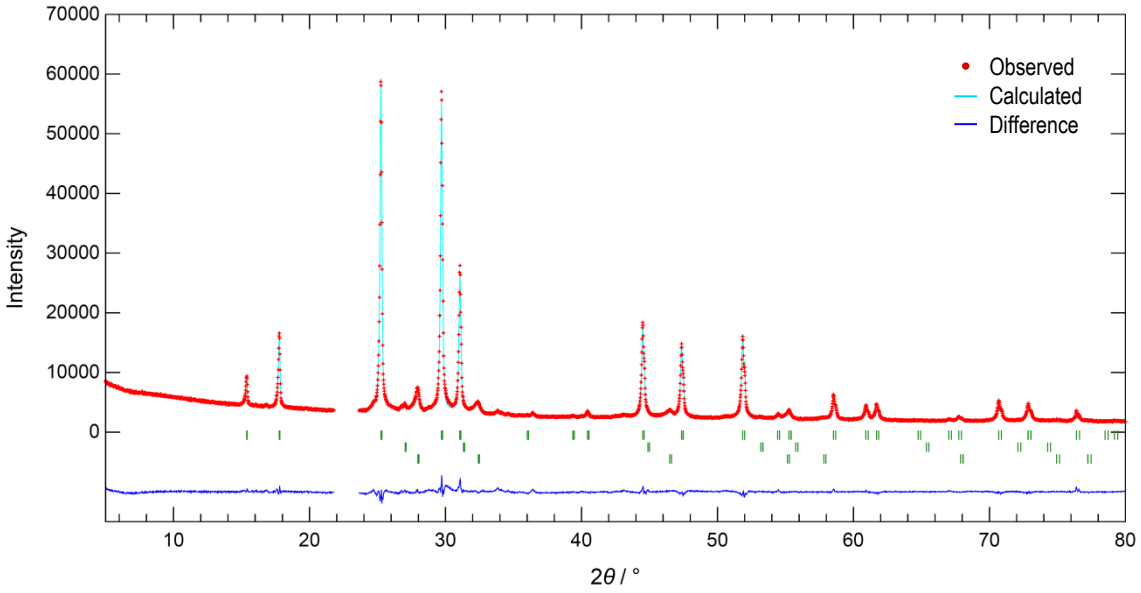

Figure S2. Rietveld refinement profile of X-ray powder diffraction data for Li_6PS_5Br (LP-550) recorded at room temperature. Red dots and light blue line denote the observed and calculated XRD patterns, respectively. The green sticks mark the position of the reflections for Li_6PS_5Br, Li_2S, and LiBr. The difference between the observed and calculated patterns is signified by the blue line. The XRD pattern in the region of 21.8−23.6° includes the unknown peaks and was not considered.

