

Supplementary Information

Deciphering the critical role of interstitial volume in glassy sulfide superionic conductors

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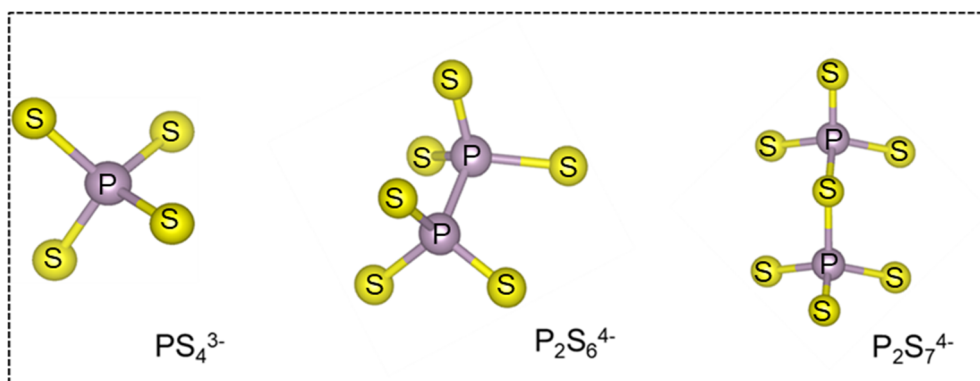


Fig. S1 Structures of typical anion clusters in 75Li₂S-25P₂S₅ glass.

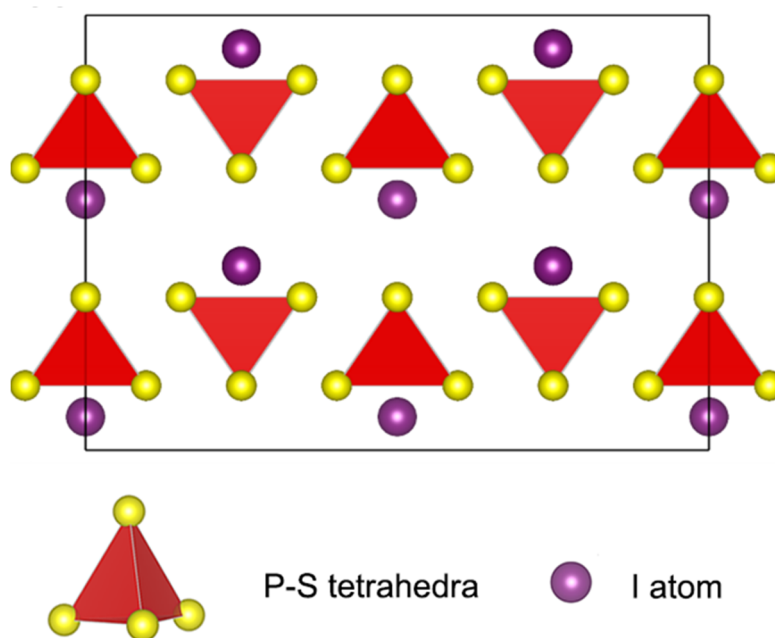


Fig. S2 The crystal structure of Li₄PS₄I.

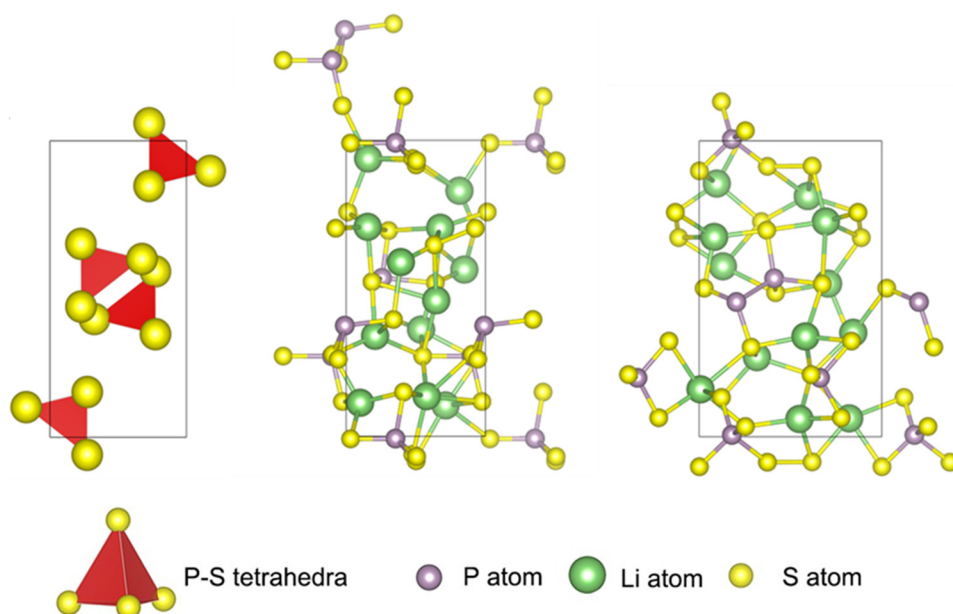
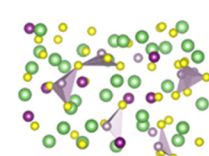
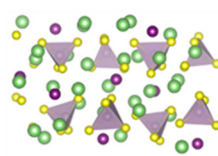
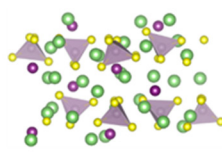
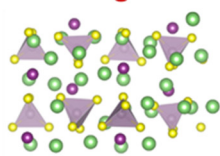


Fig. S3 Melt-quenching simulation results of β - Li_3PS_4 . The structure of anion clusters in the β - Li_3PS_4 crystal (**left**). A snapshot of $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass exhibiting the existence of $\text{P}_2\text{S}_7^{4-}$ after equilibrium (**middle**). A snapshot of $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ glass exhibiting the existence of $\text{P}_2\text{S}_6^{4-}$ after equilibrium (**right**).

Annealing



Cooling

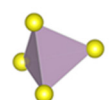
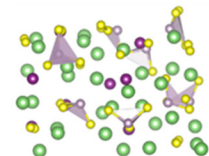
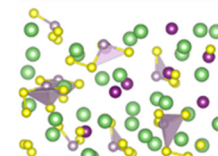
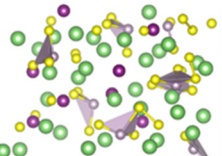
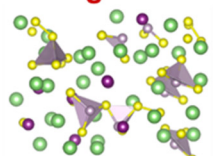


Fig. S4 Snapshots of $\text{Li}_4\text{PS}_4\text{I}$ at different temperatures during the annealing-cooling process.

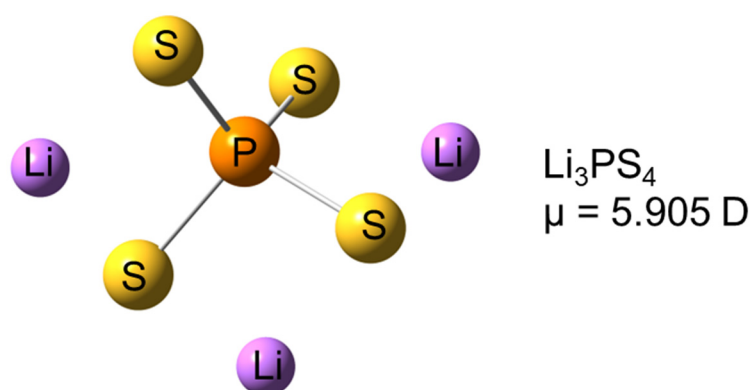


Fig. S5 The dipole moment of the Li_3PS_4 molecule.

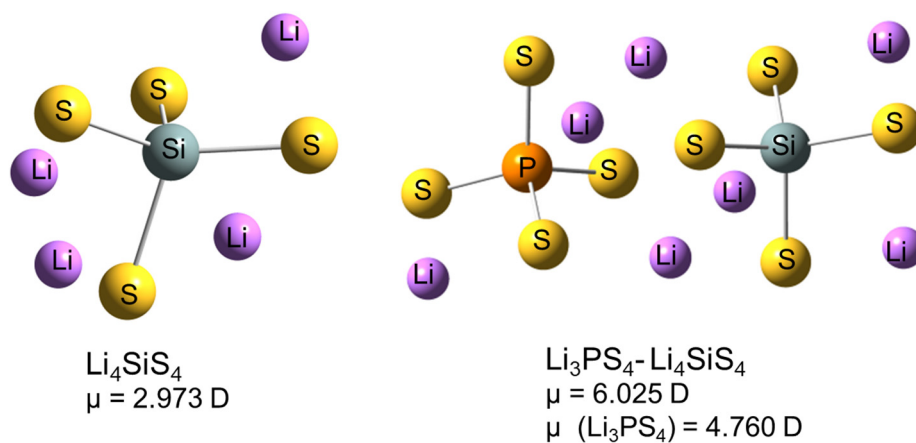


Fig. S6 The dipole moment of the Li_4SiS_4 molecule, $\text{Li}_3\text{PS}_4\text{-Li}_4\text{SiS}_4$ complex and Li_3PS_4 molecule after complexing with Li_4SiS_4 .

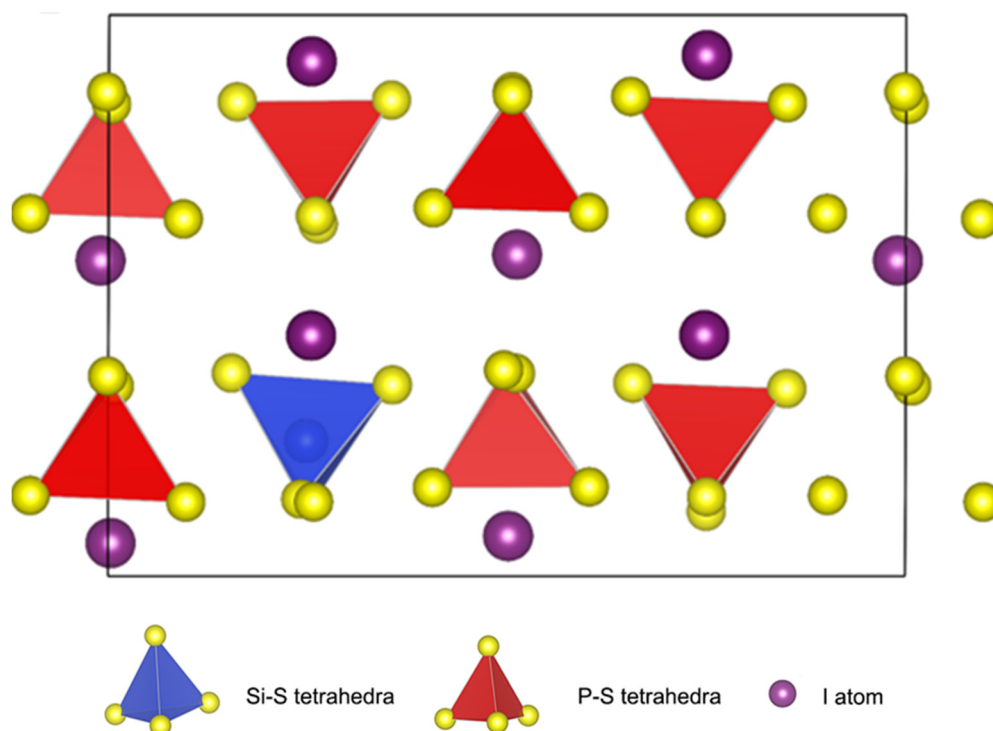
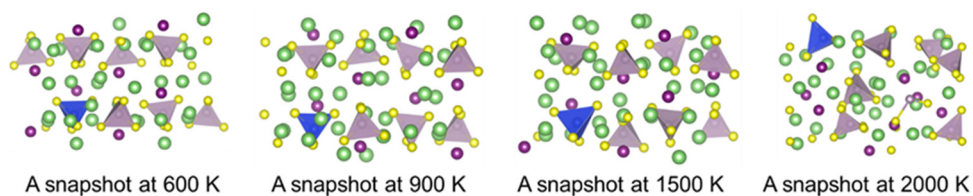


Fig. S7 The crystal structure of $\text{Li}_{4.125}\text{Si}_{0.125}\text{P}_{0.875}\text{S}_4\text{I}$.

