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Tailoring Li_6PS_5Br ionic conductivity and understanding of its role in cathode mixtures for high performance all-solid-state Li-S batteries

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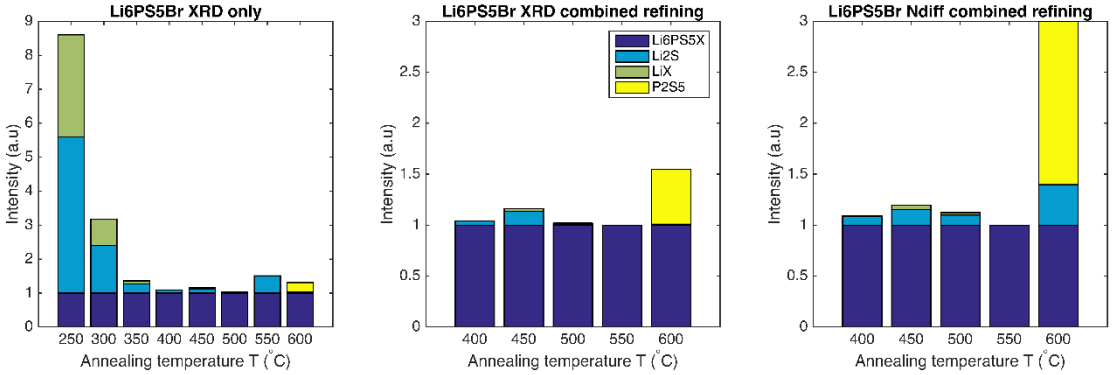

Figure S1. *The phase fraction from XRD and ND refinement results of Li_6PS_5Br annealed at various temperatures (250, 300, 350, 400, 450, 500, 550, and 600 °C).*

Table S1. *Lattice parameters, fractional atomic coordinates, isotropic atomic displacement parameters (Uiso) and site occupancies resulting from the simultaneous Rietveld refinement of X-ray and neutron diffraction data of cubic Li_6PS_5Br prepared by solid-state method (400 °C/10 h) at room temperature.*

	Atom	Fractional coordinates			Wyckoff	Occupancy	Uiso
		X	Y	Z			($Å^2$)
Li_6PS_5Br(400°C)	Li	0.1980	0.1980	0.0244	48*h*	0.5000	0.0754
F-43m	P	0.5	0.5	0.5	4*b*	1.0	0.0215
a=9.975(3) Å	S(0)	0.6180	0.6180	0.6180	16*e*	1.0	0.0339
	Br(1)	0.0	0.0	0.0	4*a*	0.7969	0.0340
	S(1)	0.0	0.0	0.0	4*a*	0.2031	0.0340
	Br(2)	0.25	0.25	0.25	4*c*	0.3489	0.0352
	S(2)	0.25	0.25	0.25	4*c*	0.6511	0.0352

Table S2. *Lattice parameters, fractional atomic coordinates, isotropic atomic displacement parameters (Uiso) and site occupancies resulting from the simultaneous Rietveld refinement of X-ray and neutron diffraction data of cubic Li_6PS_5Br prepared by solid-state method (450 °C/10 h) at room temperature.*

	Atom	Fractional coordinates			Wyckoff	Occupancy	Uiso
		X	Y	Z			($Å^2$)
Li_6PS_5Br(450°C)	Li	0.1953	0.1953	0.0235	48*h*	0.5000	0.0768
F-43m	P	0.5	0.5	0.5	4*b*	1.0	0.0174
a=9.970(1) Å	S(0)	0.6180	0.6180	0.6180	16*e*	1.0	0.0307
	Br(1)	0.0	0.0	0.0	4*a*	0.9739	0.0403
	S(1)	0.0	0.0	0.0	4*a*	0.0261	0.0403
	Br(2)	0.25	0.25	0.25	4*c*	0.3366	0.0338
	S(2)	0.25	0.25	0.25	4*c*	0.6634	0.0338

