Supporting Information

Incorporation of halogen (Cl, Br, I) in Li-P-S-O system for exploring new sulfide solid electrolytes with high conductivity and superior electrochemical performance in solid-state batteries

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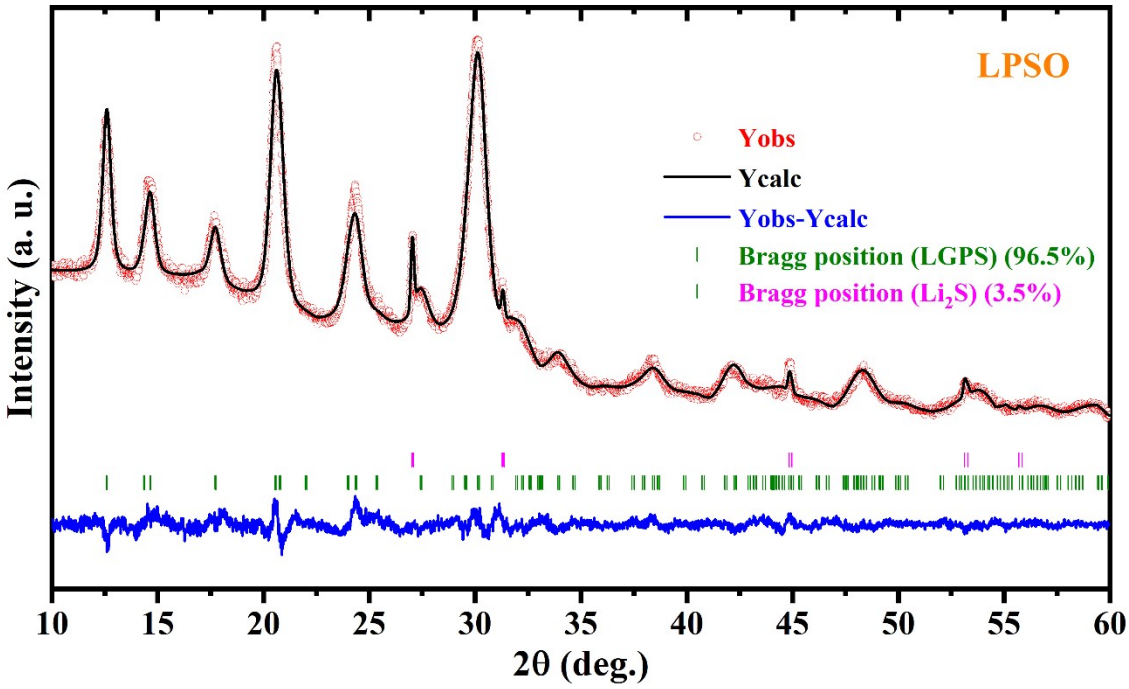

Figure S1. Rietveld refinement patterns of LPSO samples, in the refinement graphs, experimental plot is shown by dotted line (red), calculated by solid line (black), Bragg reflection peaks by

vertical lines of LGPS phase (green) and Li_2S phase (violet) and difference plot by background line (blue).

Table S2. Rietveld refinement results of LPSO

Refinement Results	**LPSO**	**Li_2S**
a (Å)	8.5518(8)	5.7118(2)
b (Å)	8.5518(8)	5.7118(2)
c (Å)	12.342(1)	5.7118(2)
V (Å^3)	902.6(1)	186.3(1)
R_p (%)	2.64	
R_{wp} (%)	3.34	
R_{expt} (%)	3.33	
R_{bragg} (%)	2.93	
R_F (%)	1.32	
χ^2(%)	1.01	
Phase Content (wt.%)	96.53	3.47