Annealing



Cooling

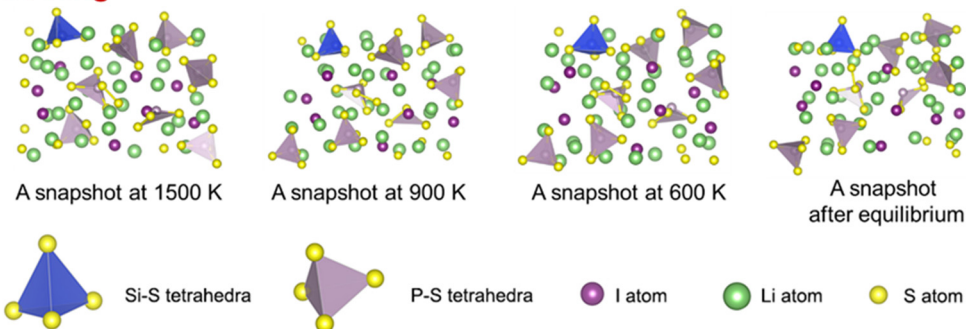


Fig. S8 Snapshots of $\text{Li}_{4.125}\text{Si}_{0.125}\text{P}_{0.875}\text{S}_4\text{I}$ at different temperatures during the annealing-cooling process.

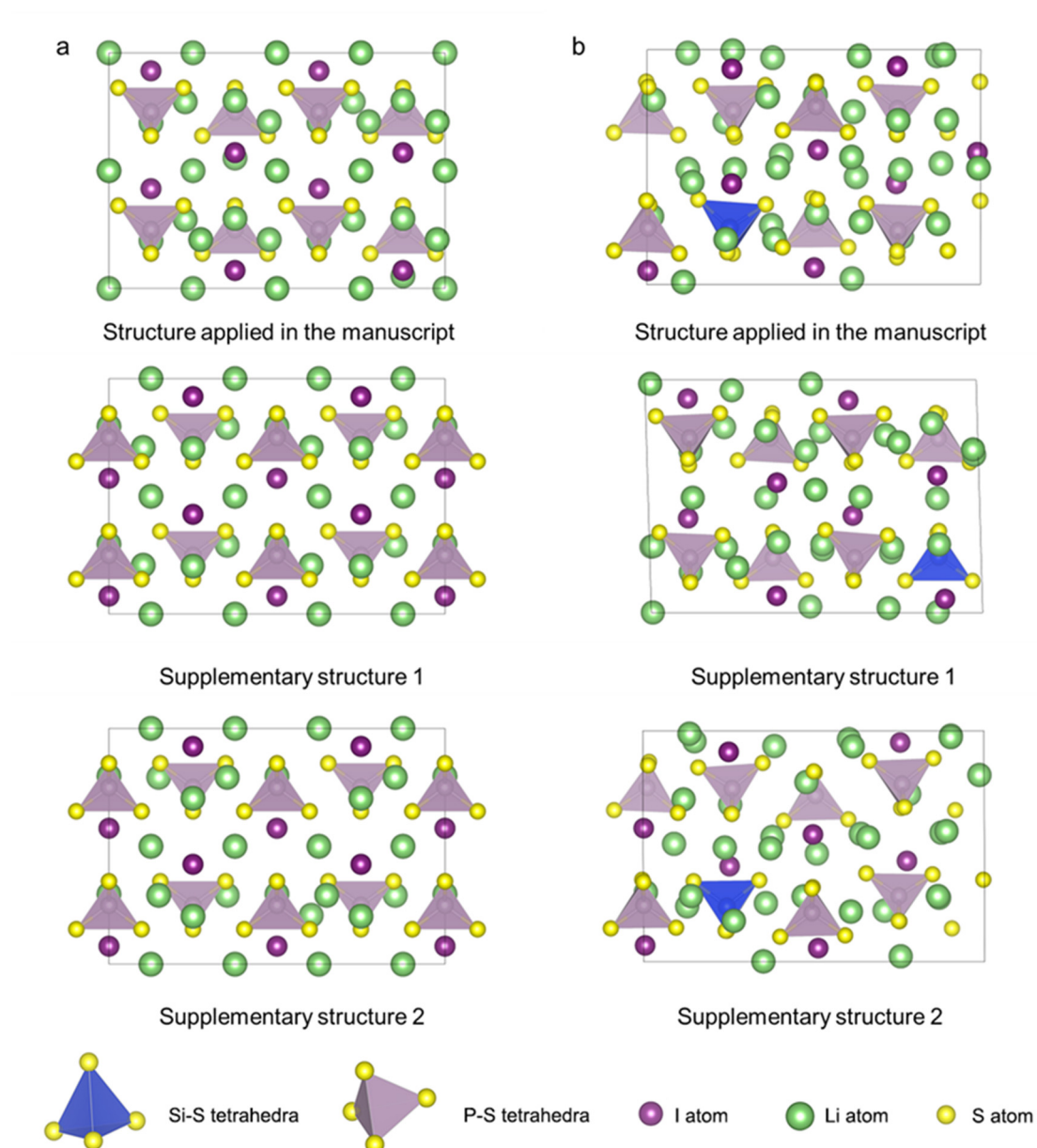


Fig. S9 The crystal structures of $\text{Li}_4\text{PS}_4\text{I}$ and $\text{Li}_{4.125}\text{Si}_{0.125}\text{P}_{0.875}\text{S}_4\text{I}$ applied in the manuscript and employed for validation. **a** The crystal structure of $\text{Li}_4\text{PS}_4\text{I}$ applied in the manuscript and other two additional structure employed for supplementary validation. **b** The crystal structure of $\text{Li}_{4.125}\text{Si}_{0.125}\text{P}_{0.875}\text{S}_4\text{I}$ applied in the manuscript and other two additional structure employed for supplementary validation.

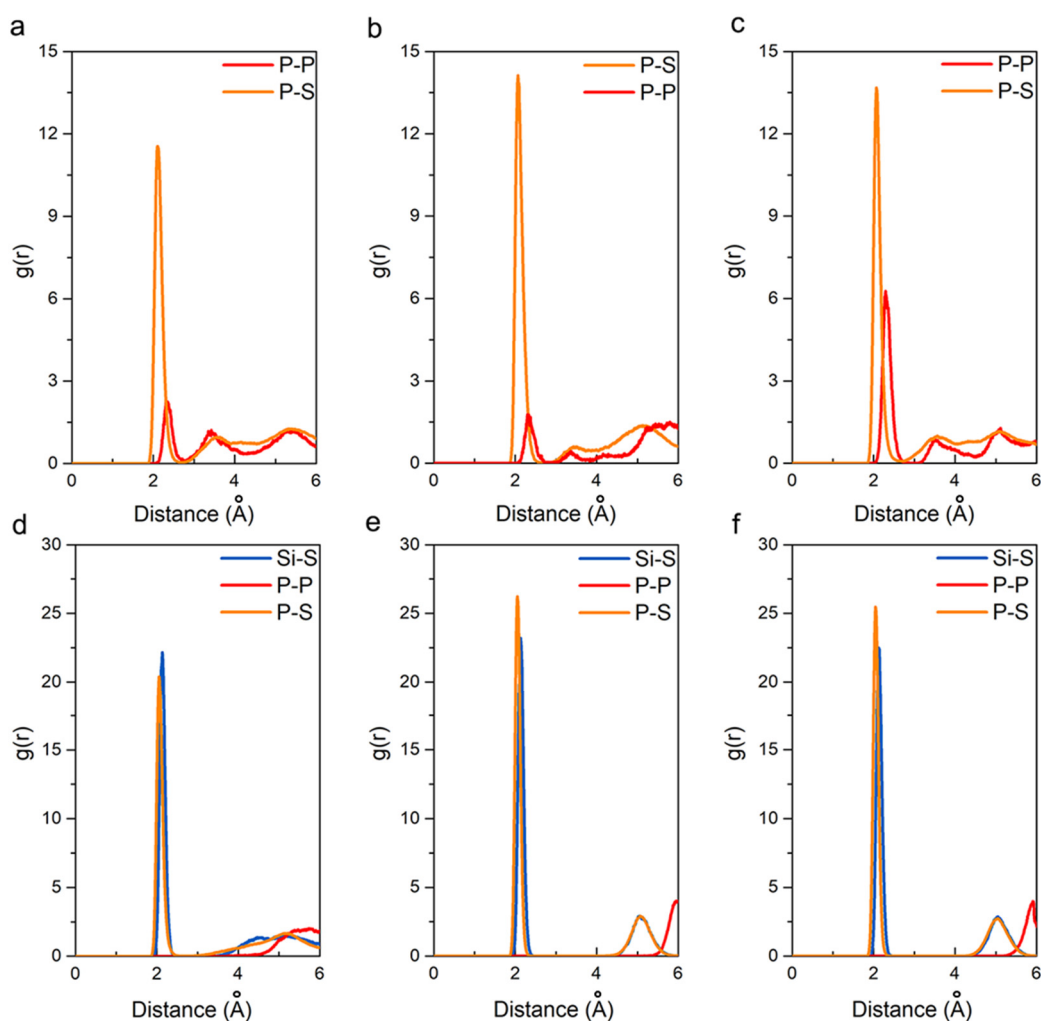


Fig. S10 The comparison of $g(r)$ profiles in simulated glassy electrolytes with different initial structures. **a** The $g(r)$ profiles of P-P and P-S pairs in the $\text{Li}_4\text{PS}_4\text{I}$ glass with the structure applied in the manuscript. **b** The $g(r)$ profiles of P-P and P-S pairs in the $\text{Li}_4\text{PS}_4\text{I}$ glass with the Supplementary structure 1. **c** The $g(r)$ profiles of P-P and P-S pairs in the $\text{Li}_4\text{PS}_4\text{I}$ glass with the Supplementary structure 2. **d** The $g(r)$ profiles of Si-S, P-P and P-S pairs in the $\text{Li}_{4.125}\text{Si}_{0.125}\text{P}_{0.875}\text{S}_4\text{I}$ glass with the structure applied in the manuscript. **e** The $g(r)$ profiles of Si-S, P-P and P-S pairs in the $\text{Li}_{4.125}\text{Si}_{0.125}\text{P}_{0.875}\text{S}_4\text{I}$ glass with the Supplementary structure 1. **f** The $g(r)$ profiles of Si-S, P-P and P-S pairs in the $\text{Li}_{4.125}\text{Si}_{0.125}\text{P}_{0.875}\text{S}_4\text{I}$ glass with the Supplementary structure 2.

