Supporting Information

Revealing the annealing effects of annealing on Li-ion mobility in the Li_6PS_5Br solid electrolyte synthesized by a mechanical milling route

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Table S1. *Room temperature X-ray diffraction patterns including Rietveld refinement of the (a) Li_6PS_5Br, (b) AN-Li_6PS_5Br, (c) and AN-BM-Li_6PS_5Br materials.*

	Atom	Fractional coordinates			Wyckoff	Occupancy	U_{iso}
		X	Y	z			(Å^2)
	Li	0.174(5)	0.174(5)	0.029(0)	48h	0.47(3)	0.172(7)
BM- Li_6PS_5Br	P	0. 5	0.5	0.5	4b	1.0	0.080(5)
F-43m	S(0)	0.617(3)	0.617(3)	0.617(3)	16e	1.0	0.074(3)
a=9.941(7) Å	S(1)	0.0	0.0	0.0	4c	0.52(5)	0.080(6)
	Br(1)	0.0	0.0	0.0	4c	0.47(5)	0.025(3)
	S(2)	0.25	0.25	0.25	4a	0.56(3)	0.065(6)
	Br(2)	0.25	0.25	0.25	4a	0.43(7)	0.055(8)
		$Li_{5.67}PS_{5.09}Br_{0.91}$, Average crystallite size: 15 nm					

	Atom	Fractional coordinates			Wyckoff	Occupancy	U_{iso}
		X	Y	z			(Å^2)
	Li	0.196(3)	0.196(3)	0.021(8)	48h	0.48(2)	0.141(4)
AN-BM-Li_6PS_5Br	P	0. 5	0.5	0.5	4b	1.0	0.054(7)
F-43m	S(0)	0.618(6)	0.618(6)	0.618(6)	16e	1.0	0.064(8)
a=9.974(4) Å	S(1)	0.0	0.0	0.0	4c	0.24(6)	0.070(6)
	Br(1)	0.0	0.0	0.0	4c	0.75(4)	0.075(8)
	S(2)	0.25	0.25	0.25	4a	0.85(3)	0.061(5)
	Br(2)	0.25	0.25	0.25	4a	0.14(7)	0.050(7)
		$Li_{5.78}PS_{5.1}Br_{0.90}$, Average crystallite size: 74 nm					

	Atom	Fractional coordinates			Wyckoff	Occupancy	U_{iso}
		X	Y	z			($Å^2$)
	Li	0.173(1)	0.173(1)	0.037(5)	48h	0.46(7)	0.169(1)
BM-AN-BM-Li_6PS_5Br	P	0. 5	0.5	0.5	4b	1.0	0.067(8)
	S(0)	0.617(2)	0.617(2)	0.617(2)	16e	1.0	0.055(4)
F-43m	S(1)	0.0	0.0	0.0	4c	0.53(3)	0.076(2)
a=9.971(4) Å	Br(1)	0.0	0.0	0.0	4c	0.47(5)	0.032(1)
	S(2)	0.25	0.25	0.25	4a	0.64(5)	0.088(5)
	Br(2)	0.25	0.25	0.25	4a	0.35(5)	0.031(4)
	$Li_{5.60}PS_{5.18}Br_{0.82}$, Average crystallite size: 22 nm						

