Electronic Supplementary Information for

Structural Mapping and Tuning Mixed Halide Ions in Amorphous Sulfides for Fast Li-Ion Conduction and High Deformability

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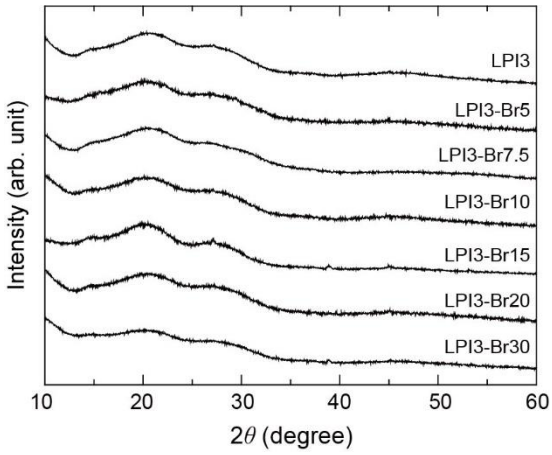

Fig. S1 Anionic structural changes in delithiated sulfide SEs. Laboratory X-ray diffraction patterns of all LPI3-Br series samples. All these samples exhibit an amorphous phase. LPI3, LPI3-Br5, -Br7.5, -Br10, -Br15, -Br20, and -Br30 indicate $[(Li_2S)_{0.658}(LiI)_{0.342}]_{0.825}[P_2S_5]_{0.175}$, $[(Li_2S)_{0.658}(LiI_{0.95}LiBr_{0.05})_{0.342}]_{0.825}[P_2S_5]_{0.175}$, $[(Li_2S)_{0.658}(LiI_{0.925}LiBr_{0.075})_{0.342}]_{0.825}[P_2S_5]_{0.175}$, $[(Li_2S)_{0.658}(LiI_{0.90}LiBr_{0.10})_{0.342}]_{0.825}[P_2S_5]_{0.175}$, $[(Li_2S)_{0.658}(LiI_{0.85}LiBr_{0.15})_{0.342}]_{0.825}[P_2S_5]_{0.175}$, $[(Li_2S)_{0.658}(LiI_{0.80}LiBr_{0.20})_{0.342}]_{0.825}[P_2S_5]_{0.175}$, and $[(Li_2S)_{0.658}(LiI_{0.70}LiBr_{0.30})_{0.342}]_{0.825}[P_2S_5]_{0.175}$ samples, respectively.

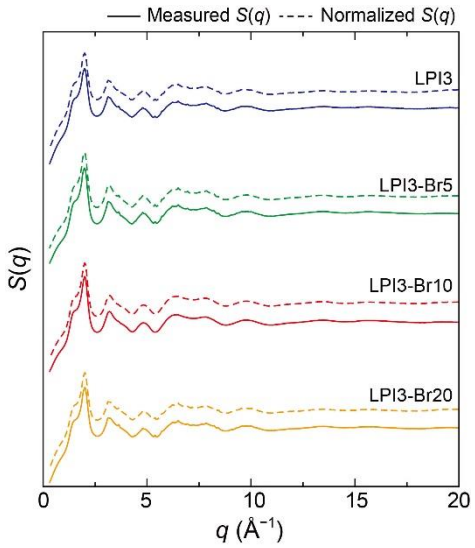

Fig. S2 Comparison of measured and normalized structural factor $S(q)$ in LPI3-Br series. The normalized $S(q)$ was obtained during RMC simulations to correct measurement errors.