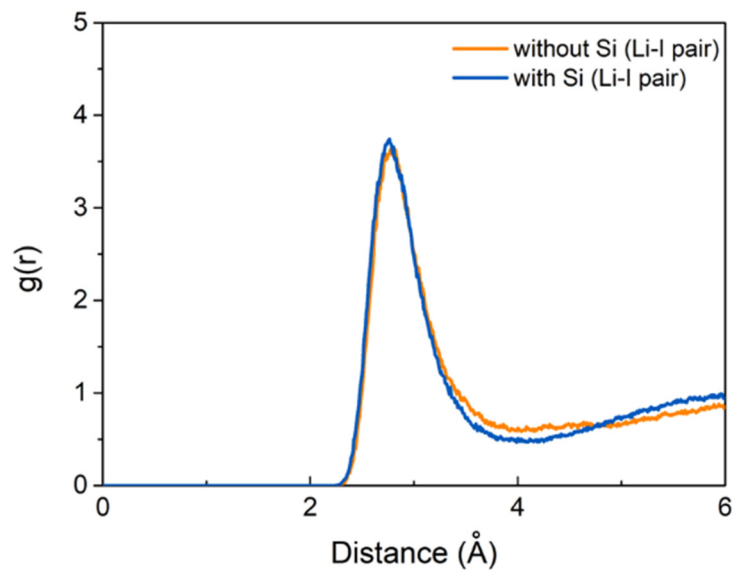


Fig. S11 The $g(r)$ profiles of the Li-I pair in the $\text{Li}_4\text{PS}_4\text{I}$ glass and the Si-doped $\text{Li}_{4.125}\text{Si}_{0.125}\text{P}_{0.875}\text{S}_4\text{I}$ glass.

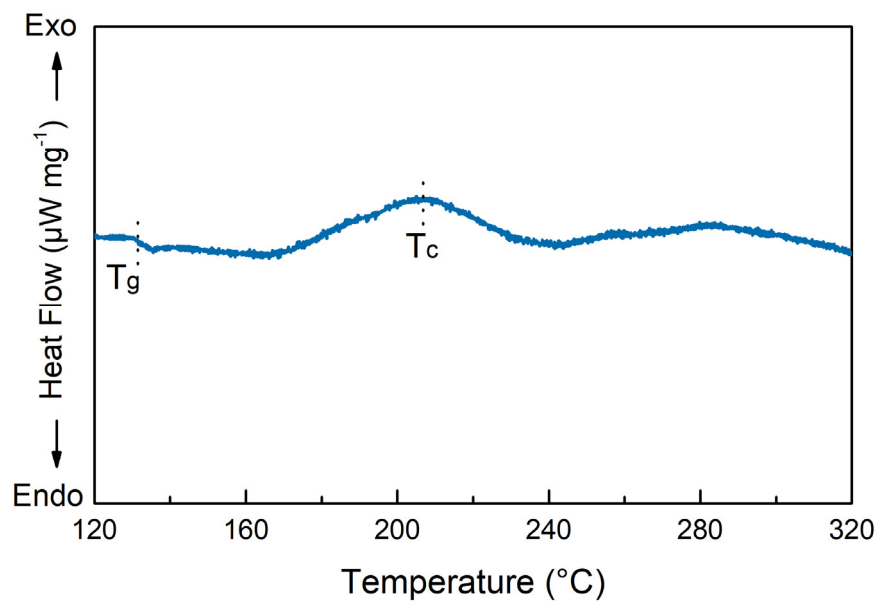


Fig. S12 The differential scanning calorimetry curve of the P:Si = 6 electrolyte in N_2 flow.

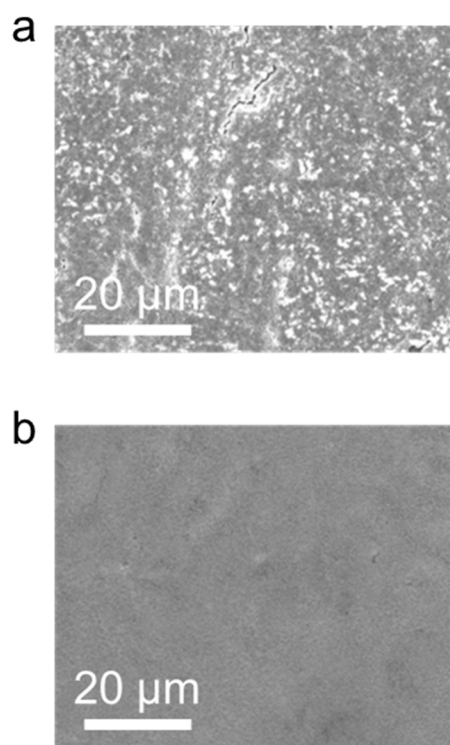


Fig. S13 The surface morphology of the cold-pressed and hot-pressed P:Si = 6 electrolytes.

a The surface morphology of the cold-pressed P:Si = 6 electrolyte. **b** The surface morphology of the highly-densified hot-pressed P:Si = 6 electrolyte.

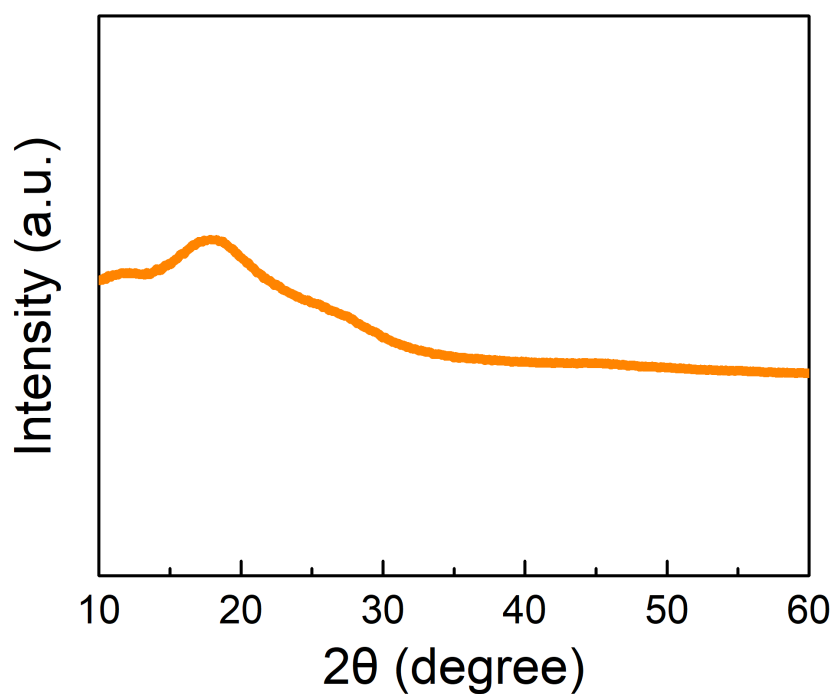


Fig. S14 The XRD spectrum of the hot-pressed P:Si = 6 electrolyte.

Table S1 The calculation of relative density of the P:Si = 6 electrolyte.

Composition	Theoretical Density / (g cm^{-3})	Weight / (mg)	Thickness / (mm)	Real Density / (g cm^{-3})	Relative Density
P:Si = 6	2.483	158.6	0.869	2.325	0.936

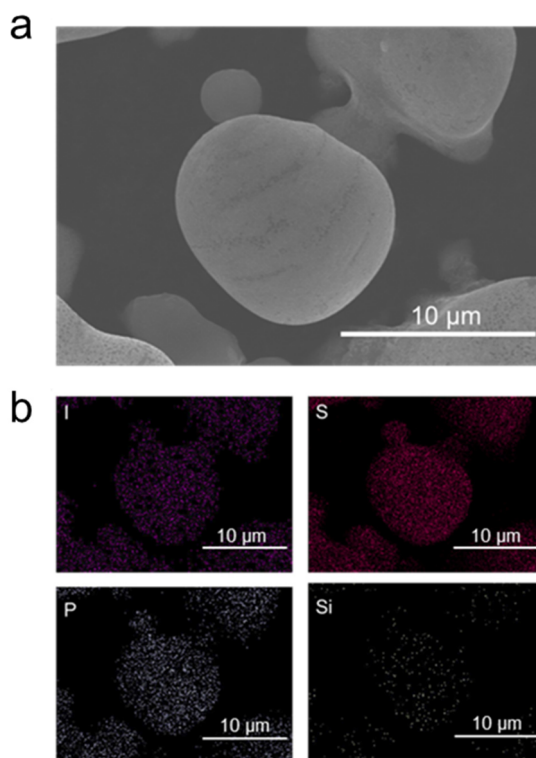


Fig. S15 The morphology and elemental distribution of the P:Si = 6 particle. **a** The particle morphology of the P:Si = 6 particle and **b** the corresponding EDS mapping results.

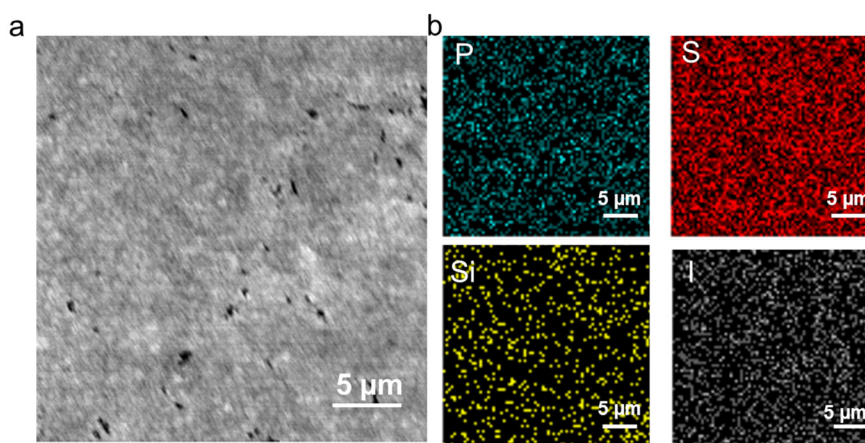


Fig. S16 The morphology and elemental distribution of the P:Si = 6 pellet. **a** The surface morphology of the P:Si = 6 pellet and **b** the corresponding EDS mapping results.

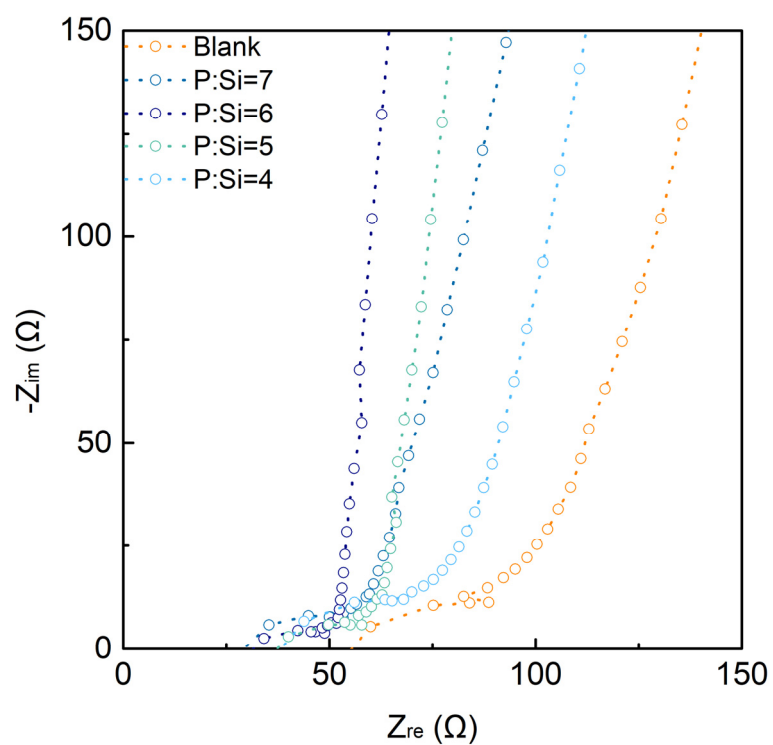


Fig.S17 Nyquist plots of electrolytes with different P/Si ratios at 298 K.

Table S2 The summary of the ionic conductivity and density of electrolytes with different P/Si ratios.

Composition	Blank	P:Si = 7	P:Si = 6	P:Si = 5	P:Si = 4
Resistance / (ohms)	101.20	58.68	50.17	61.83	73.18
Thickness / (mm)	0.885	0.872	0.869	0.874	0.879
Ionic conductivity / (mS cm ⁻¹)	1.11	1.90	2.21	1.80	1.53

Table S3 The summary of the reported ionic conductivity of glass sulfide electrolytes.