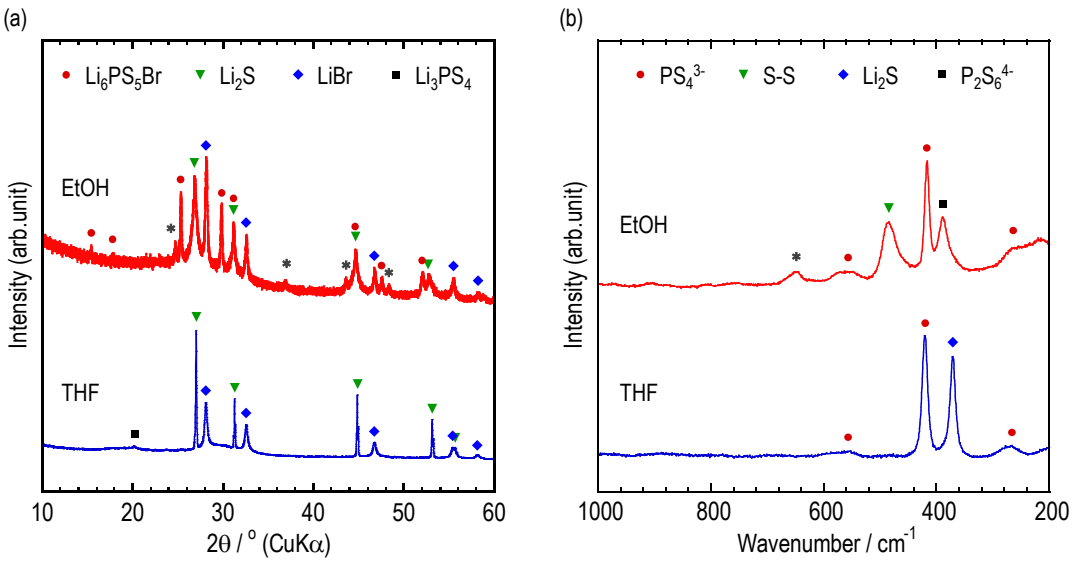

Figure S3. (a) XRD patterns and (b) Raman spectra of the samples prepared with EtOH only and THF only, respectively. Asterisks indicate unknown peaks.

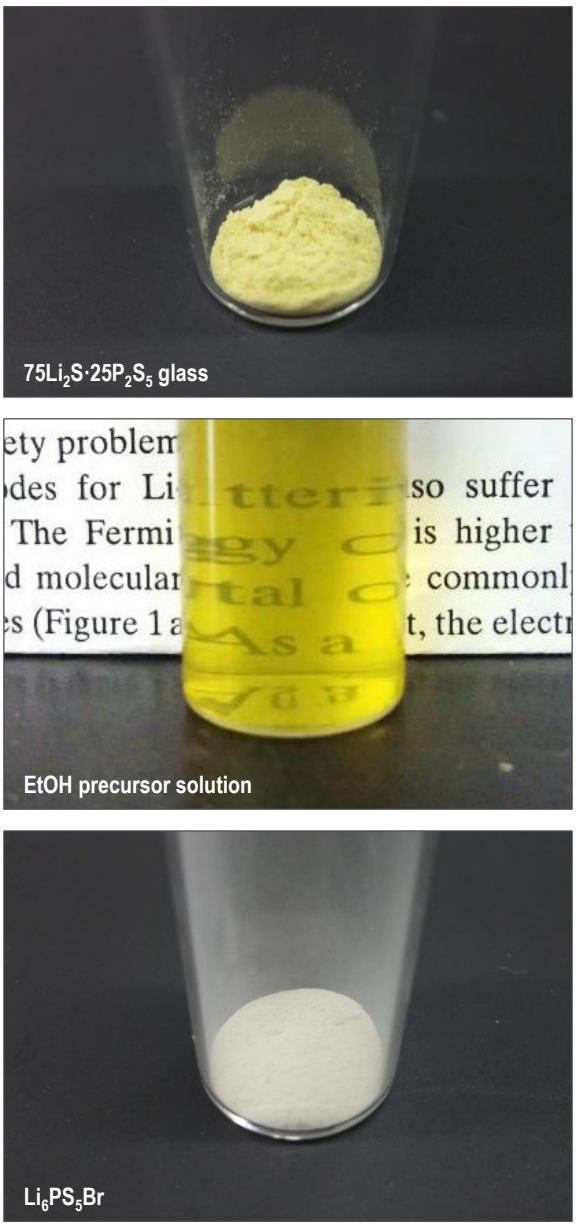

Figure S4. Photographic images of $75Li_2S{\cdot}25P_2S_5$ glass powder, EtOH precursor solution, and Li_6PS_5Br powder synthesized from Li_2S, LiBr, and $75Li_2S{\cdot}25P_2S_5$ glass with EtOH solvent.