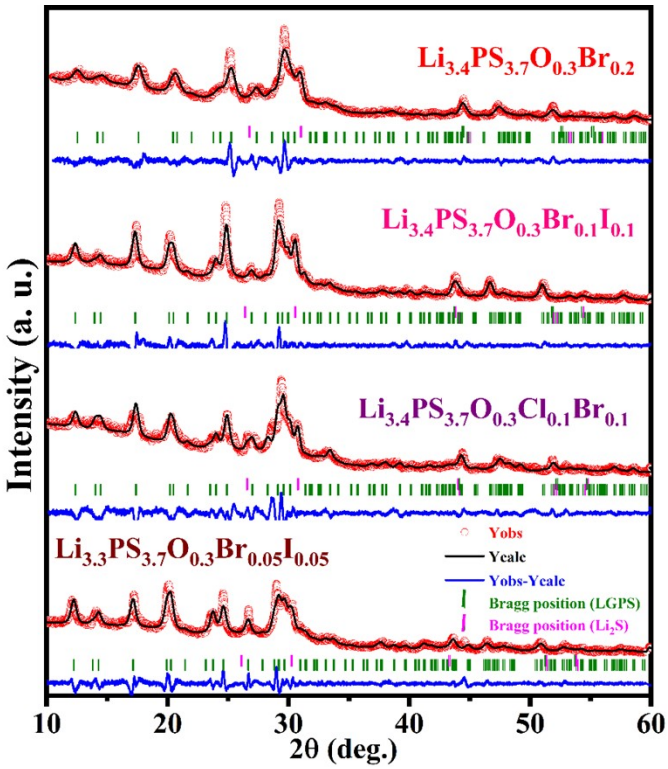

Figure S3. Le Bail Rietveld refinement graphs of solid electrolytes.

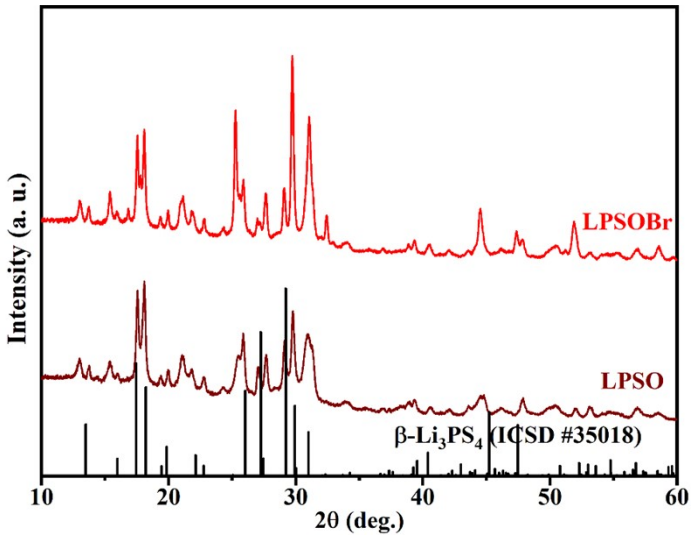

Figure S4. XRD patterns of LPSO and LPSOBr calcined at 350 °C in quartz tube.