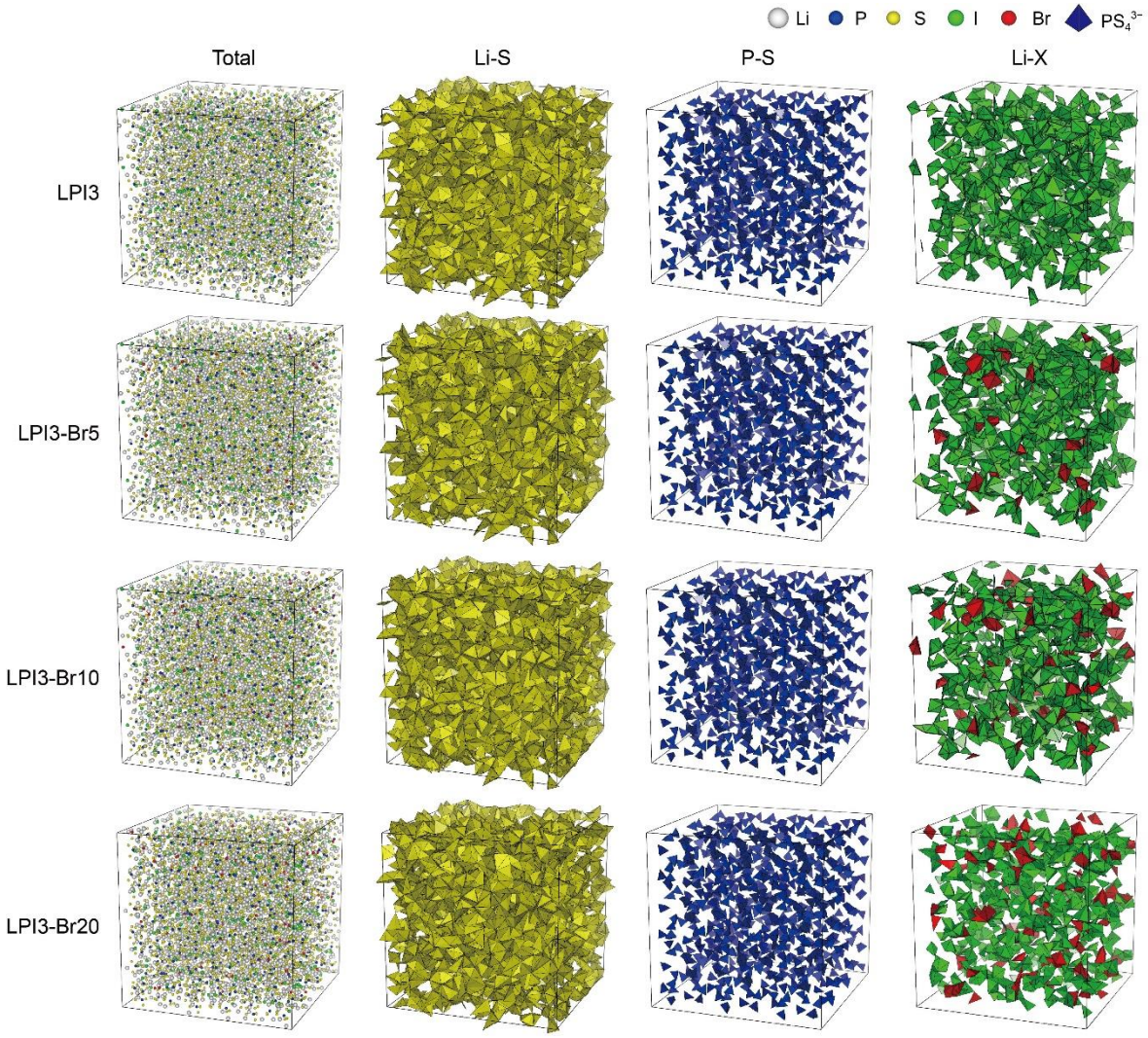

Fig. S3 Atomic structure of LPI3-Br series samples reconstructed by reverse Monte-Carlo (RMC) simulation. The white, blue, yellow, brown and red spheres indicate the Li, P, S, I, and Br atoms, respectively. The yellow, blue, green, and red polyhedrons indicate the Li-S, P-S, Li-I, and Li-Br bonds, respectively.