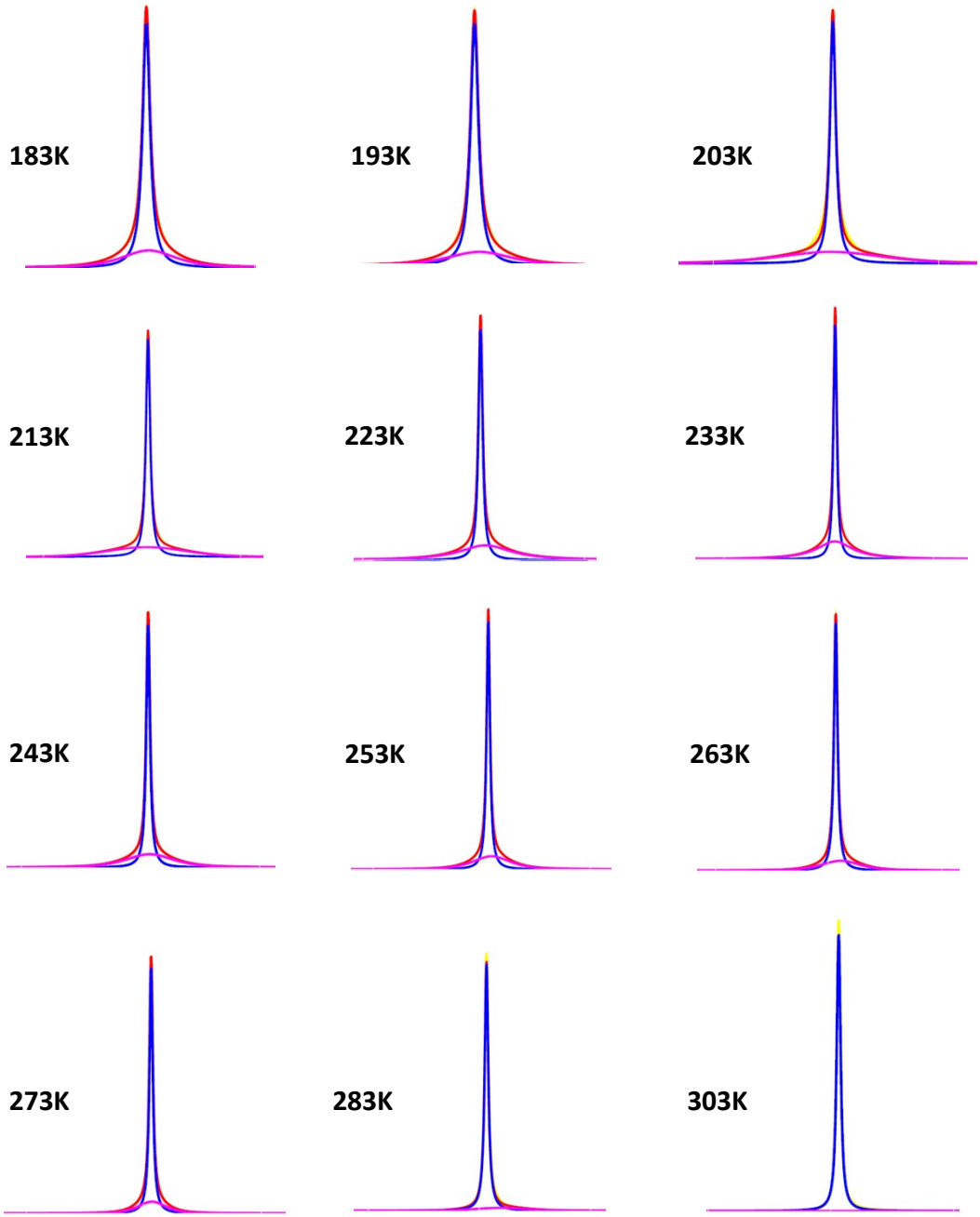

Figure S1. *The line shape of Li_6PS_5Br measured from 183 to 303 K, which are fit as a sum of Gaussian (broad) and Lorentzian component (narrow) associated with slow and fast lithium ion motilities. Here, the fit results of AN-Li_6PS_5Br is shown as an example.*

