## Supporting information for

## Effect of Boron Element in Li-P-S system

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Figure S1. XRD patterns of the nominal chemical composition  $0.6Li_3PS_4$ -  $0.4Li_3BS_3$  at different annealing temperature between 450°C and 700°C. New peaks corresponding to the LGPS type structure are identified starting at 500°C (highlighted in blue), Impurities have been identified as:  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> (\*) and Li<sub>7</sub>PS<sub>6</sub> ( $\Delta$ ) phases.



Figure S2. (a) Nyquist diagram of the sample  $Li_3P_{0.6}B_{0.4}S_{3.6}$  at different temperature and (b) Fitted curve with the associated equivalent circuit for the Nyquist diagram at -20°C.

Temperature	-35°C	-20°C	0°C	20°C
R1	9 245 Ohm	3 167 Ohm	N/A	N/A
	(± 280)	(± 102)		
Q1	$0.534 9e-9 F.s^{(a-1)}$	$0.545 \ 2e-9 \ F.s^{(a-1)}$	N/A	N/A
	(± 6.2 e-11)	(± 2.5 e-11)		
al	1	1	N/A	N/A
R2	459 394 Ohm	100 862 Ohm	16 643 Ohm	3 607 Ohm
	(± 316)	(± 121)	(± 32.2)	(± 6.3)
Q2	20.14e-9 F.s <sup>(a - 1)</sup>	32.06e-9 F.s <sup>(a - 1)</sup>	$69.52e-9 \text{ F.s}^{(a-1)}$	75.7 e-9 $F.s^{(a-1)}$
	(± 6.2 e-11)	(± 1.3 e-10)	(± 3.0 e-9)	(± 5.2 e-9)
a2	0.639	0.622	0.574	0.585
	$(\pm 0.38 \text{ e-3})$	$(\pm 0.45 \text{ e-3})$	(± 3.42 e-3)	(± 6.17 e-3)
Q3	7.498e-6 F.s <sup>(a - 1)</sup>	23.47e-6 F.s <sup>(a - 1)</sup>	75.77e-6 F.s <sup>(a - 1)</sup>	$0.155 \text{ e-} 3 \text{ F.s}^{(a-1)}$
	(± 2.1 e-8)	$(\pm 6.5 \text{ e-8})$	(± 0.38 e-6)	(± 0.42 e-6)
a3	0.361	0.414	0.5158	0.585
	(± 1.32 e-3)	(± 1.43 e-3)	(± 1.11 e-3)	(± 1.61 e-3)

Table S1 Values from fitted diagram from sample  $Li_3P_{0.6}B_{0.4}S_{3.6}$  at each temperature

Temperature	25°C	40°C	60°C	80°C
R2	2 553 Ohm	1 027 Ohm	377 Ohm	162 Ohm
	$(\pm 8.0)$	(± 3.2)	(± 1.17)	(± 1.27)
Q2	$27.44e-9 \text{ F.s}^{(a-1)}$	45.52e-9 F.s <sup>(a - 1)</sup>	$0.229e-6 \text{ F.s}^{(a-1)}$	N/A
	(± 4.6 e-9)	(± 4.71 e-9)	(± 1.3 e-8)	
a2	0.595	0.623	0.513	N/A
	(± 4.8 e-3)	$(\pm 6.5 \text{ e-3})$	(± 0.18 e-3)	
Q3	$0.180e-3 F.s^{(a-1)}$	$0.277e-3 F.s^{(a-1)}$	$0.433e-3 F.s^{(a-1)}$	$0.607 \text{ e-} 3 \text{ F.s}^{(a-1)}$
	(± 0.57 e-6)	(± 0.59 e-6)	(± 0.77 e-6)	(± 1.87 e-6)
a3	0.603	0.623	0.661	0.651
	(± 2.2 e-3)	$(\pm 1.3 \text{ e-3})$	$(\pm 0.97 \text{ e-3})$	$(\pm 1.63 \text{ e-3})$



Figure S3. a) Arrhenius plot with associated activation energy of composition  $Li_3P_{1-x}B_xS_{4-x}$ (0.15<x<0.45) in binary system, and b) Arrhenius plot with associated activation energy of compositions of the ternary  $Li_2S-P_2S_3$  system as given in the table 1.



Figure S4. Contrast color of the activation energy in function of the composition inside the  $Li_2S-P_2S_5-B_2S_3$  ternary.



Figure S5. Polarization profile of symmetric cell made from compound a)  $Li_3P_{1-x}B_xS_{4-x}$  (0.15<x<0.5) and b) other composition of the ternary  $Li_2S-P_2S_5-B_2S_3$  at different current density