Glass Sulfide-based SE	Ionic Conductivity / (mS cm ⁻¹)	Ref.
Blank(60(0.75Li ₂ S·0.25P ₂ S ₅)-40LiI)	1.11	*This Work
P : Si = 7	1.90	*This Work
P : Si = 6	2.21	*This Work
P : Si = 5	1.80	*This Work
P : Si = 4	1.53	*This Work
75Li ₂ S·25P ₂ S ₅	0.50	1
70(0.75Li ₂ S·0.25P ₂ S ₅)-30LiI	1.78	2
Li _{0.84} B _{0.40} Si _{0.2} O _{0.4} S _{0.84} I _{0.36}	2.10	3
67(0.75Li ₂ S·0.25P ₂ S ₅)-33LiBH ₄	1.60	4
0.26B ₂ S ₃ -0.30Li ₂ S-0.44LiI	1.70	5
0.28SiS ₂ -0.42Li ₂ S-0.30LiI	1.80	6
77.5Li ₂ S·22.25P ₂ S ₅ ·0.25P ₂ O ₅	1.11	7
30LiI·70(0.07Li ₂ O·0.68Li ₂ S·0.25P ₂ S ₅)	1.30	8
0.07Li ₂ O·0.68Li ₂ S·0.25P ₂ S ₅	0.25	8
80(0.7Li ₂ S·0.3P ₂ S ₅)·20LiBr	0.34	9
75Li ₂ S·21P ₂ S ₅ ·4P ₂ O ₅	0.10	10

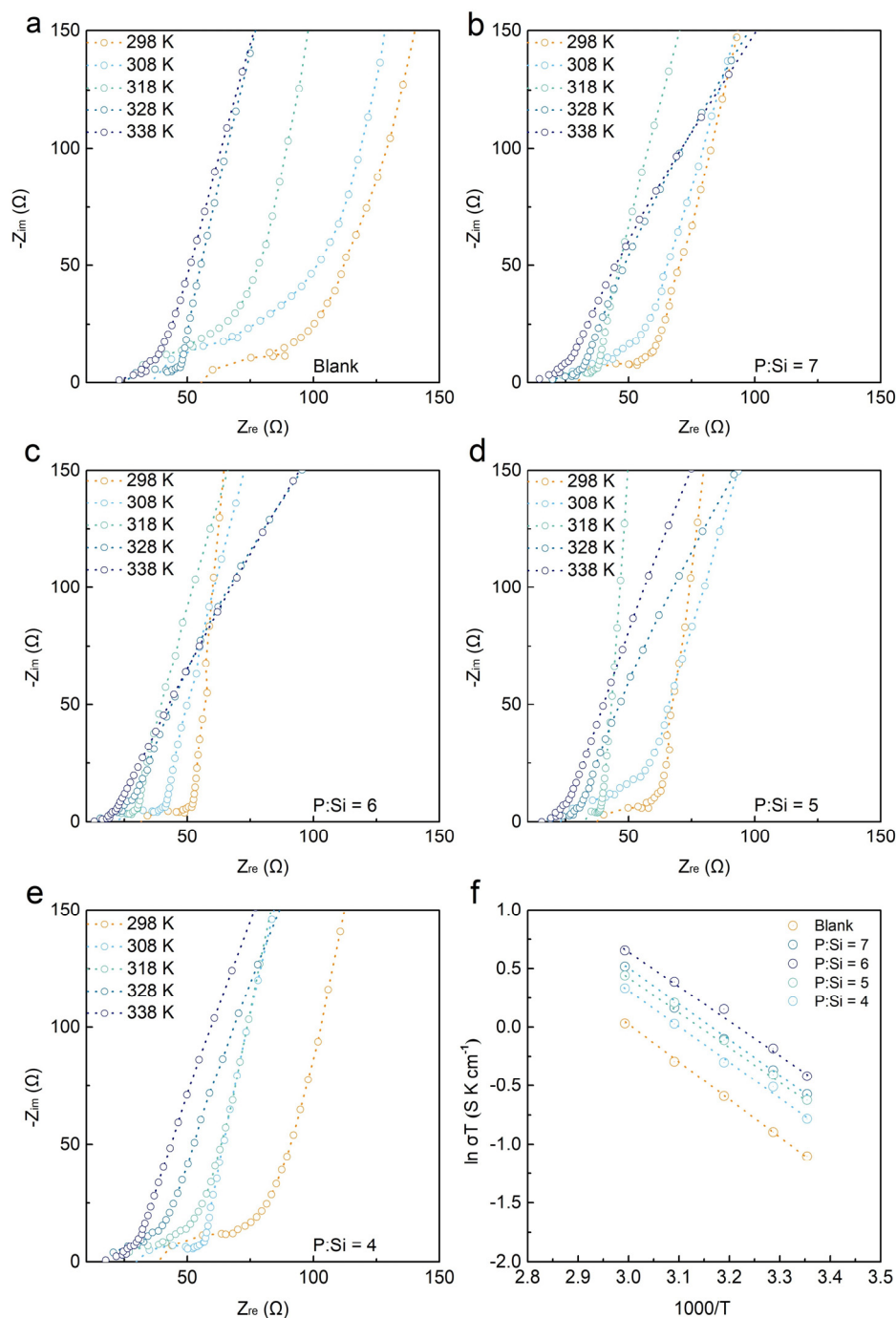


Fig. S18 The temperature-dependent Nyquist plots of synthesized electrolytes and the derived Arrhenius plot. **a** The temperature-dependent Nyquist plots of the blank electrolyte. **b** The temperature-dependent Nyquist plots of the P:Si = 7 electrolyte. **c** The temperature-dependent Nyquist plots of the P:Si = 6 electrolyte. **d** The temperature-dependent Nyquist plots of the P:Si = 5 electrolyte. **e** The temperature-dependent Nyquist plots of the P:Si = 4 electrolyte. **f** Arrhenius plots of electrolytes with different P/Si ratios.

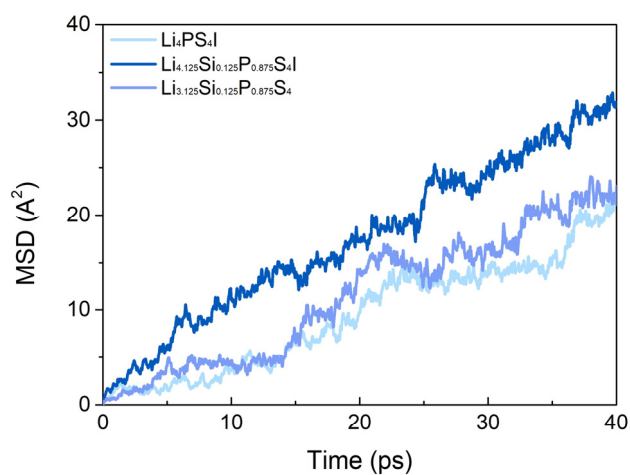


Fig. S19 The lithium MSD plots for $\text{Li}_4\text{PS}_4\text{I}$, $\text{Li}_{4.125}\text{Si}_{0.125}\text{P}_{0.875}\text{S}_4\text{I}$ and $\text{Li}_{3.125}\text{Si}_{0.125}\text{P}_{0.875}\text{S}_4$ at 600 K from AIMD simulations.

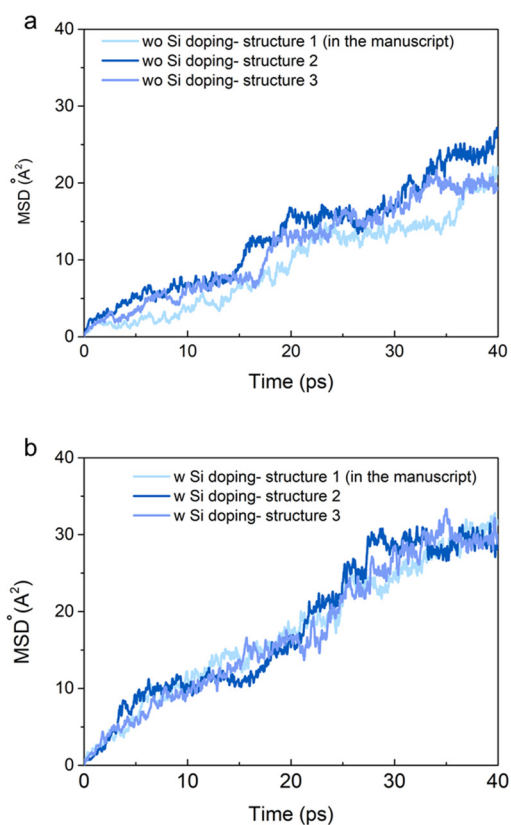


Fig. S20 The lithium MSD plots for three structures of $\text{Li}_4\text{PS}_4\text{I}$ and $\text{Li}_{4.125}\text{Si}_{0.125}\text{P}_{0.875}\text{S}_4\text{I}$ glass. **a** The lithium MSD plots for three structures of $\text{Li}_4\text{PS}_4\text{I}$ glass at 600 K from AIMD simulations. **b** The lithium MSD plots for three structures of $\text{Li}_{4.125}\text{Si}_{0.125}\text{P}_{0.875}\text{S}_4\text{I}$ glass at 600 K from AIMD simulations.

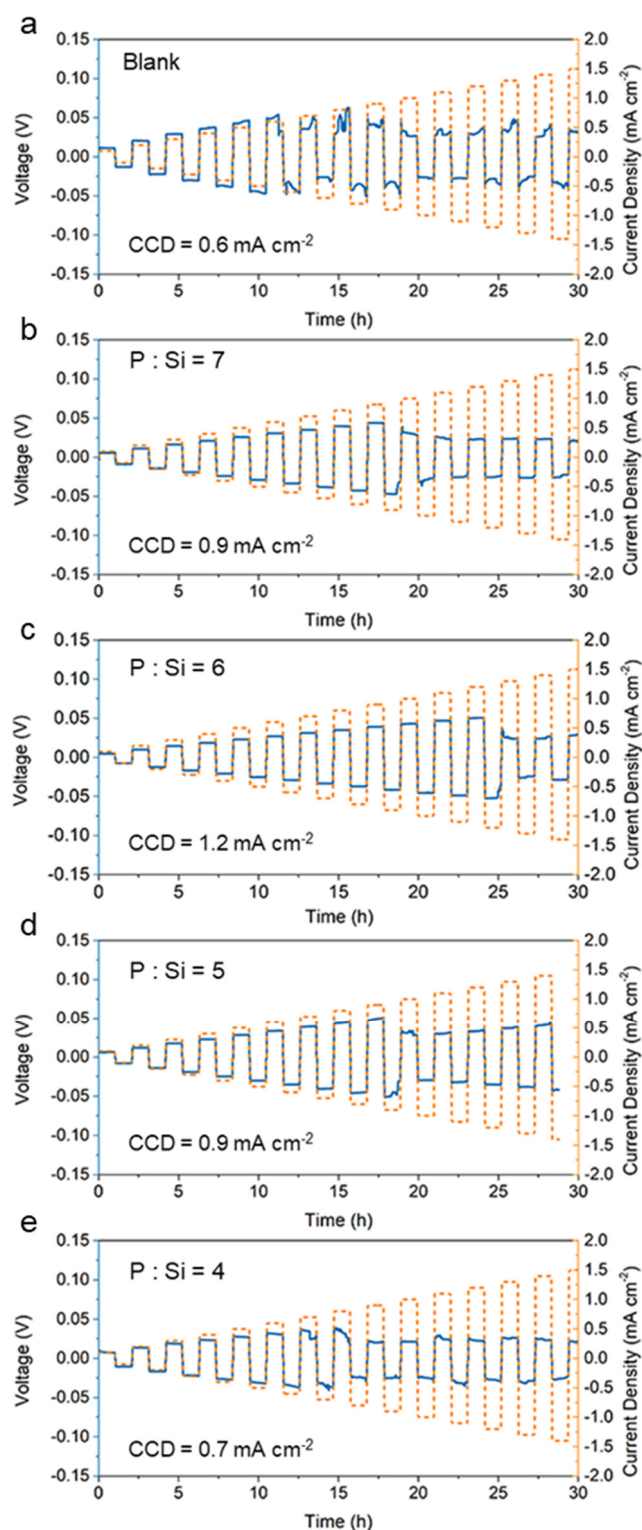


Fig. S21 CCD tests of synthesized electrolytes. **a-e** The voltage profiles of blank (**a**), P:Si = 7 (**b**), P:Si = 6 (**c**), P:Si = 5 (**d**) and P:Si = 4 (**e**) electrolytes during the CCD test. The step size of current density was set to be 0.1 mA cm⁻². And the charging/discharging time was set to be 1 h.