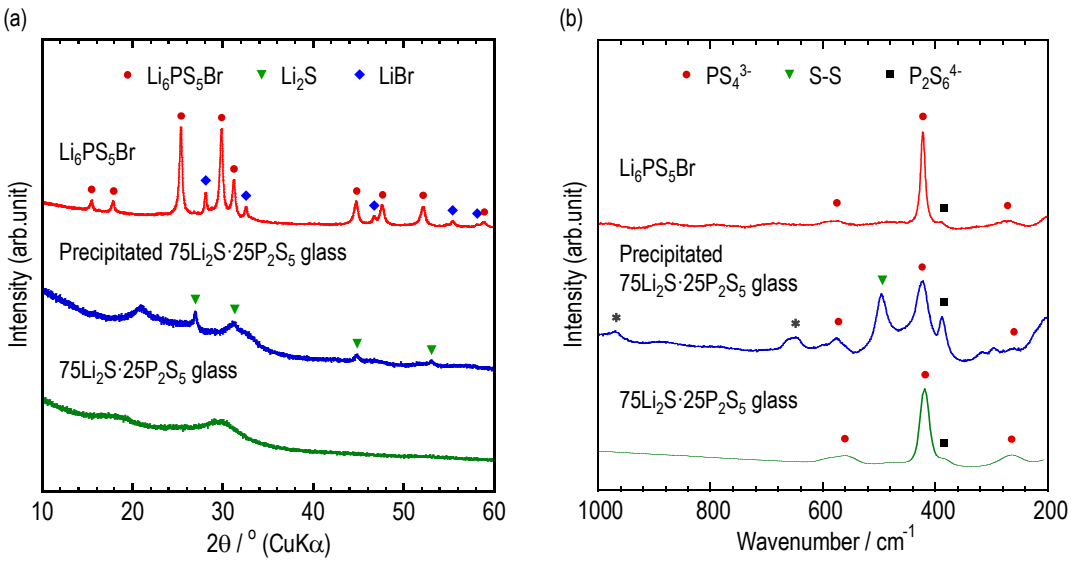

Figure S5. (a) XRD patterns and (b) Raman spectra of Li_6PS_5Br synthesized from Li_2S, LiBr, and $75Li_2S{\cdot}25P_2S_5$ glass with EtOH solvent, $75Li_2S{\cdot}25P_2S_5$ glass precipitated from EtOH solvent, and $75Li_2S{\cdot}25P_2S_5$ glass. Asterisks indicate unknown peaks.

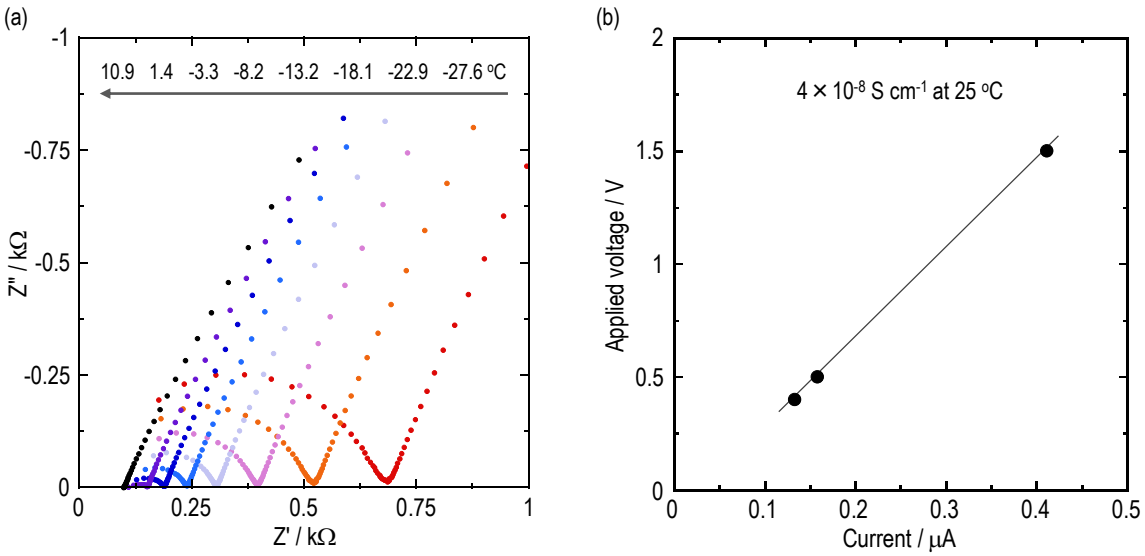

Figure S6. (a) Nyquist plots of LP-550 sintered body at temperatures between -27.6 °C and 10.9 °C. A resistance of more than 100 Ω was used for analyzing the temperature-dependence of the conductivity. (b) Relationship between the applied voltage and current, measured by DC polarization technique to determine the electronic conductivity, for the LP-550 green compact pressed at 360 MPa.

