Electronic Supporting Information

Crucial role of oxygen substitution in argyrodite solid electrolytes from bulk to surface under atmospheric conditions

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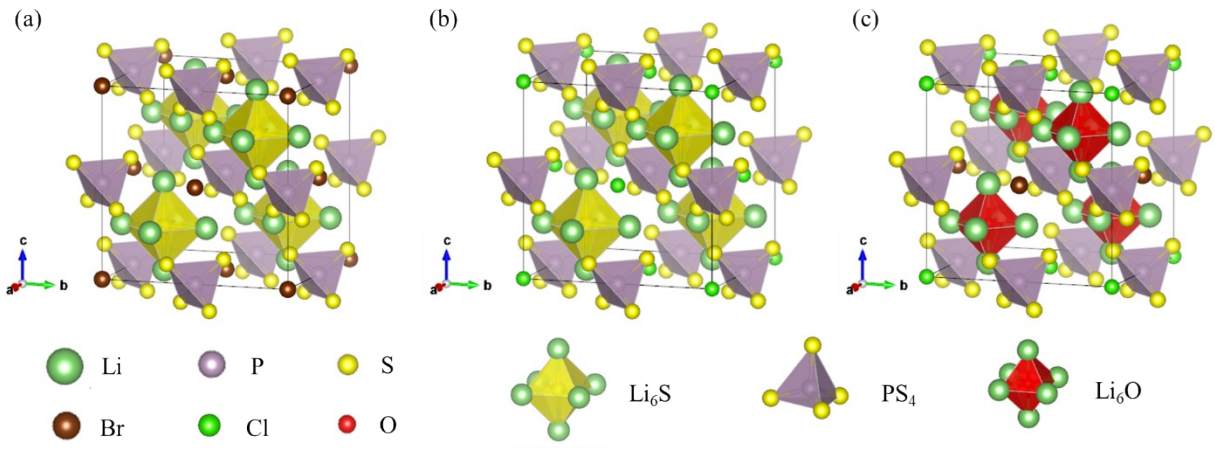

Fig. S1 Atomic structures of (a)Li_6PS_5Br, (b)Li_6PS_5Cl and (c)$Li_6POS_4Br_{0.5}Cl_{0.5}$.