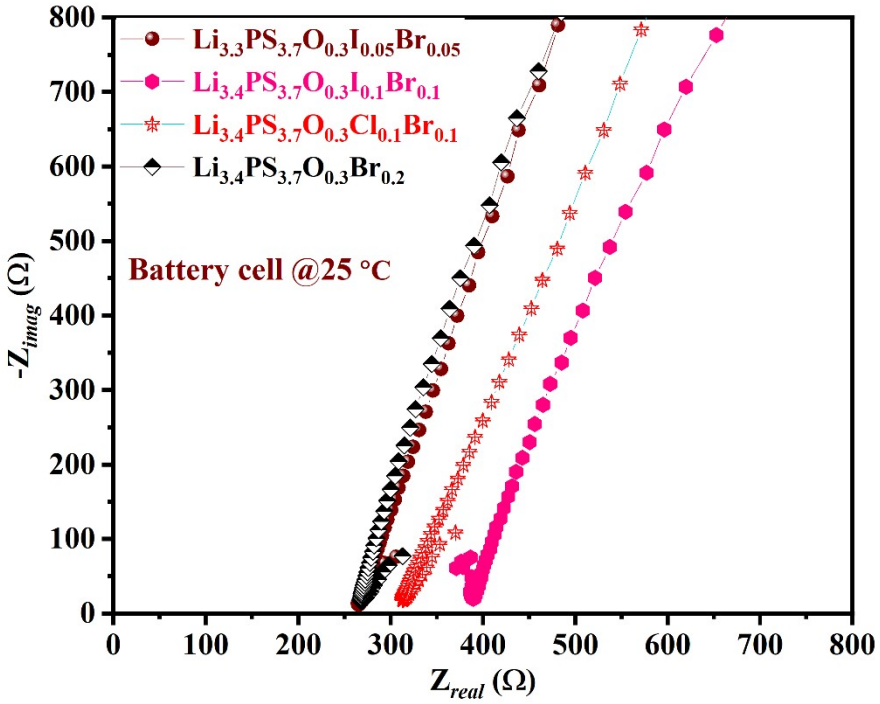

Figure S5. Nyquist plots of samples prepared with composition $Li_{3.2+y}PS_{3.7}O_{0.3}X_y$ (X = Cl, Br, I and y = 0.1, 0.2) recorded in steel/SE/steel cell at 25 °C.

Table S6. EIS results and relative density of solid electrolytes prepared with composition $Li_{3.2+y}PS_{3.7}O_{0.3}X_y$ (X = Cl, Br, I and y = 0.1, 0.2) recorded in steel/SE/steel cell at 25 °C.

Sample	**Results in steel/SE/steel cell**	
	R_{ct} (Ω)	**σ (mS cm^{-1})**
$Li_{3.3}PS_{3.7}O_{0.3}I_{0.05}Br_{0.05}$	264	0.47
$Li_{3.4}PS_{3.7}O_{0.3}I_{0.1}Br_{0.1}$	390	0.32
$Li_{3.4}PS_{3.7}O_{0.3}Cl_{0.1}Br_{0.1}$	312	0.40
$Li_{3.4}PS_{3.7}O_{0.3}Br_{0.2}$	267	0.46

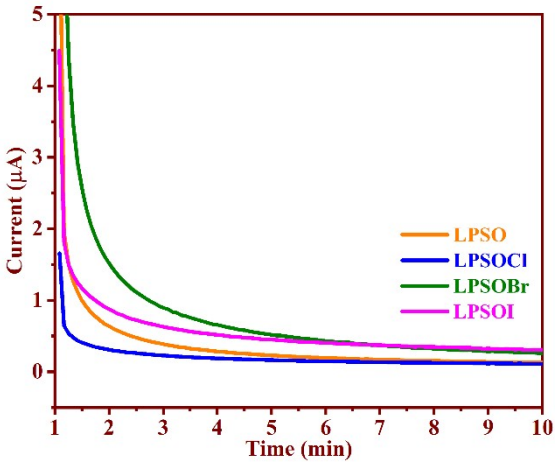

Figure S7. DC polarization curves of LPSO, LPSOCl, LPSOBr and LPSOI.