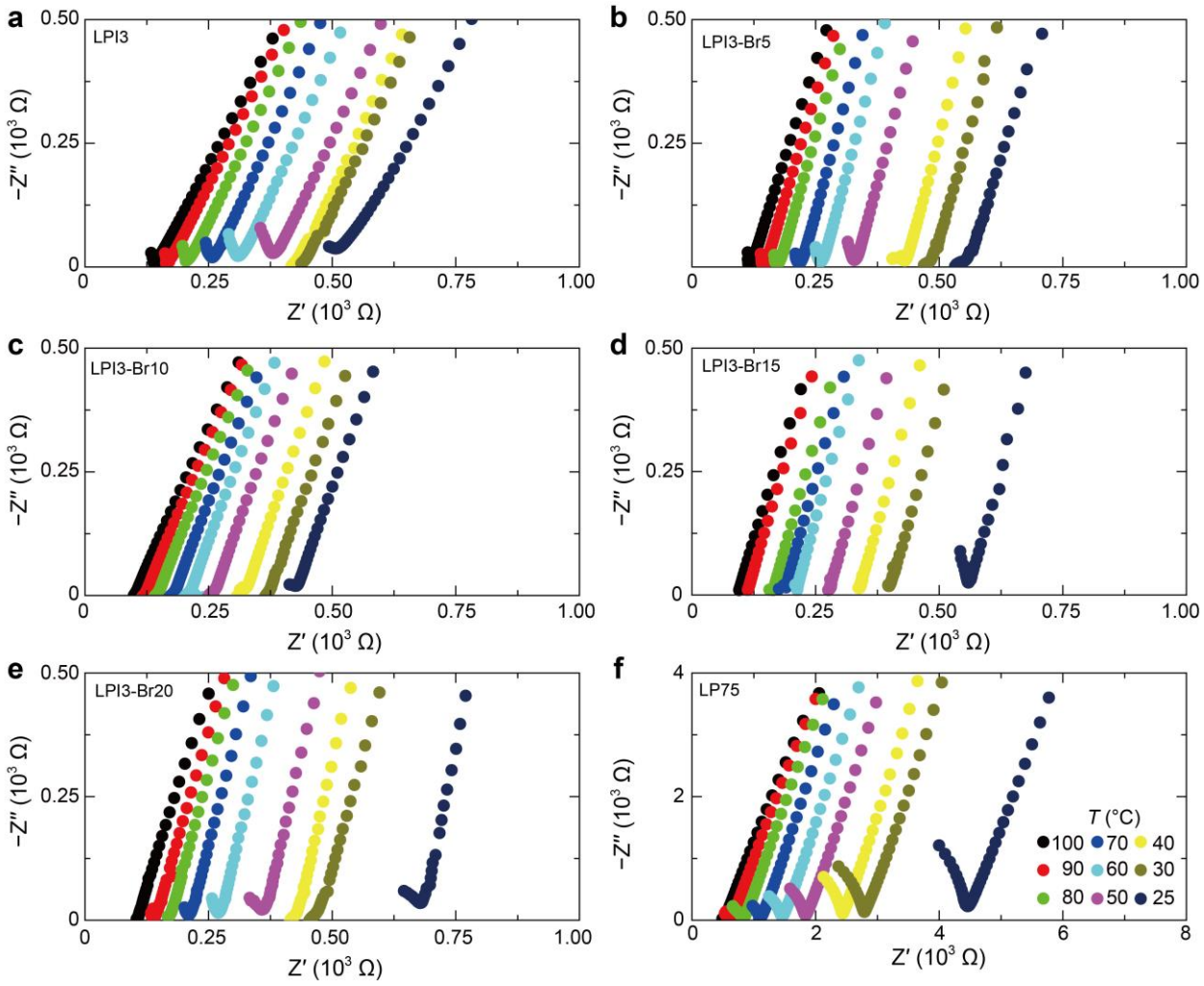

Fig. S4 Impedance spectral changes of LP75 and LPI3-Br series samples with temperature (*T*). (a) LPI3, (b) LPI3-Br5, (c) LPI3-Br10, (d) LPI3-Br15, (e) LPI3-Br20, and (f) LP75.