Table S4 The summarization of the reported CCD values for glass sulfide electrolytes.

Glass Sulfide-based SE	CCD / (mA cm ⁻²)	Capacity / (mAh cm ⁻²)	Ref.
P : Si = 6	1.2	1.2	*This Work
P : Si = 6	4.0	0.1	*This Work
75Li ₂ S-25P ₂ S ₅	0.4	0.4	2
70(0.75Li ₂ S-0.25P ₂ S ₅)-30LiI	1.0	1.0	1
0.67Li ₂ S- 0.33(0.2P ₂ O ₅ -0.8SiS ₂)	0.3	0.3	11
60Li ₂ S-28P ₂ S ₅ -12SiS ₂ (<u>Wafer</u>)	1.8 (3MPa)	0.9	12
60Li ₂ S-28P ₂ S ₅ -12SiS ₂ (<u>Wafer</u>)	0.6(1MPa)	0.3	12

Table S5 The summarization of the reported Li symmetric cell performances for glass sulfide electrolytes.

Glass Sulfide-based SE	Current Density / (mA cm ⁻²)	Capacity / (mAh cm ⁻²)	Cycling Time / (h)	Ref.
P : Si = 6	0.1	0.5	8000	*This Work
P : Si = 6	0.2	0.2	2000	*This Work
P : Si = 6	1.0	0.1	1500	*This Work
70(0.75Li ₂ S-0.25P ₂ S ₅)-30LiI	0.3	0.3	200	2
75Li ₂ S-25P ₂ S ₅	0.3	0.3	18	13
Li _{0.84} B _{0.40} Si _{0.2} O _{0.4} S _{0.84} I _{0.36}	0.1	0.1	110	3
77.5Li ₂ S-22.25P ₂ S ₅ -0.25P ₂ O ₅	0.1	0.1	120	7

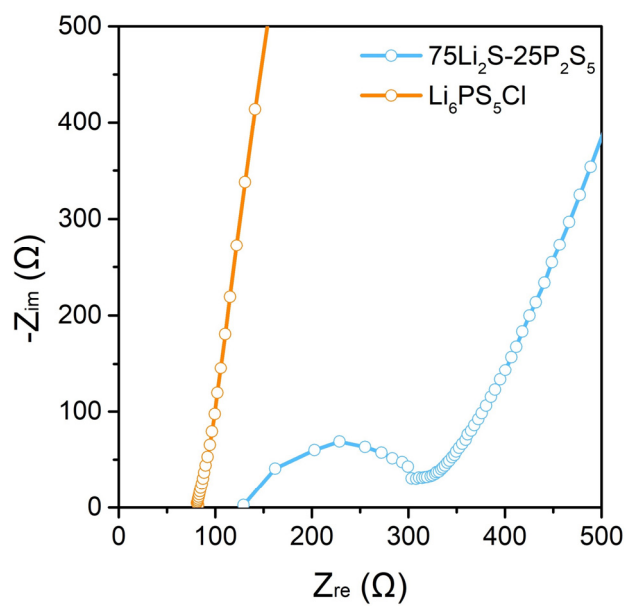


Fig. S22 Nyquist plots of $\text{Li}_6\text{PS}_5\text{Cl}$ and $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ electrolytes at 298 K.

Table S6 The summary of relative density of $\text{Li}_6\text{PS}_5\text{Cl}$ and $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ electrolytes.

Composition	Theoretical Density / (g cm^{-3})	Weight/ (mg)	Thickness / (mm)	Real Density / (g cm^{-3})	Relative Density
$\text{Li}_6\text{PS}_5\text{Cl}$	1.864	159.1	1.284	1.578	0.848
$75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$	1.865	157.3	1.181	1.697	0.910

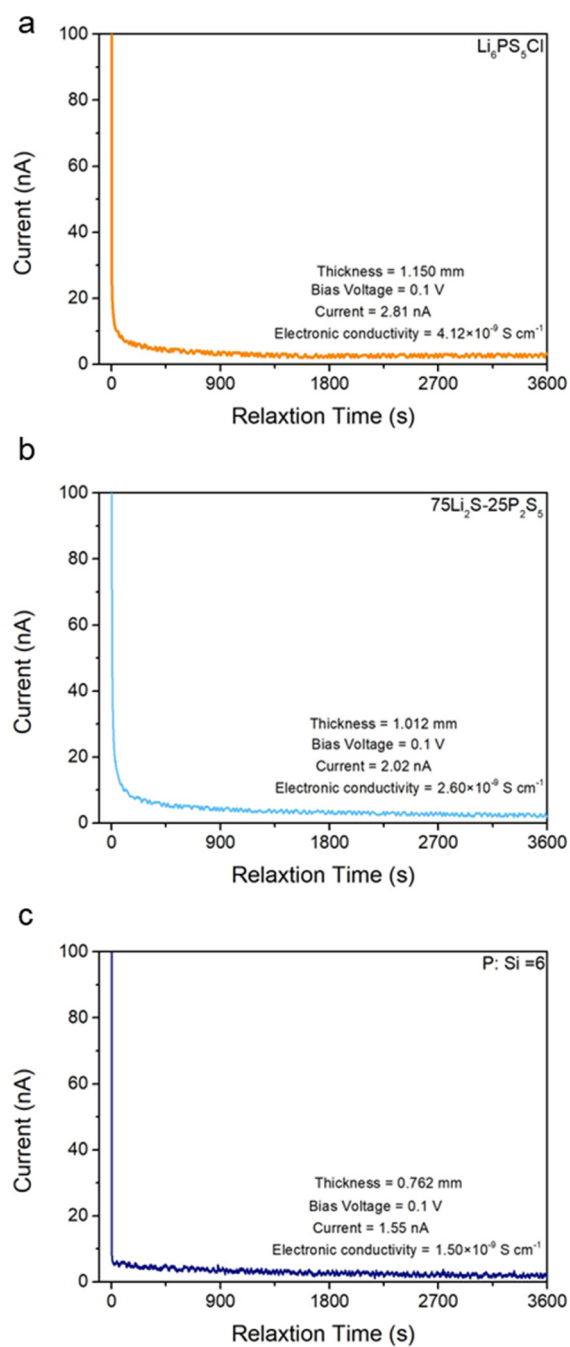


Fig. S23 The measurement of electronic conductivity for state-of-the-art sulfides and the P:Si = 6 electrolyte. **a-c** The DC polarization curves of (a) $\text{Li}_6\text{PS}_5\text{Cl}$, (b) $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ and (c) P:Si = 6 electrolyte at a bias voltage of 0.1V.

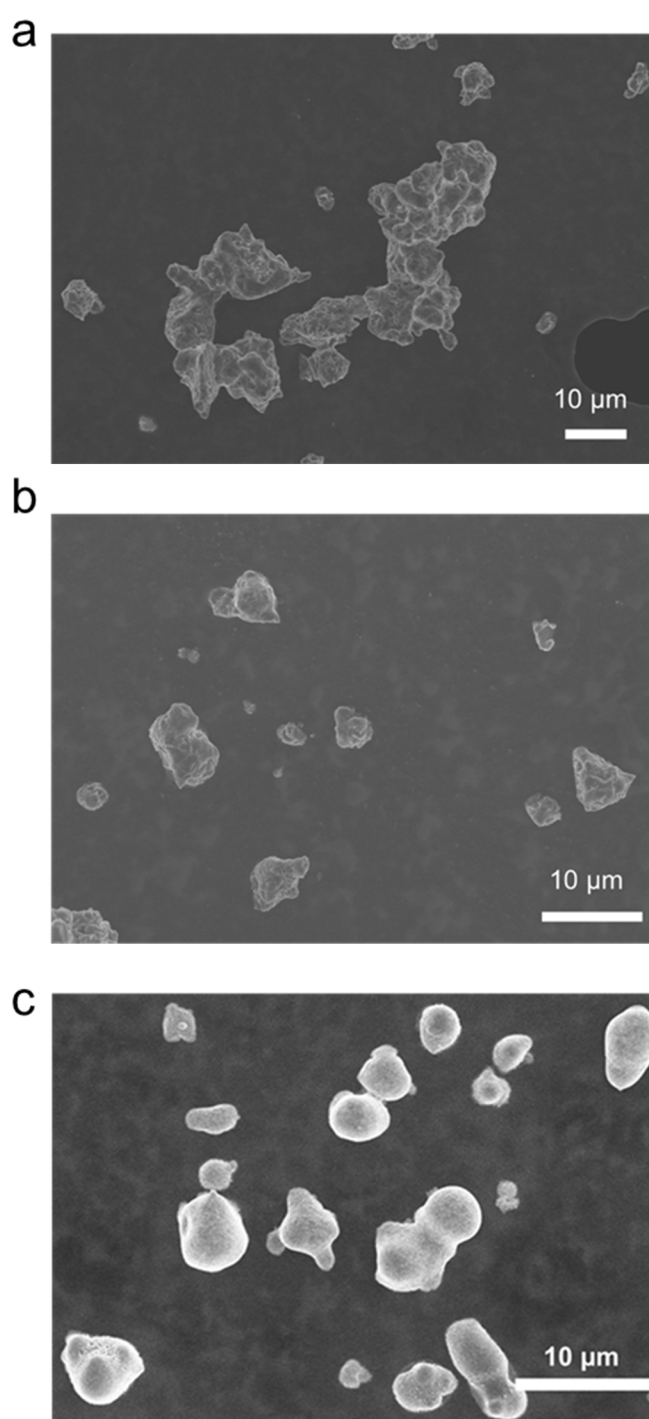


Fig. S24 The morphology of electrolyte particles for state-of-the-art sulfides and the P:Si = 6 electrolyte. **a** The morphology of distributing $\text{Li}_6\text{PS}_5\text{Cl}$ particles. **b** The morphology of distributing $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ particles. **c** The morphology of distributing P:Si = 6 particles.