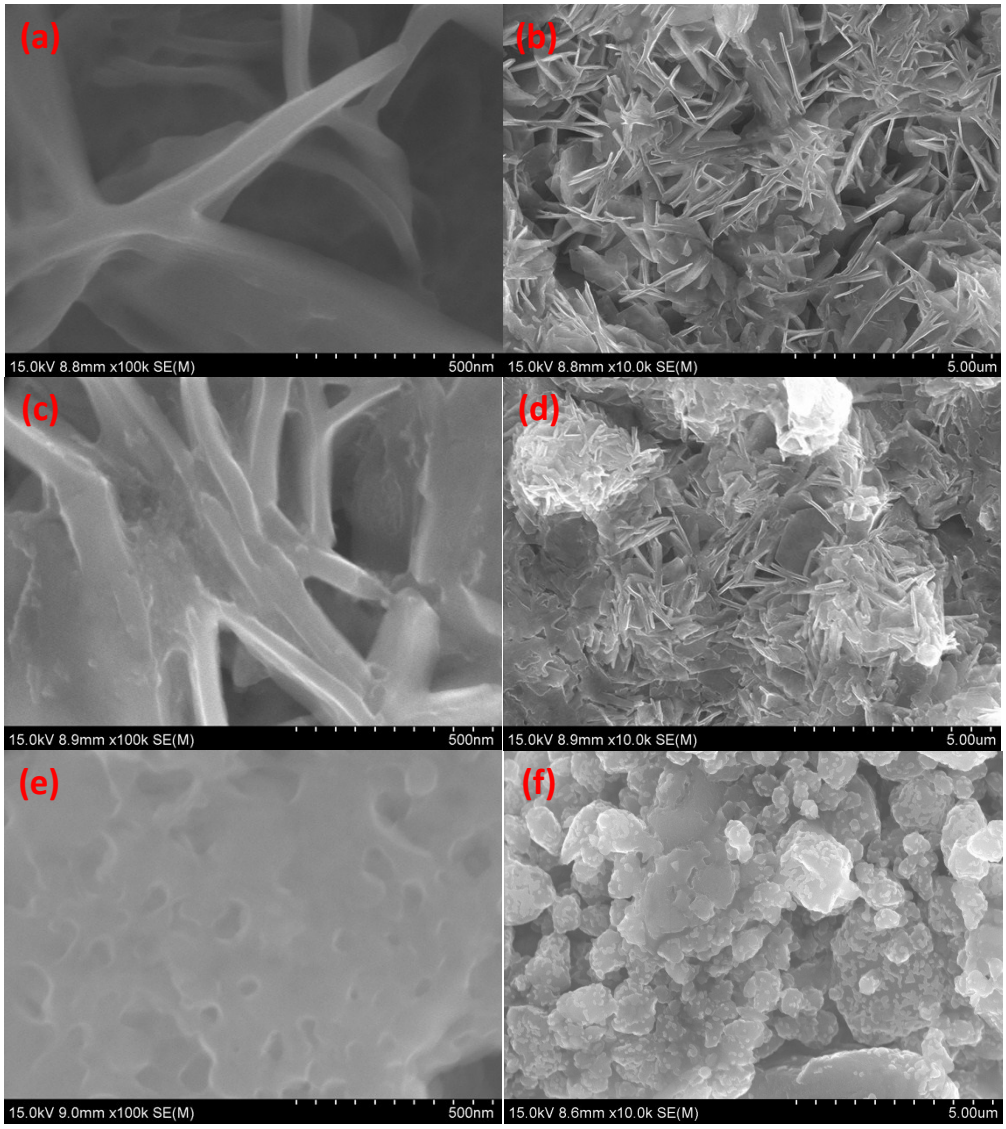

Figure S2. SEM images of the samples (a-b) Li_6PS_5Br, (c-d) AN-Li_6PS_5Br, and (e-f) AN-BM-Li_6PS_5Br.

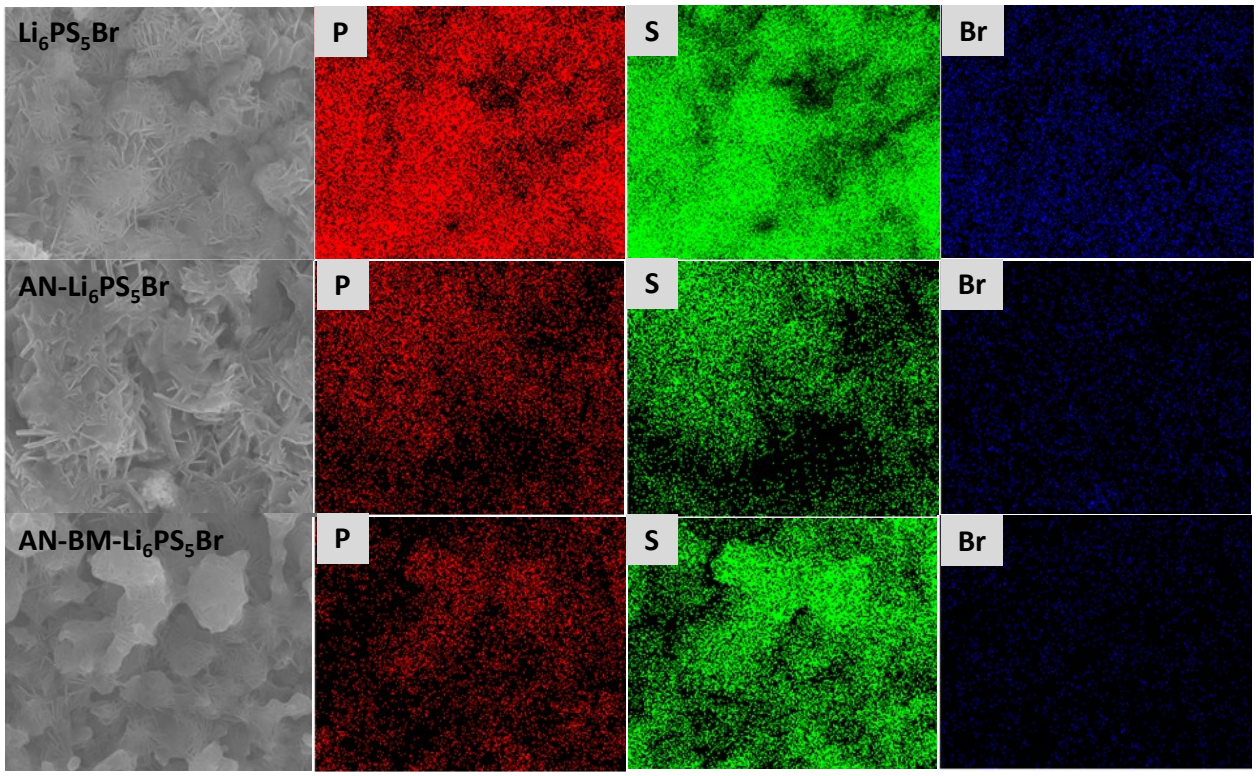

Figure S3. The EDS mapping of the samples (a-b) Li_6PS_5Br, (c-d) AN-Li_6PS_5Br, and (e-f) AN-BM-Li_6PS_5Br.