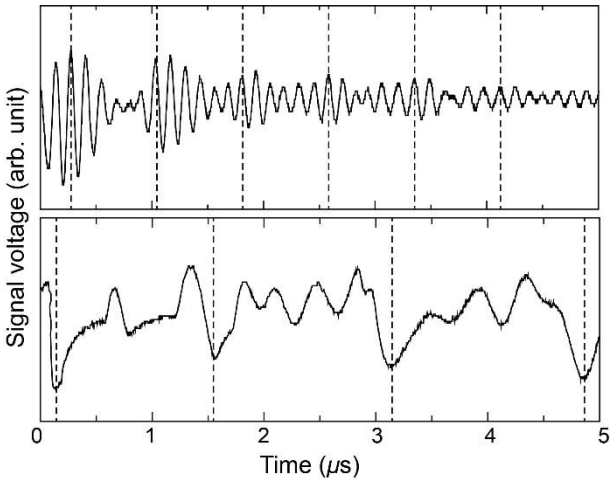

Fig. S5 Wave patterns of a LPI3-Br10 sample measured by ultrasonic pulse-echo technique: longitudinal (top) and shear (bottom) modes. The dotted vertical lines indicate the time-of-flight difference.

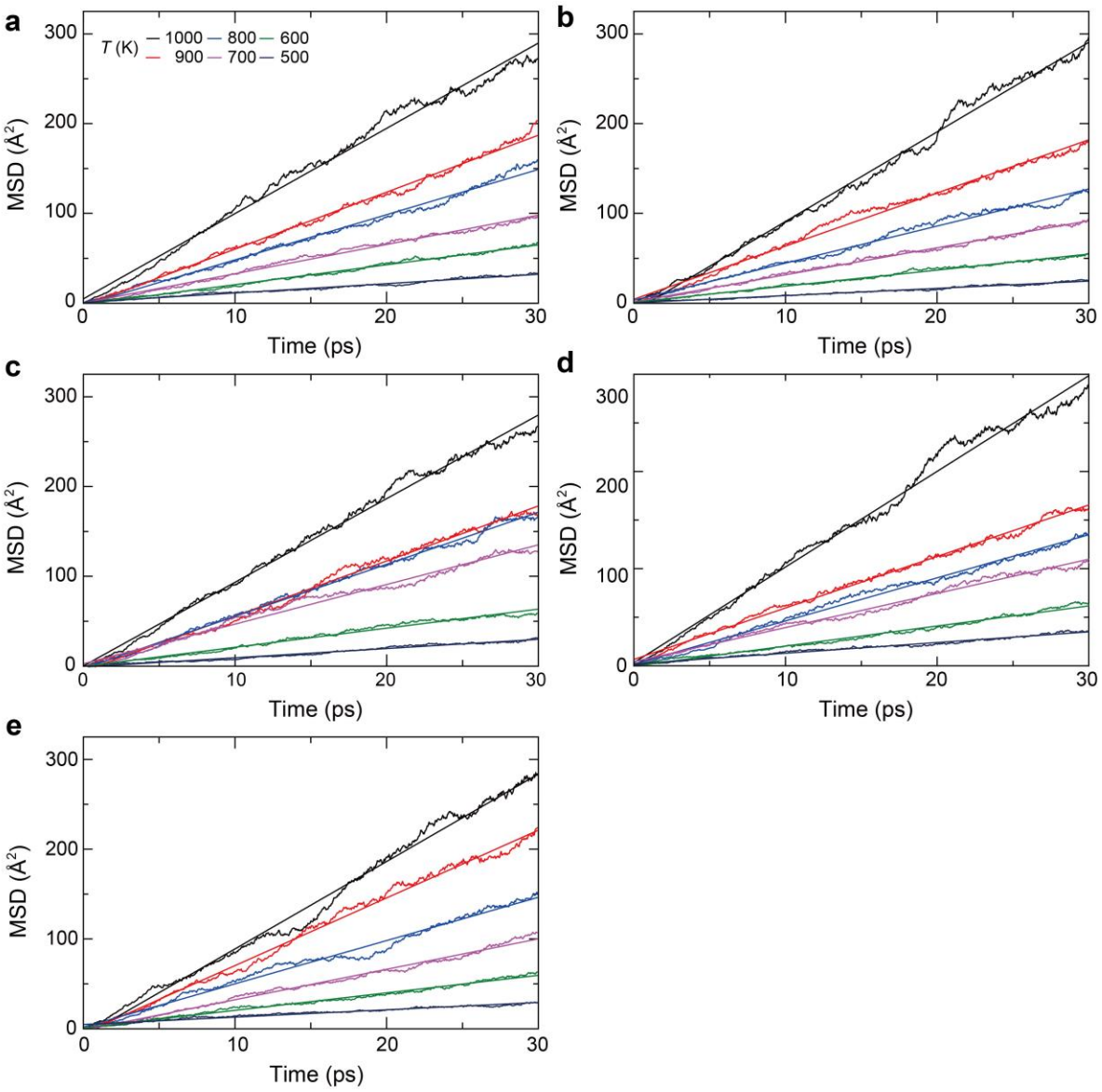

Fig S6. Mean square displacement (MSD) of Li ions obtained by ab initio molecular dynamics (AIMD) simulations. (a) LPI3, (b) LPI3-Br5, (c) LPI3-Br10, (d) LPI3-Br15, and (e) LPI3-Br20. LPI3, LPI3-Br5, -Br10, -Br15, and -Br20 indicate $[(Li_2S)_{0.658}(LiI)_{0.342}]_{0.825}[P_2S_5]_{0.175}$, $[(Li_2S)_{0.658}(LiI_{0.95}LiBr_{0.05})_{0.342}]_{0.825}[P_2S_5]_{0.175}$, $[(Li_2S)_{0.658}(LiI_{0.90}LiBr_{0.10})_{0.342}]_{0.825}[P_2S_5]_{0.175}$, $[(Li_2S)_{0.658}(LiI_{0.85}LiBr_{0.15})_{0.342}]_{0.825}[P_2S_5]_{0.175}$, and $[(Li_2S)_{0.658}(LiI_{0.80}LiBr_{0.20})_{0.342}]_{0.825}[P_2S_5]_{0.175}$ samples, respectively.