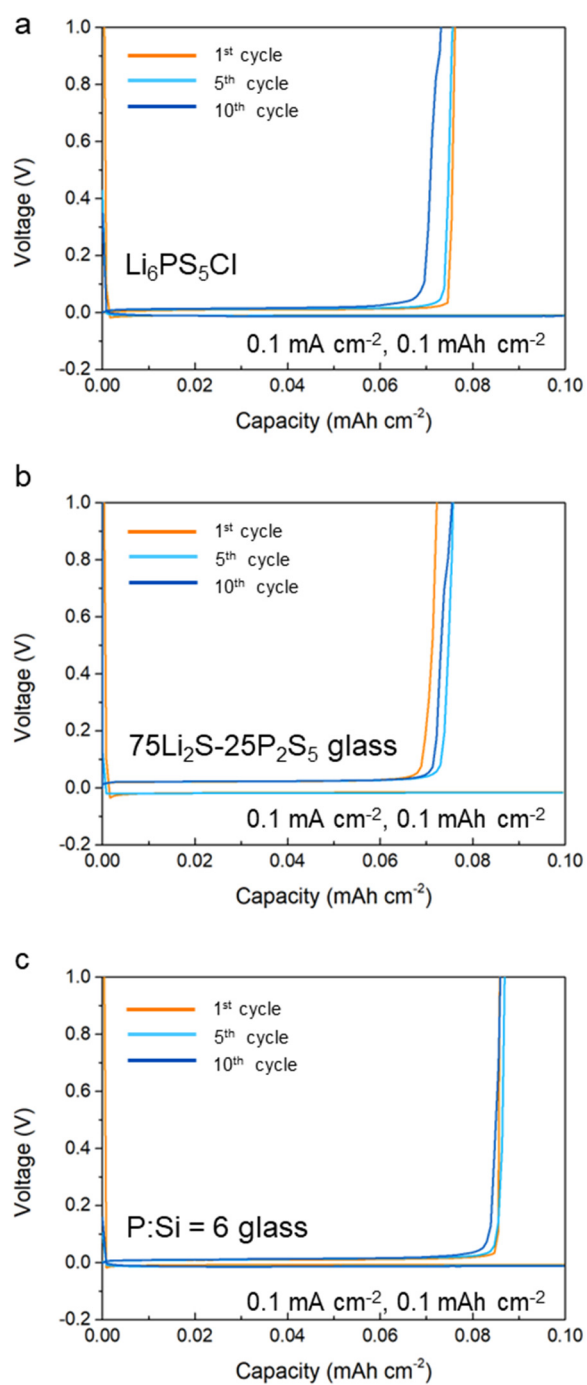


Fig. S25 The voltage profiles of Li||SS half cells. **a-c** The voltage profiles of Li||SS half cells using (a) $\text{Li}_6\text{PS}_5\text{Cl}$, (b) $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ and (c) P:Si = 6 electrolytes as the interlayer in the 1st, 5th and 10th cycles.

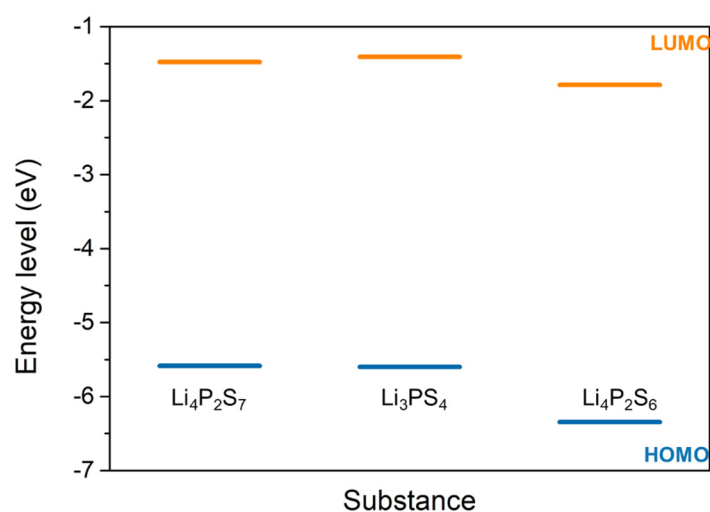


Fig. S26 The calculated HOMO/LUMO values for $\text{Li}_4\text{P}_2\text{S}_7$, Li_3PS_4 and $\text{Li}_4\text{P}_2\text{S}_6$ molecules.

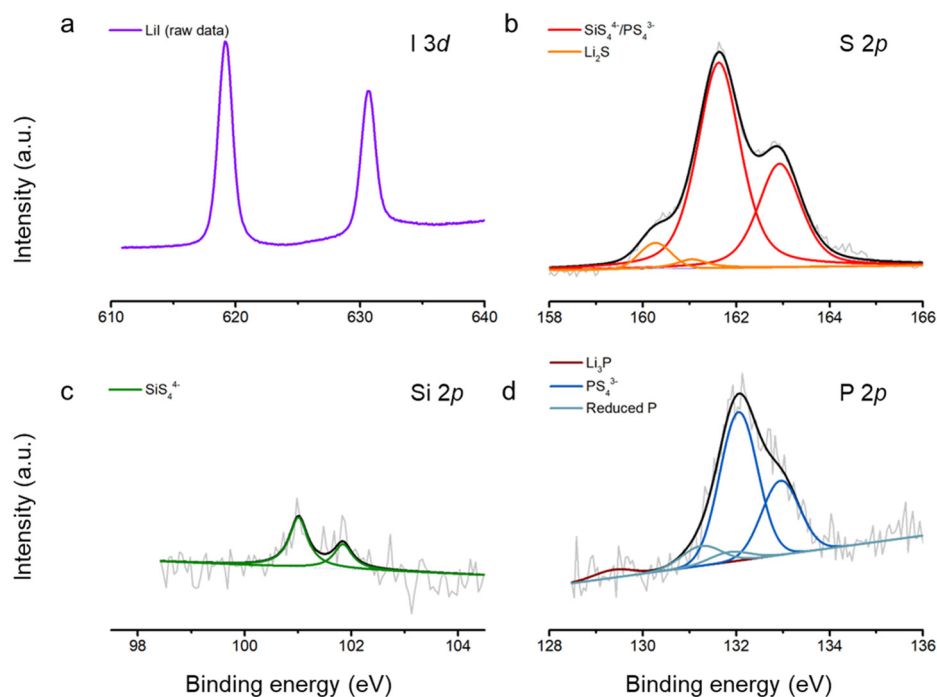


Fig. S27 The XPS characterization of the Li/P:Si = 6 interface. **a** The I 3d spectrum of the Li/P:Si = 6 interface. **b** The S 2p spectrum of the Li/P:Si = 6 interface. The raw data is plotted in a grey line. **c** The Si 2p spectrum of the Li/P:Si = 6 interface. The raw data is plotted in a grey line. **d** The P 2p spectrum of the Li/P:Si = 6 interface. The raw data is plotted in a grey line.

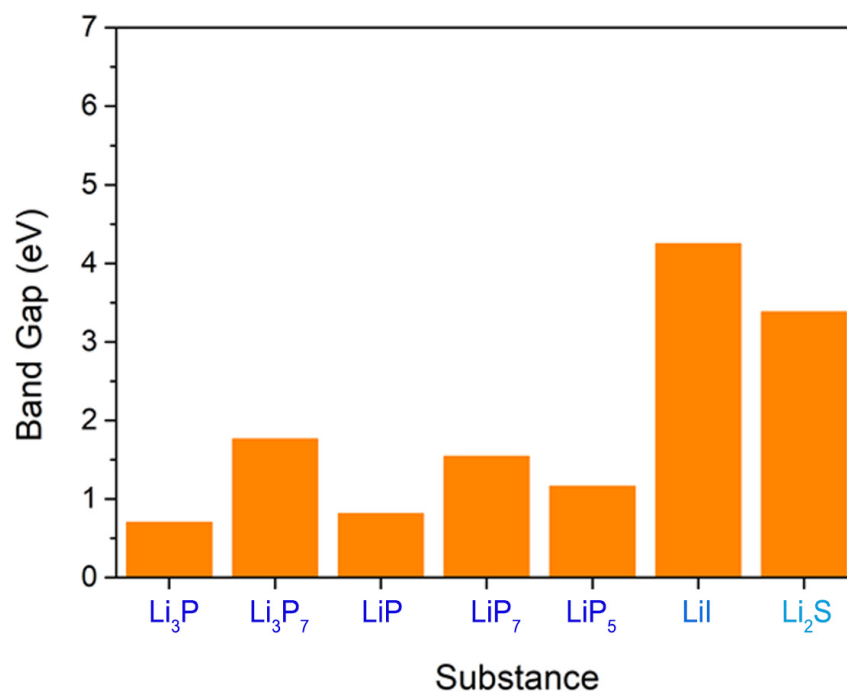


Fig. S28 The summarized band gap of the possible SEI components in L-P-S-I systems from Materials Project.



Fig. S29 The optical image of the mold cell and the holder for X-ray CT tests.

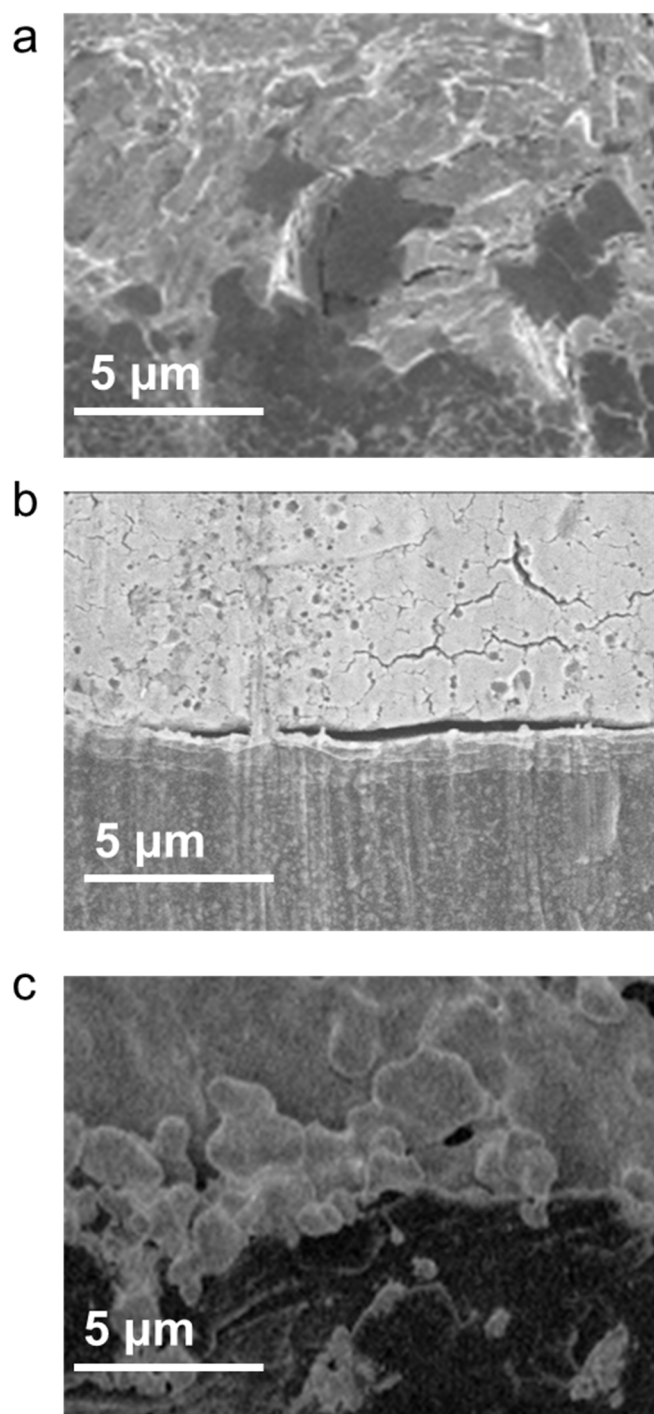


Fig. S30 The morphology of Li/SSE interface after cycling. **a** The cross-sectional image of Li/Li₆PS₅Cl interface after cycles. **b** The cross-sectional image of Li/75Li₂S-25P₂S₅ interface after cycles. **c** The cross-sectional image of Li/P:Si = 6 interface after cycles.