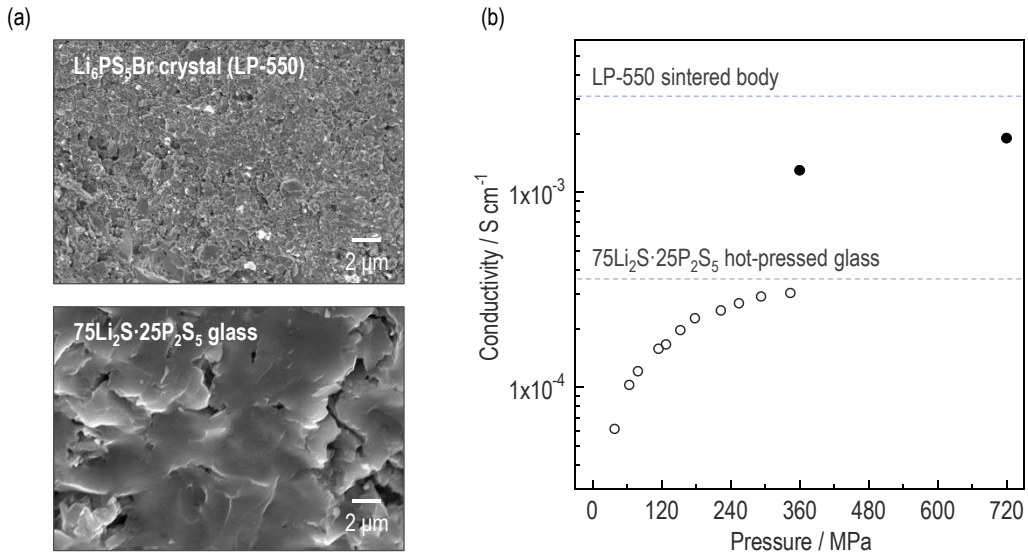

Figure S7. (a) SEM images of fracture cross sections of Li_6PS_5Br crystal (LP-550) and $75Li_2S \cdot 25P_2S_5$ glass[10] green compacts pressed at 360 MPa at room temperature. (b) Relationships between molding pressures and ionic conductivities of Li_6PS_5Br crystal (LP-550, closed circle) and $75Li_2S \cdot 25P_2S_5$ glass (open circle). Dashed line indicates the conductivity of $75Li_2S \cdot 25P_2S_5$ hot-pressed glass[10] and LP-550 sintered body.

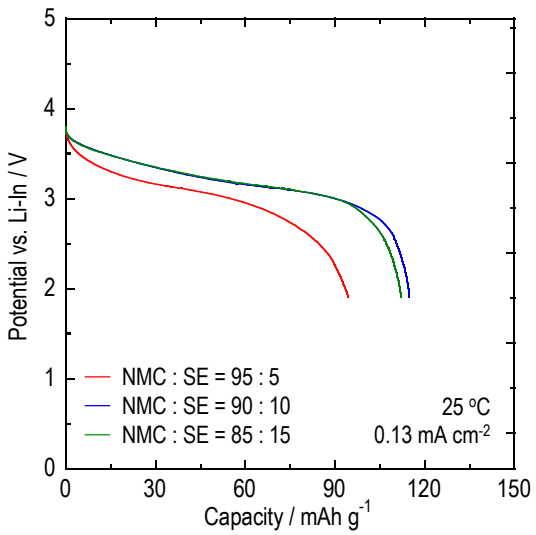

Figure S8. Discharge curves of cells with SE-coated NMC electrodes. The NMC/SE weight ratios were *x*:100-*x* (*x* = 85, 90, 95).