Table S3. *Lattice parameters, fractional atomic coordinates, isotropic atomic displacement parameters (Uiso) and site occupancies resulting from the simultaneous Rietveld refinement of X-ray and neutron diffraction data of cubic Li_6PS_5Br prepared by solid-state method (500 °C/10 h) at room temperature.*

	Atom	Fractional coordinates			Wyckoff	Occupancy	Uiso
		X	Y	Z			(Å^2)
Li_6PS_5Br(500ºC)	Li	0.1954	0.1954	0.0236	48*h*	0.5000	0.0791
F-43m	P	0.5	0.5	0.5	4*b*	1.0	0.0201
a=9.975(8) Å	S(0)	0.6179	0.6179	0.6179	16*e*	1.0	0.0321
	Br(1)	0.0	0.0	0.0	4*a*	0.9777	0.0386
	S(1)	0.0	0.0	0.0	4*a*	0.0223	0.0386
	Br(2)	0.25	0.25	0.25	4*c*	0.3273	0.0346
	S(2)	0.25	0.25	0.25	4*c*	0.6727	0.0346

Table S4. *Lattice parameters, fractional atomic coordinates, isotropic atomic displacement parameters (Uiso) and site occupancies resulting from the simultaneous Rietveld refinement of X-ray and neutron diffraction data of cubic Li_6PS_5Br prepared by solid-state method (550 ºC/10 h) at room temperature.*

	Atom	Fractional coordinates			Wyckoff	Occupancy	Uiso
		X	Y	Z			(Å^2)
Li_6PS_5Br(550ºC)	Li	0.2020	0.2020	0.0243	48*h*	0.5000	0.0684
F-43m	P	0.5	0.5	0.5	4*b*	1.0	0.0224
a=9.983(5) Å	S(0)	0.6172	0.6172	0.6172	16*e*	1.0	0.0307
	Br(1)	0.0	0.0	0.0	4*a*	0.8179	0.0387
	S(1)	0.0	0.0	0.0	4*a*	0.1821	0.0387
	Br(2)	0.25	0.25	0.25	4*c*	0.2715	0.0322
	S(2)	0.25	0.25	0.25	4*c*	0.7285	0.0322

Table S5. *Lattice parameters, fractional atomic coordinates, isotropic atomic displacement parameters (Uiso) and site occupancies resulting from the simultaneous Rietveld refinement of X-ray and neutron diffraction data of cubic Li_6PS_5Br prepared by solid-state method (600 ºC/10 h) at room temperature.*

	Atom	Fractional coordinates			Wyckoff	Occupancy	Uiso
		X	Y	Z			($Å^2$)
Li_6PS_5Br(600ºC)	Li	0.1935	0.1935	0.0143	48*h*	0.5000	0.0824
F-43m	P	0.5	0.5	0.5	4*b*	1.0	0.0271
a=9.991(4) Å	S(0)	0.6179	0.6179	0.6179	16*e*	1.0	0.0318
	Br(1)	0.0	0.0	0.0	4*a*	0.9778	0.0359
	S(1)	0.0	0.0	0.0	4*a*	0.0222	0.0359
	Br(2)	0.25	0.25	0.25	4*c*	0.4168	0.0386
	S(2)	0.25	0.25	0.25	4*c*	0.5832	0.0386