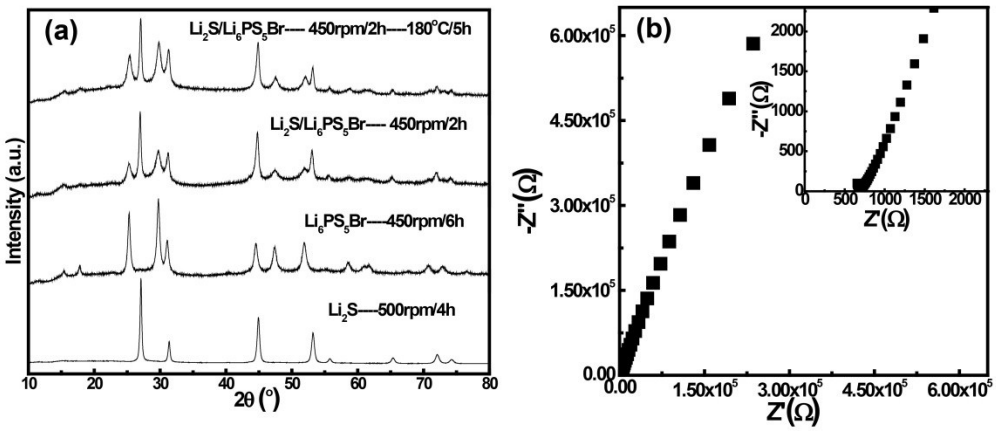

Figure S4. (*a) XRD patterns of Li_2S cathode, Li_6PS_5Br electrolyte and the mixture of those two. (b) The complex impedance plot for the mixture of Li_2S and Li_6PS_5Br ball milled with 450 rpm for 2 h.*

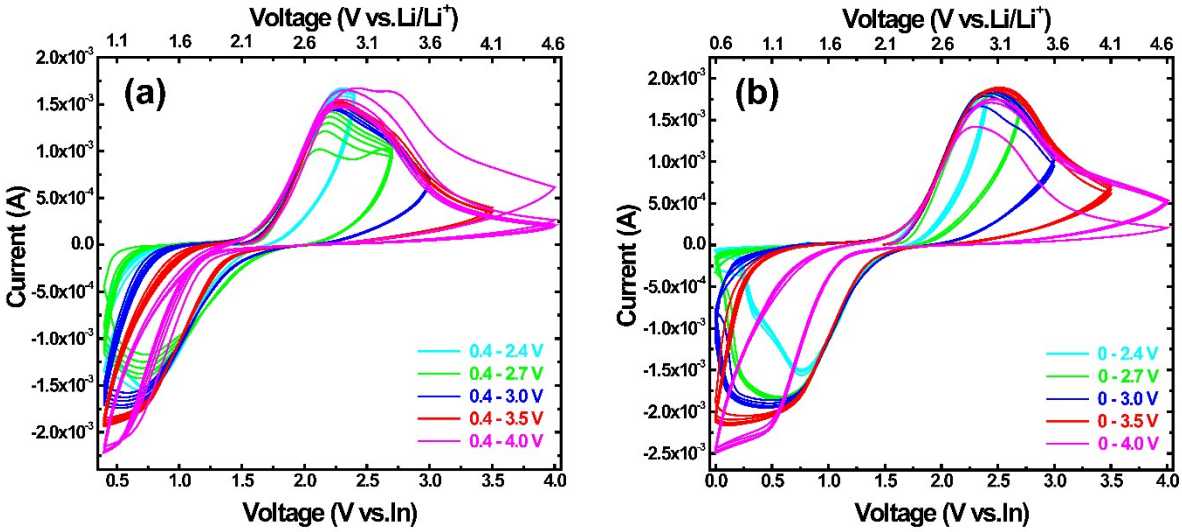

Figure S5. *Cyclic voltammograms of the nano-Li2S/AN-Li6PS5Br/Li-In all-solid-state batteries for different voltage cut-off windows (a) 0.4 - 2.4, 0.4 - 2.7, 0.4 - 3.0, 0.4 - 3.5, and 0.4 to 4.0 V and (b) 0 - 2.4, 0 - 2.7, 0 - 3.0, 0 - 3.5, and 0 - 4.0 V; all vs. In, at a scanning rate of 0.5 mV/s. The bottom X-axis shows the values of the voltage versus In, the top X-axis shows the corresponding values of voltage versus Li/Li⁺.*