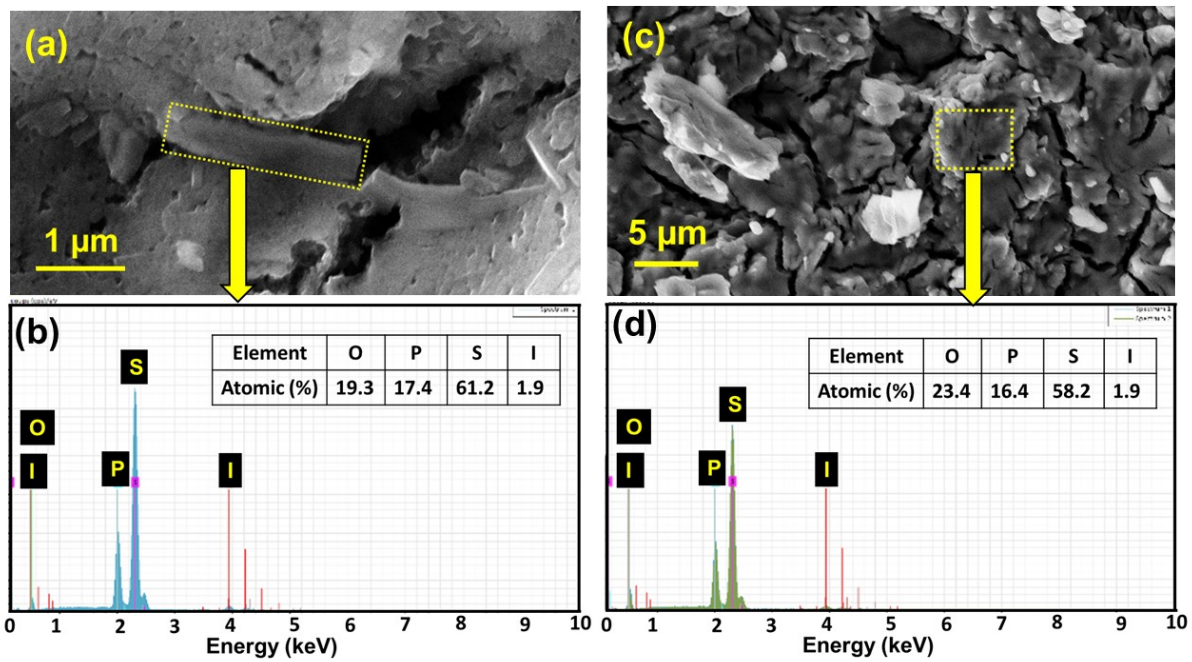

Figure S8. Elemental analysis of LPSOI by SEM-EDS of (a, b) French fries, (c, d) microstructure at low magnification.

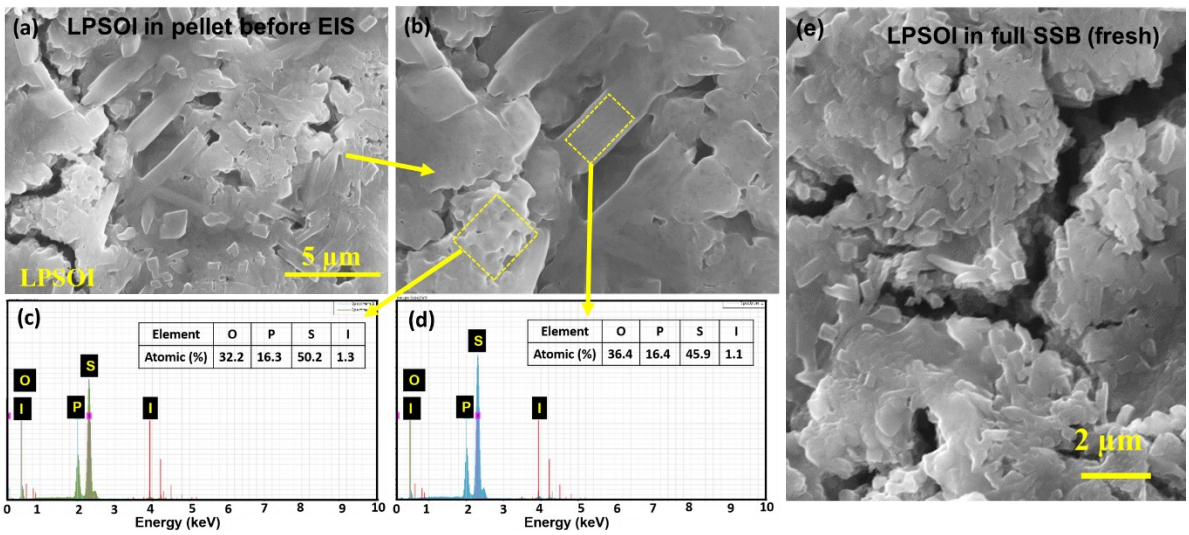

Figure S9. (a-d) Microstructure and elemental analysis of LPSOI pellet before EIS measurement by SEM-EDS, and (e) microstructure of LPSOI layer in full SSB before charge-discharge cycle.