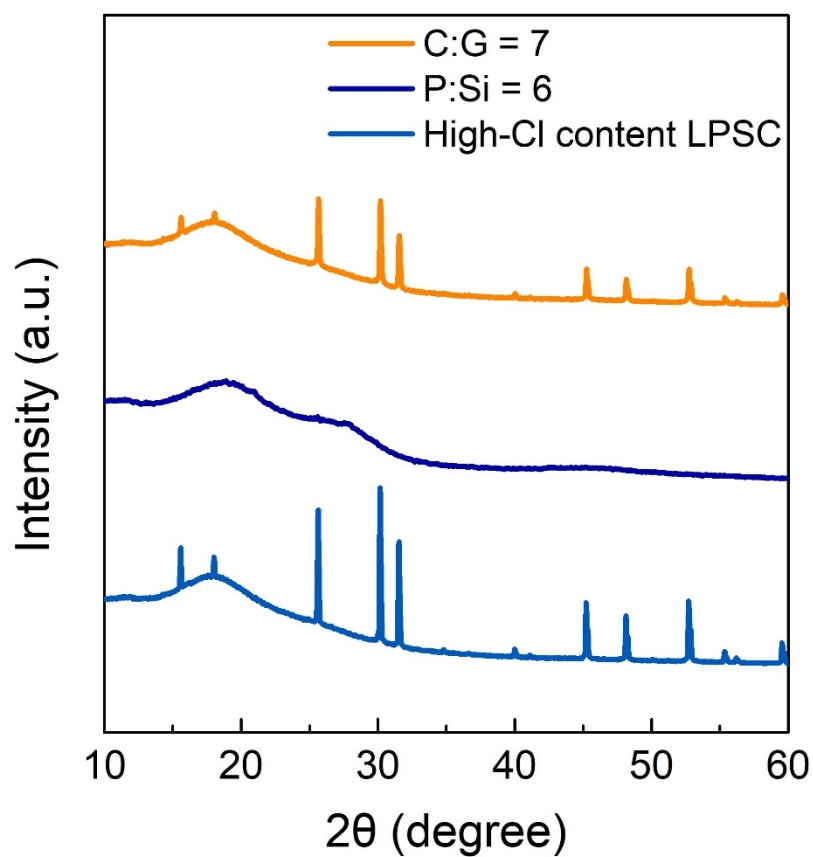


Fig. S31 XRD spectra of C:G = 7, P:Si = 6 and high-Cl content LPSC electrolytes.

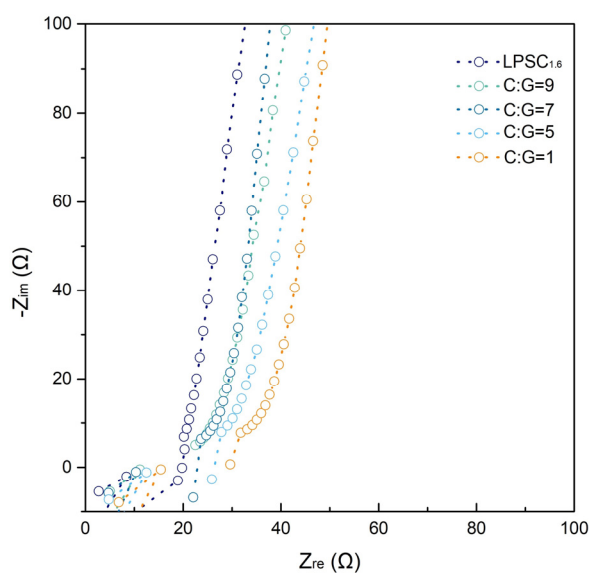


Fig. S32 Nyquist plots of electrolytes with different C/G ratios at 298 K.

Table S7 The summary of the relative density of composite electrolytes with different C/G ratios.

Composition	Theoretical Density / (g cm ⁻³)	Weight / (mg)	Thickness / (mm)	Real Density / (g cm ⁻³)	Relative Density
LPSCl _{1.6}	1.880	139.0	1.122	1.578	0.839
C:G = 9	1.928	142.3	1.079	1.681	0.872
C:G = 7	1.940	145.0	1.068	1.730	0.892
C:G = 5	1.961	149.3	1.084	1.754	0.894
C:G = 1	2.146	147.5	0.971	1.935	0.902

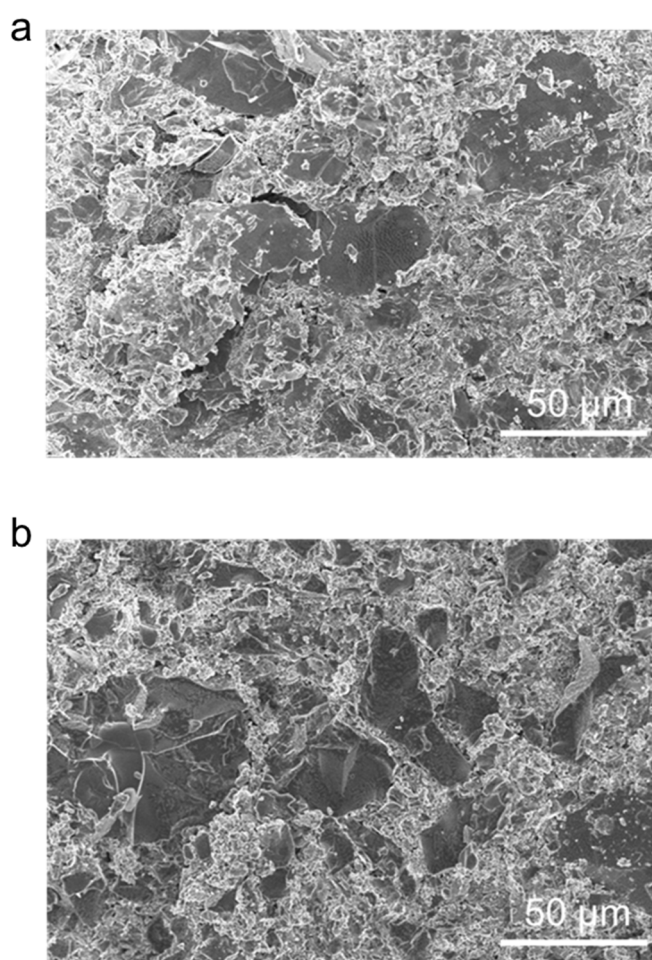


Fig. S33 The morphology comparison between cold-pressed Li_{5.4}PS_{4.4}Cl_{1.6} and C:G = 7. **a** The surface morphology of the cold-pressed Li_{5.4}PS_{4.4}Cl_{1.6} electrolyte. **b** The surface morphology of the C:G = 7 electrolyte.

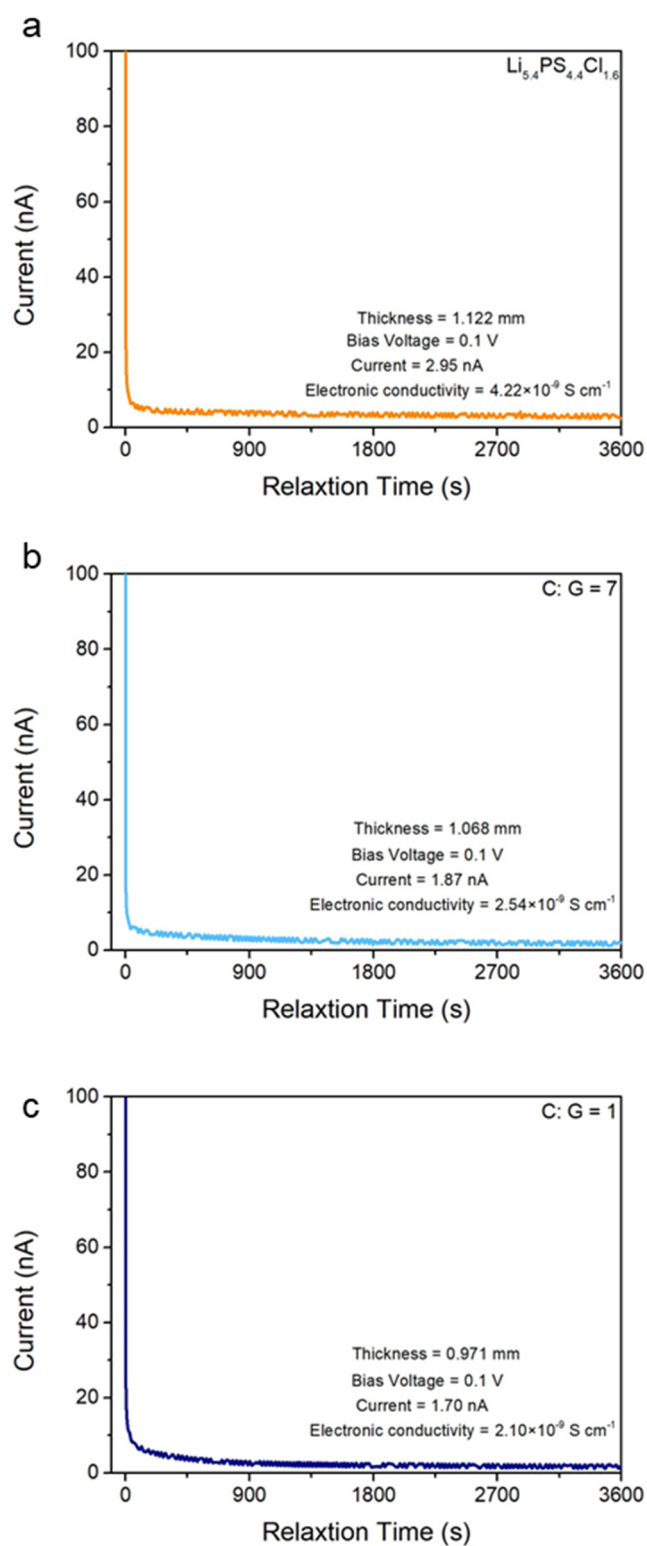


Fig. S34 The measurement of electronic conductivity for $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$, C:G = 7 and C:G = 1 electrolytes. **a-c** The DC polarization curves of (a) $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$, (b) C:G = 7, and (c) C:G = 1 electrolyte at a bias voltage of 0.1V.