Table S1 Summary of cut-off distances for LPI3-Br series in RMC simulations.

Atom *i*	Atom *j*	Cut-off distance (Å)	Atom *i*	Atom *j*	Cut-off distance (Å)
Li	Li	2.80	I	S	3.30
Li	I	2.60	Br	Br	3.30
Li	Br	2.40	Br	P	3.40
Li	P	3.10	Br	S	3.30
Li	S	2.25	P	P	2.90
I	I	3.30	P	S	1.80
I	Br	3.30	S	S	2.90
I	P	3.10	-	-	-

Table S2 Detailed information on Arrhenius plots of AIMD results for LPI3-Br series. D_{Li} indicates the diffusivity of Li ions. The D_{ion} at 300 K was obtained from the extrapolated values.

T (K)	D_{Li} (10^{-6} cm^2 s^{-1})				
	LPI3	LPI3-Br5	LPI3-Br10	LPI3-Br15	LPI3-Br20
1200	1.75	1.55	1.55	1.76	1.62
1000	1.06	0.99	1.02	0.95	1.26
900	0.79	0.69	0.97	0.74	0.80
800	0.60	0.50	0.74	0.56	0.56
700	0.35	0.30	0.35	0.34	0.33
600	0.14	0.14	0.20	0.18	0.14
300	0.0012	0.0013	0.0034	0.0023	0.0010