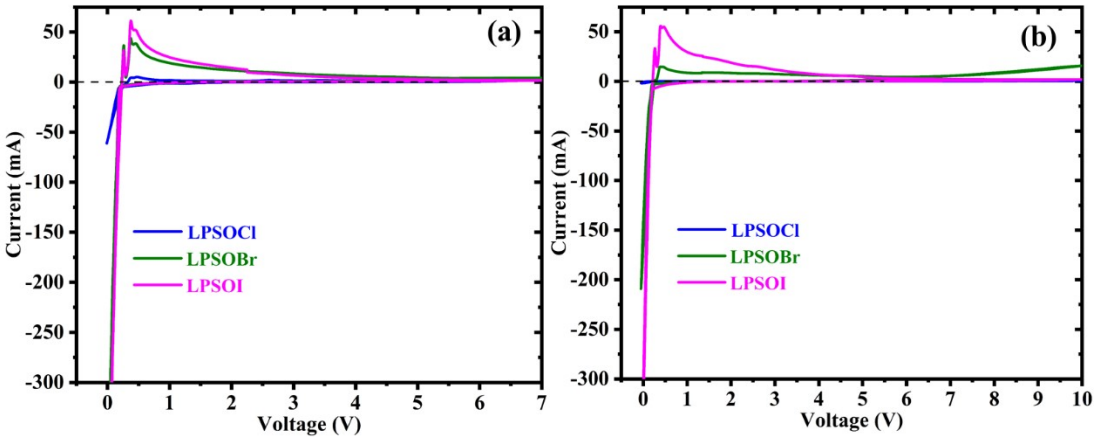

Figure S10. CV curves of Li/SE/Au cells at a scan rate of 1 mV s^{-1} in the voltage range of (a) -0.01 - 7V, (b) -0.05-10V.