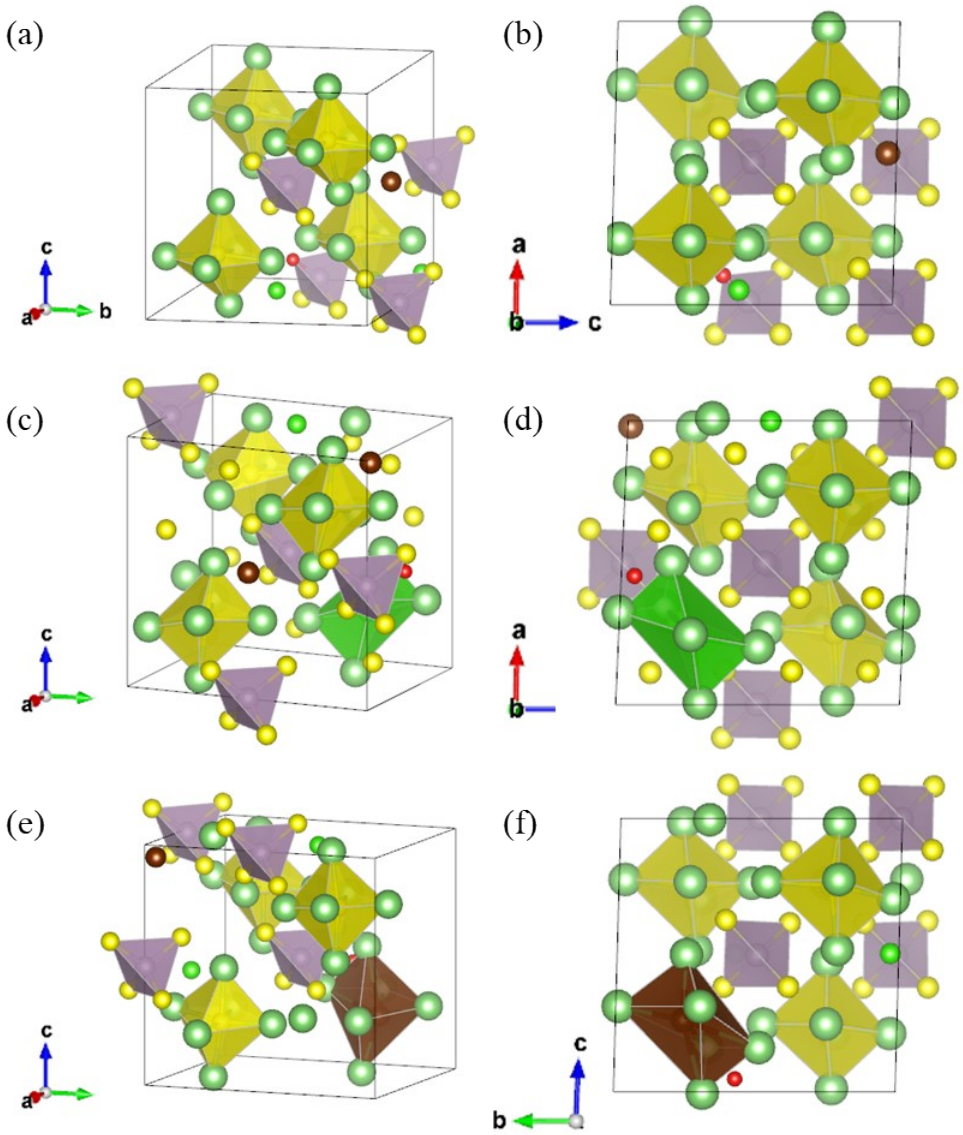

Fig. S2 Atomic structures of (a,b)16e site $Li_6PO_{0.25}S_{4.75}Br_{0.5}Cl_{0.5}$ (c,d for Cl and e,f for Br) 4a site inversed $Li_6PO_{0.25}S_{4.75}Br_{0.5}Cl_{0.5}$.

Table. S1 Lattice constants of (a,b)16e site $Li_6PO_{0.25}S_{4.75}Br_{0.5}Cl_{0.5}$ (c,d for Cl and e,f for Br) 4a site inversed $Li_6PO_{0.25}S_{4.75}Br_{0.5}Cl_{0.5}$.

	a	*b*	*c*	alpha	beta	gamma
16e site $Li_6PO_{0.25}S_{4.75}Br_{0.5}Cl_{0.5}$	10.17	10.17	10.23	88.50	91.51	88.14
Cl - 4a site inversed $Li_6PO_{0.25}S_{4.75}Br_{0.5}Cl_{0.5}$	10.08	10.39	10.39	90.21	88.42	91.58
Br - 4a site inversed $Li_6PO_{0.25}S_{4.75}Br_{0.5}Cl_{0.5}$	10.51	10.08	10.08	92.55	90.37	90.37

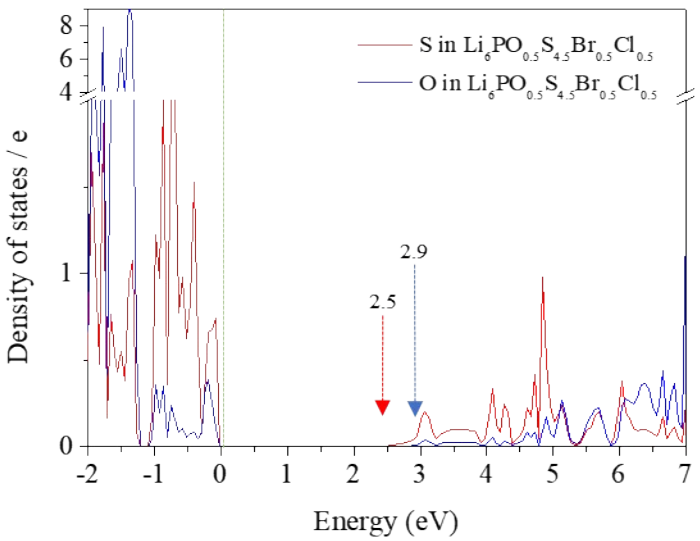

Fig. S3 Density of states for S and O in $Li_6PO_{0.5}S_{4.5}Br_{0.5}Cl_{0.5}$.(Dotted arrows are band gaps).