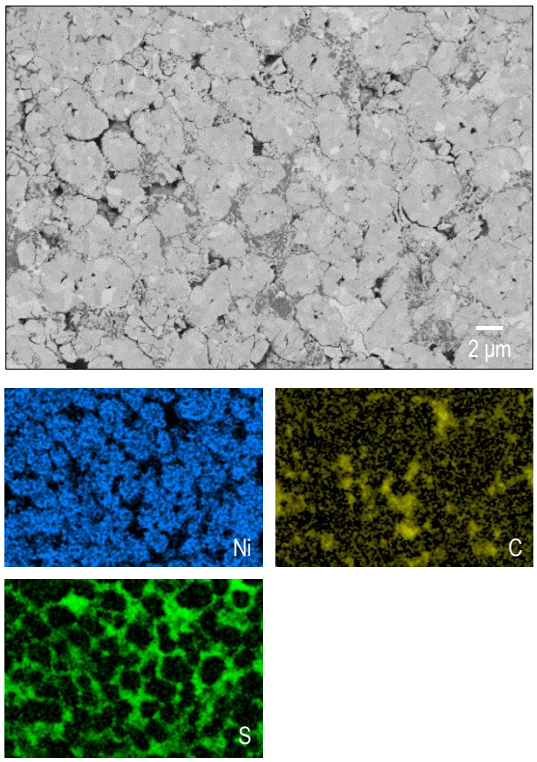

Figure S9. Cross-sectional FE-SEM image and EDX maps of nickel, carbon, and sulfur for the infiltrated NMC electrode.

Table S1. Conditions for LP synthesis of Li_6PS_5Br SEs: starting material, solvent, and heat treatment temperature .

	LP	(a)	(b)	(c)	MC
Synthesis technique	LP	LP	LP	MC, LP	MC
Staring material	Li_2S, P_2S_5, LiBr	Li_2S, P_2S_5, LiBr	Li_2S, P_2S_5, LiBr	Li_2S, LiBr, Li_3PS_4	Li_2S, P_2S_5, LiBr
Solvent	THF, EtOH	EtOH	THF	EtOH	-
Heat treatment temperature / °C	550	150	150	150	550
Label	LP-550	-	-	-	MC-550

Table S2. Crystallographic data and Rietveld refinement of XRD powder data for Li_6PS_5Br crystal (LP-550)

Crystal system	Cubic	Lattice parameter	a = 9.9641(2) Å	R_{wp} = 3.88, R_e = 1.59, R_B = 5.04
Space group	$F\bar{4}3m$ (no. 216)	Volume	V = 989.27(3) Å^3	Goodness of the fit S = 2.44

Atom	Wyckoff site	Occ.	x	y	z	B / Å^2
Li	48*h*	0.5	0.2966(9)	0.009(2)	= 1 - x(Li)	5.0
P	4*b*	1.0	0.0	0.0	0.5	2.0
S1	4*a*	= 1 - g(Br1)	0.0	0.0	1.0	2.0
S2	4*d*	= g(Br1)	0.25	0.25	0.75	2.0
S3	16*e*	1.0	0.1180(1)	= -x(S3)	= 0.5 + x(S3)	2.0
Br1	4*a*	0.689(2)	0.0	0.0	1.0	2.0
Br2	4*d*	= 1 - g(Br1)	0.25	0.25	0.75	2.0

Table S3 Ionic conductivities and activation energies of Li_6PS_5Br synthesized from Li_2S, P_2S_5, and LiBr using THF and EtOH solvents and Li_6PS_5Br synthesized from Li_2S, LiBr, and $75Li_2S \cdot 25P_2S_5$ glass using EtOH solvent. Green compacts were prepared by pressing at 360 MPa at room temperature.

Heat treatment temperature / °C	150	150
Starting material	Li_2S, P_2S_5, LiBr	Li_2S, LiBr, $75Li_2S \cdot 25P_2S_5$ glass
Solvent	THF + EtOH	EtOH
Pellet	Green compact	Green compact
Molding pressure / MPa	360	360
Conductivity at 25 °C / mS cm^{-1}	0.13	0.16

Table S4. Ionic conductivities and activation energies of sulfide-based SEs prepared *via* the LP techniques reported in previous studies

	Li_3PS_4 (THF)	Li_3PS_4 (EA)	$Li_7P_3S_{11}$	$Li_7P_2S_8I$	LiI-Li_4SnS_4
Measurement temperature / °C	25	R.T.	25	R.T.	30
Conductivity at 25 °C / mS cm^{-1}	0.16	0.33	1.5	0.63	0.41
Activation energy / kJ mol^{-1}	34.3	31	23	N / A	41.6
Reference	15	19	20	14	25