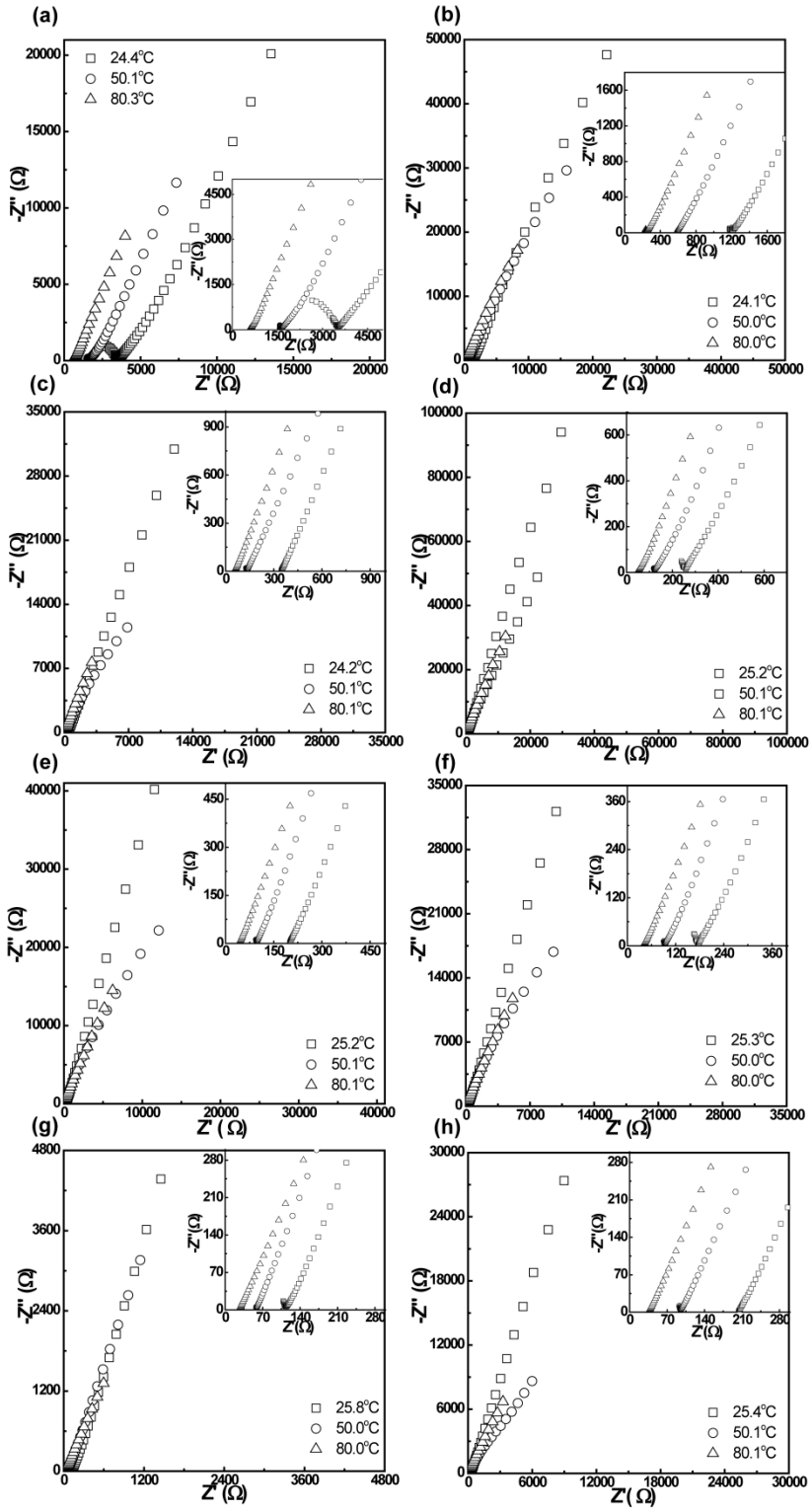

Figure S2. *Nyquist impedance plot of Li_6PS_5Br prepared by solid-state method and annealed at different temperatures for 10 h: (a) 250, (b) 300, (c) 350, (d) 400, (e) 450, (f) 500, (g) 550, and (h) 600 °C. The insets are the magnified view of the impedance at high frequencies.*

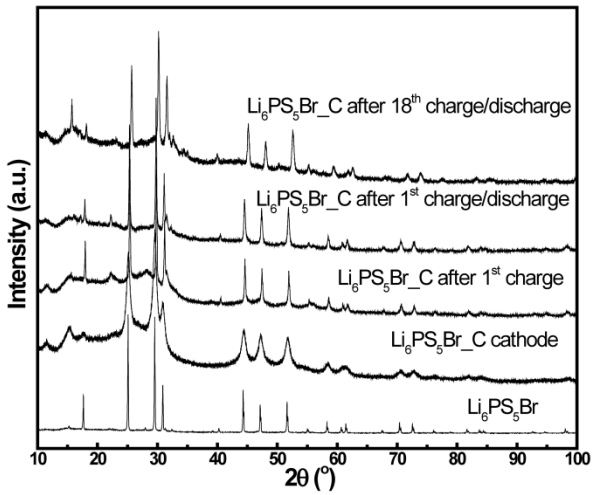

Figure S3. *Ex-situ XRD of Li_6PS_5Br-C cathode mixture for Li_6PS_5Br-C/Li_6PS_5Br/In solid-state Li-S batteries before and after different cycles.*