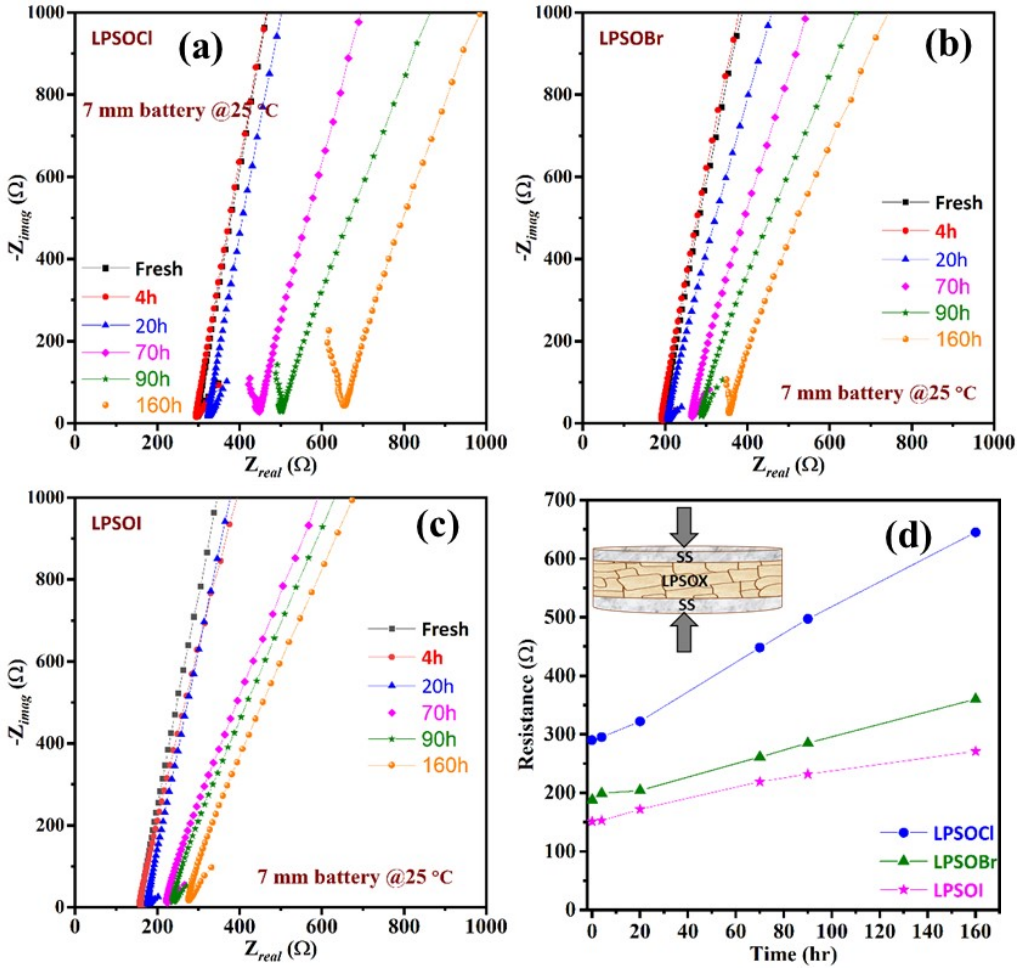

Figure S11. EIS data of LPSOX solid electrolytes with time in SS/SE/SS configuration; (a) LPSOCl, (b) LPSOBr, (c) LPSOI, and (d) comparison of total resistance

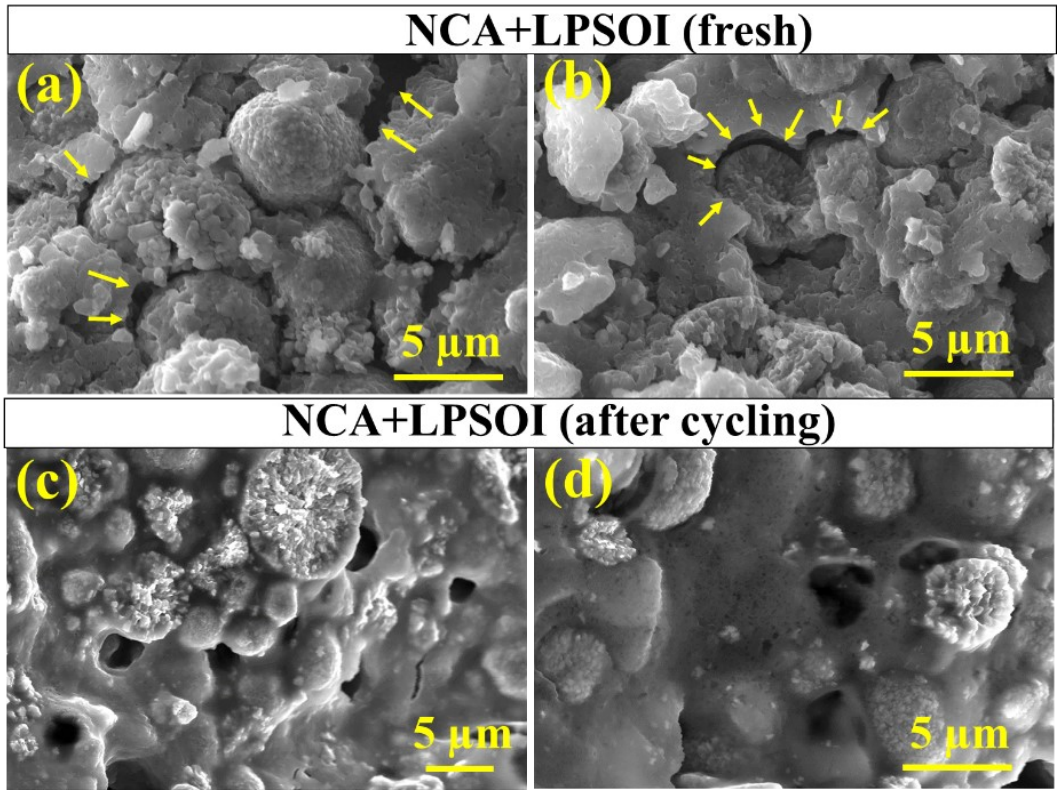

Figure S12. (a & b) cathode composite of fresh SSB cell showing micro gap between NCA particles and LPSOI electrolyte, and (c & d) cathode composite of cycled SSB cell.