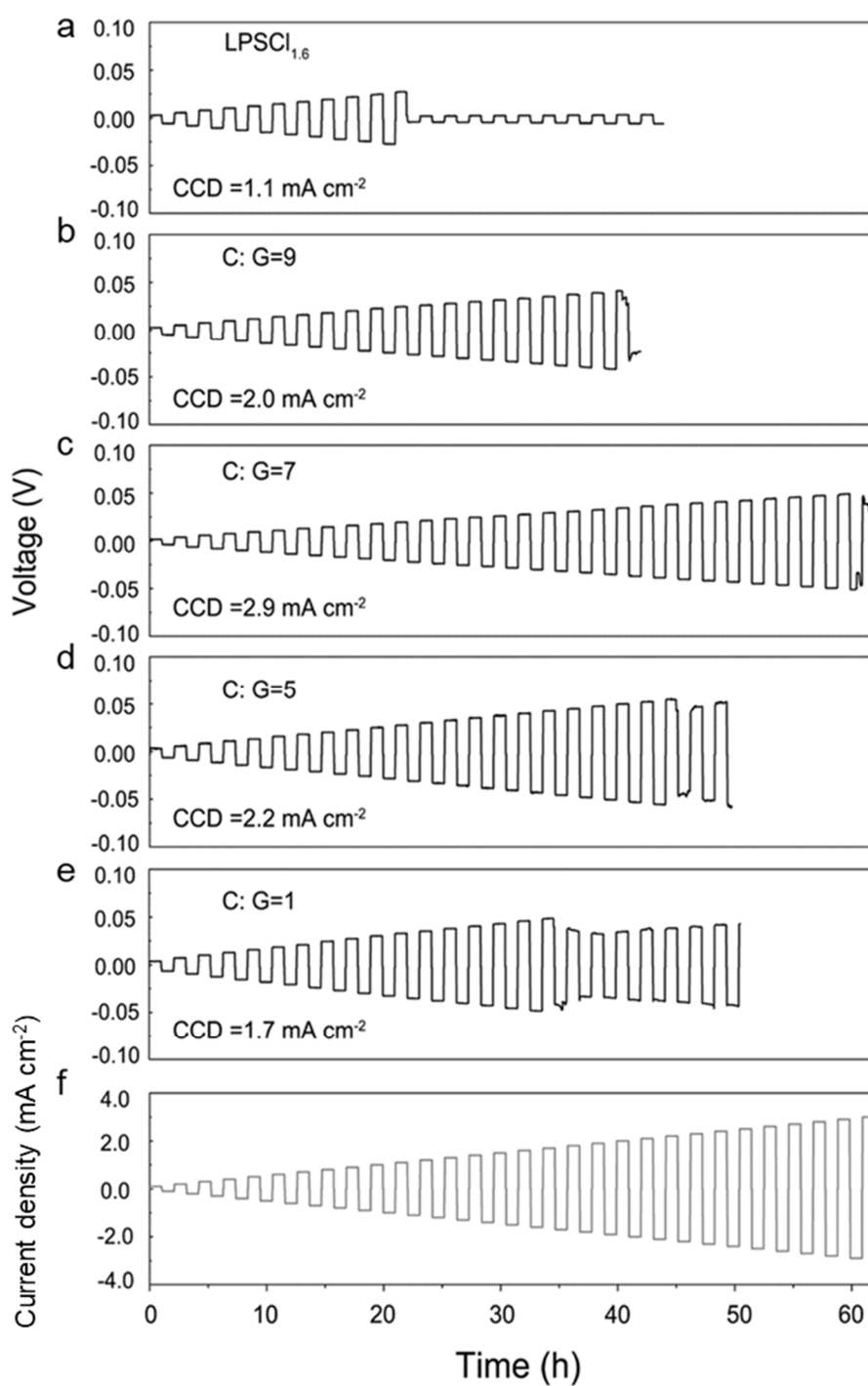


Fig. S35 The CCD tests of the glassy/crystalline composite electrolytes. **a-e** The voltage profiles of $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$ (**a**), C:G = 9 (**b**), C:G = 7 (**c**), C:G = 5 (**d**) and C:G = 1 (**e**) electrolytes during the CCD test. **f** The current density profile of the CCD test. The step size of current density was set to be 0.1 mA cm^{-2} . And the charging/discharging time was set to be 1 h.

Table S8 The summarization of the reported CCD values for sulfide-based SEs at 298 K.
(discharging/charging time = 1 h, bare Li as the electrode).

Sulfide-based SE	CCD / (mA cm^{-2})	Capacity / (mAh cm^{-2})	Ref.
C : G = 7	2.90	2.90	*This Work
$\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$	1.40	1.40	14
$\text{Li}_6\text{PS}_5\text{Cl}$ (pressure hold for 30 min)	2.15	2.15	15
$\text{Li}_{6.25}\text{PS}_{4.75}\text{Cl}_{0.25}$	1.52	1.52	16
$\text{Li}_7\text{P}_{2.88}\text{Nb}_{0.12}\text{S}_{10.7}\text{O}_{0.3}$	1.16	1.16	17
$\text{Li}_6\text{PS}_{4.7}\text{O}_{0.3}\text{Br}$	0.89	0.89	18
$\text{Li}_6\text{PS}_5\text{Cl}$	0.60	0.60	*This Work
$\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$	1.10	1.10	* This Work
$\text{Li}_7\text{P}_3\text{S}_{11}$	0.76	0.76	19
$\text{Li}_7\text{P}_{2.9}\text{Si}_{0.05}\text{S}_{10.85}$	0.80	0.80	19

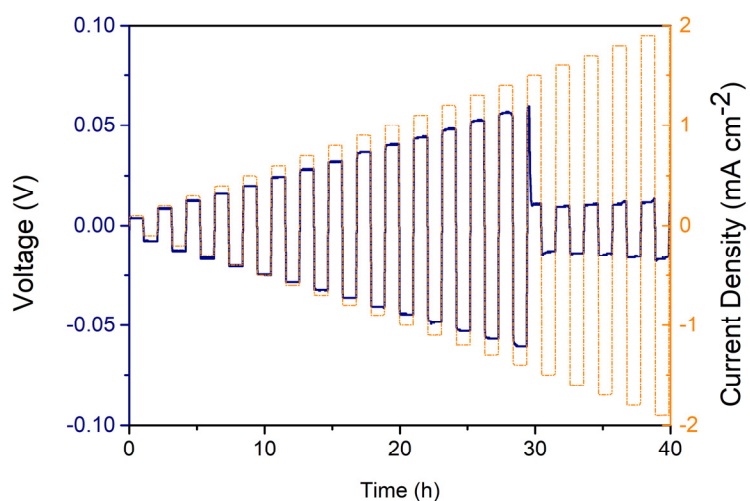


Fig. S36 The CCD profile of the $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}/75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ composite electrolyte, with a weight ratio of $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5 = 12.5\%$.

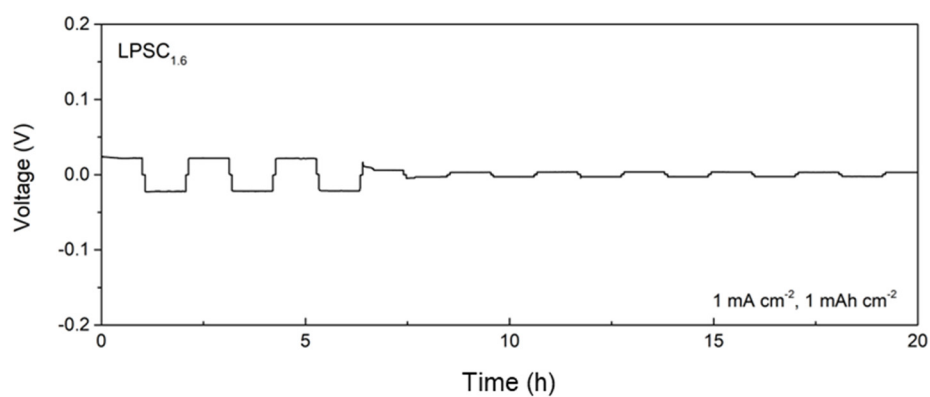


Fig. S37 The galvanostatic discharging/charging profiles of the Li symmetric cell using the $\text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6}$ electrolyte at a current density of 1 mA cm^{-2} and a cut-off capacity of 1 mAh cm^{-2} .

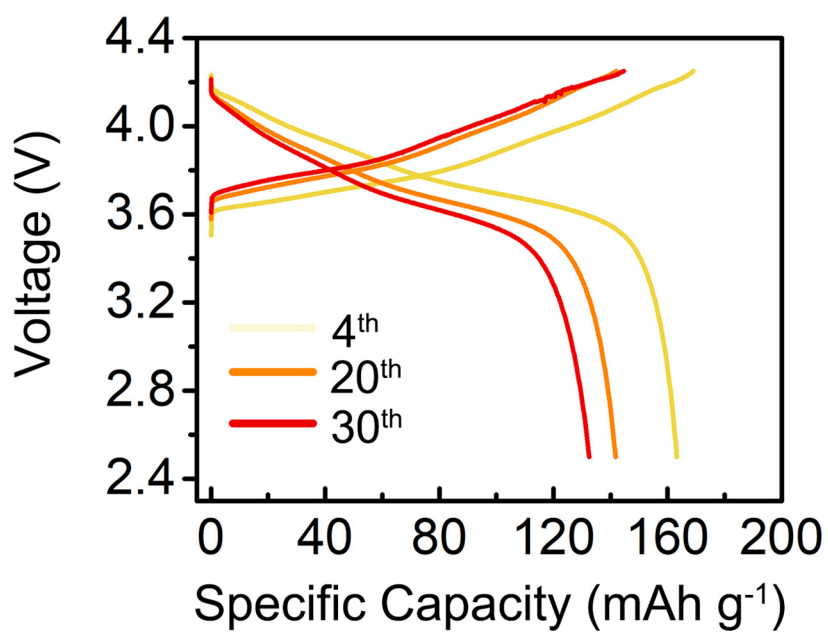


Fig. S38 The voltage profiles of $\text{Li} | \text{Li}_{5.4}\text{PS}_{4.4}\text{Cl}_{1.6} | \text{NCM83125}$ full cell at different cycles.

Table S9 The summarization of the reported Li symmetric cells' (using bare Li metal) performances for sulfide-based SEs at 298 K.

Sulfide-based SE	Current Density / (mA cm ⁻²)	Capacity / (mAh cm ⁻²)	Cycling Time / (h)	Ref.
C : G = 7	1.0	3.0	900	*This Work
C : G = 7	1.0	1.0	1200	*This Work
P : Si = 6	0.1	0.5	8000	*This Work
P : Si = 6	0.2	0.2	2000	*This Work
P : Si = 6	1.0	0.1	1500	*This Work
Li _{6.25} PS _{4.75} ClN _{0.25}	1.0	1.0	200	16
Li _{6.25} PS _{4.75} ClN _{0.25}	0.5	0.5	1000	16
Li ₇ P _{2.88} Nb _{0.12} S _{10.7} O _{0.3}	0.2	0.2	300	17
LPSI _{1.4} -gc	0.2	0.2	3200	20
Li ₆ PS _{4.7} O _{0.3} Br	0.4	0.4	350	18
LiF@Li ₁₀ GeP ₂ S ₁₂	0.1	0.1	1000	21
PEGME-SPE/LPSC	1.0	0.5	1000	22
LPSI-20Sn	1.26	1.0	200	23
Li _{5.5} PS _{4.425} O _{0.075} Cl _{1.5}	0.4	0.2	150	24
Li _{6.988} P _{2.994} Nb _{0.2} S _{10.934} O _{0.6}	0.1	0.1	100	25
Li _{5.6} Cu _{0.2} PS _{4.8} Br _{1.2}	0.2	0.2	1200	26
Li _{5.5} PS _{4.5} Cl _{1.5}	0.2	0.2	500	14
Li _{5.5} PS _{4.5} Cl _{1.5}	0.5	0.5	200	14
Li _{6.04} P _{0.98} Bi _{0.02} S _{4.97} O _{0.03} Cl	0.1	0.1	600	27

Table S10 The summarization of the reported high-voltage ASSLMBs' performances at 298 K.

Ref.	Initial Discharging Capacity / (mAh g ⁻¹)	Total cycles / (n)	Cathode	Interlayer	Capacity retention / (%)
28	125	75	NCM111	Li ₁₀ SiP ₂ S ₁₂	91
29	131	500	LiCoO ₂	Li ₁₀ GeP ₂ S ₁₂	87
30	121	25	LiCoO ₂	@Li _{3.15} Ge _{0.15} P _{0.85} S ₄ /77.5Li ₂ S-22.5P ₂ S ₅	90
31	134	50	LiCoO ₂	@Li ₁₀ GeP ₂ S ₁₂ /Li ₃ P _{0.98} Sb _{0.02} S _{3.95} O _{0.05}	79
32	110	100	NCA	75Li ₂ S-25P ₂ S ₅	84
33	170	40	NCM622	0.5LiI-Li ₃ PS ₄	74
16	136	100	LiCoO ₂	Li _{6.25} PS _{4.75} ClN _{0.25}	87
34	133	80	LiCoO ₂	Li _{5.4} PS _{4.4} Cl _{1.6}	71
14	151	100	NCM811	Li _{5.5} PS _{4.5} Cl _{1.5}	80
35	113	100	LiCoO ₂	Li ₆ PS ₅ Cl-MgF ₂	92
36	163	100	NCM811	Li ₆ PS ₅ Cl	90
*This work	172	500	NCM83125	C:G =7	82

@ Two layers of electrolytes were applied in the ASSLMBs.

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