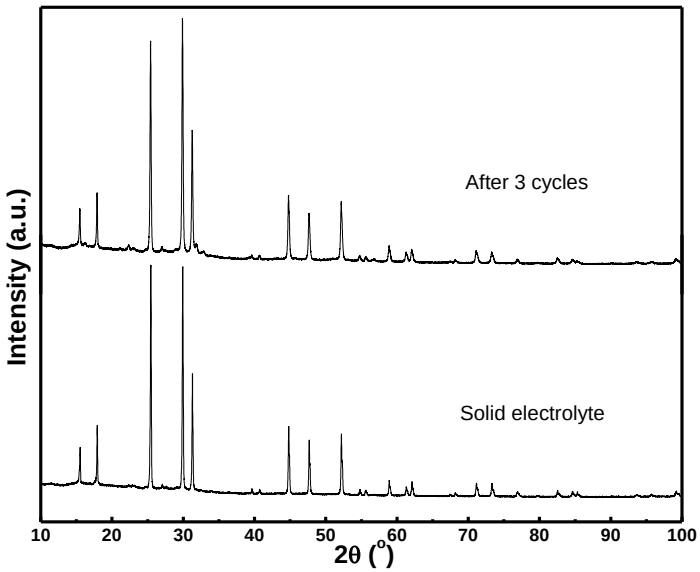

Figure S4. *Ex-situ XRD of Li_6PS_5Br working as electrolyte for Li_6PS_5Br-C/Li_6PS_5Br/In solid-state Li-S batteries before and after 3 cycles.*

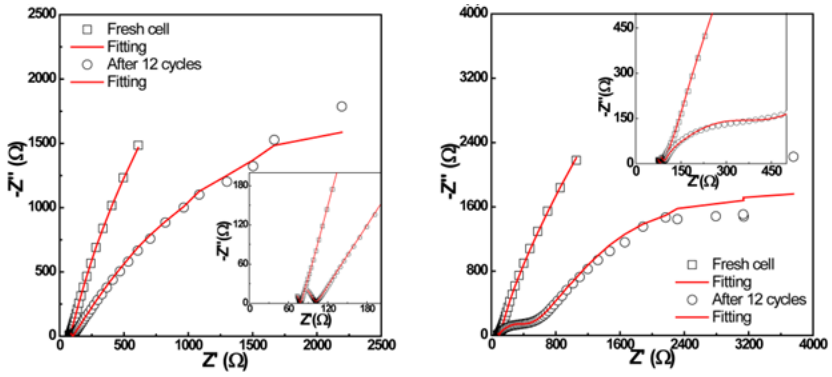

Figure S5. *Nyquist plots of the Li_6PS_5Br-C/Li_6PS_5Br/In all-solid-state Li-S battery before and after cycled at different voltage windows: (left) 0 and 3.0 V vs. In, (right) 0 and 5.0 V vs. In with the current density of 0.32 mA/cm^{2}at room temperature. The results represent fits using an equivalent circuit R(RQ)Q.*

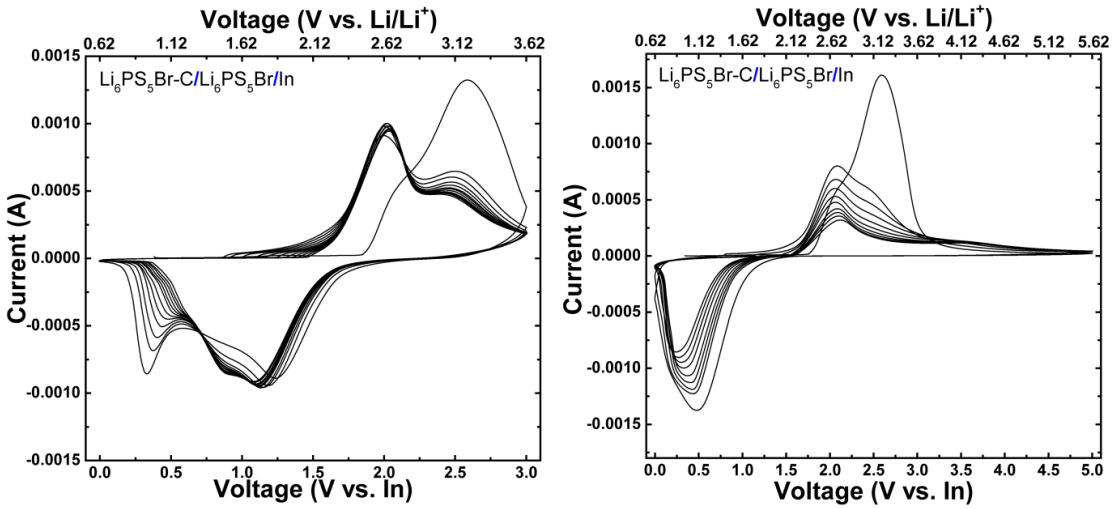

Figure S6. *Cyclic voltammograms of the Li_6PS_5Br-C/Li_6PS_5Br/In all-solid-state Li-S battery in different scan voltage windows from 0 to (**a**) 3.0 and (**b**) 5.00 V (vs. In) at a sweep rate of 0.2 mV/s. Bottom voltage axis shows the values of the voltage versus In, while top voltage axis shows the corresponding values of voltage versus Li/Li$^+$.*

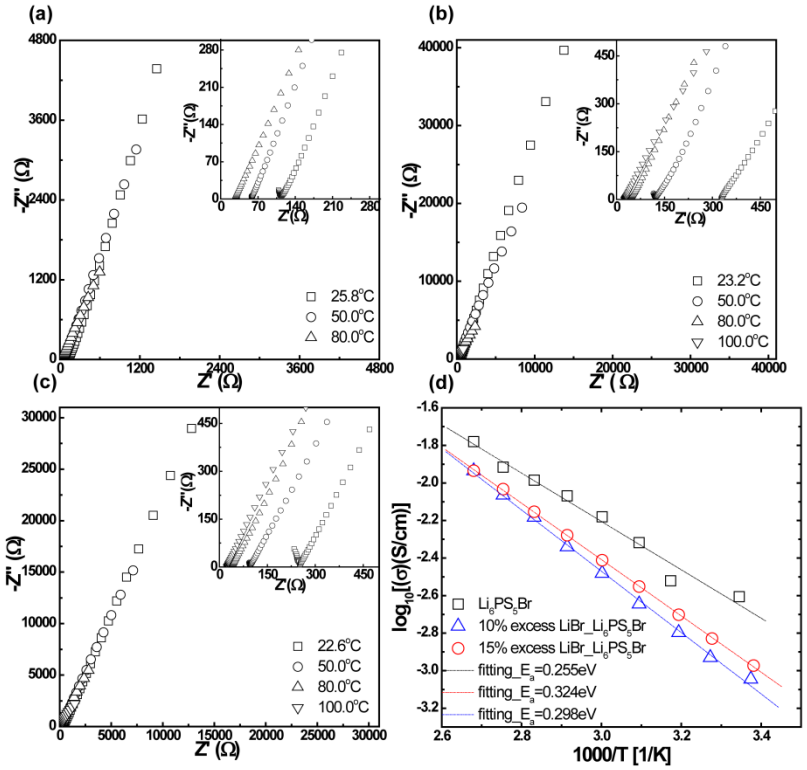

Figure S7. The *AC impedance spectroscopy at selected temperatures of (a)Li_6PS_5Br, (b)10% excess-Li_6PS_5Br, (c)15% excess-Li_6PS_5Br. (d) The corresponding temperature-dependent lithium ion conductivity.*