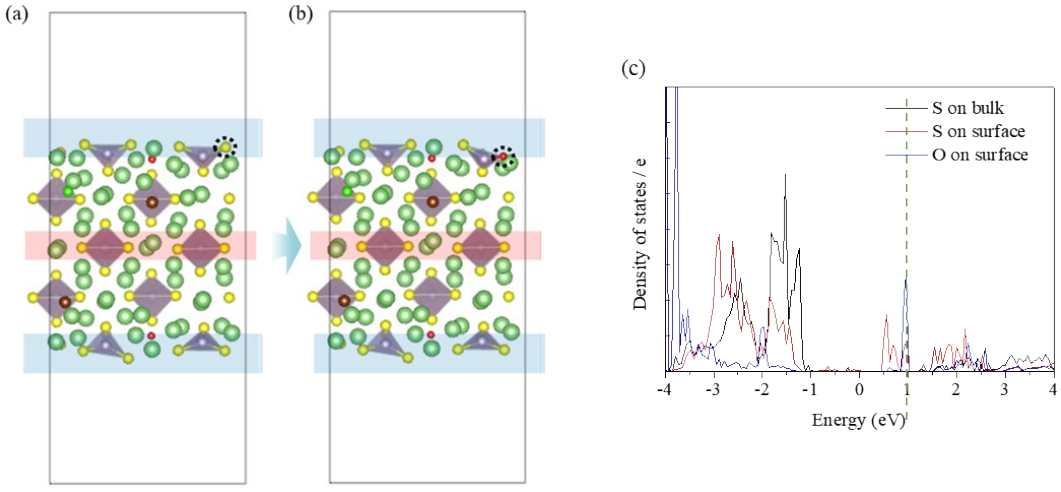

Fig. S4 Atomic structures before and after the exchange between S and O in (a, b) $Li_6PO_{0.5}S_{4.5}Br_{0.5}Cl_{0.5}$.; PDOSs of the exchanged S, O on the surface and S in the bulk for (c)$Li_6PO_{0.5}S_{4.5}Br_{0.5}Cl_{0.5}$.(blue shaded areas : surfaces, red shaded area : bulk, black dotted circle : exchanged elements).

Table S2. Average net charges of S and O at the surface before the exchange.

	S on 4d	S on 16e	O on 4d	p
$Li_6PS_5Br_{0.5}Cl_{0.5}$	-1.65	-0.80	X	1.239
$Li_6PO_{0.5}S_{4.5}Br_{0.5}Cl_{0.5}$	-1.63	-0.73	-1.69	1.25
$Li_6POS_5Br_{0.5}Cl_{0.5}$	X	-0.72	-1.69	1.25

Table S3. Average net charges of S and O at the surface After the exchange.

	S on 4d	S on 16e	Exchanged O	O on 4d	P
$Li_6PS_5Br_{0.5}Cl_{0.5}$	-1.65	-0.77	-1.51	X	1.42
$Li_6PO_{0.5}S_{4.5}Br_{0.5}Cl_{0.5}$	-1.64	-0.74	-1.46	-1.69	1.44
$Li_6POS_5Br_{0.5}Cl_{0.5}$	X	-0.72	-1.42	-1.69	1.42

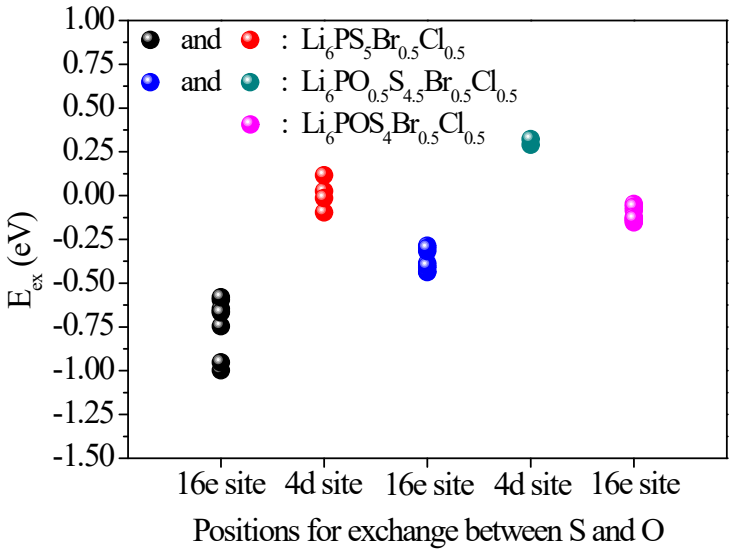

Fig. S5 Exchange energy between S and O depending on the positions in $Li_6PS_5Br_{0.5}Cl_{0.5}$, $Li_6PO_{0.5}S_{4.5}Br_{0.5}Cl_{0.5}$ and $Li_6POS_4Br_{0.5}Cl_{0.5}$.

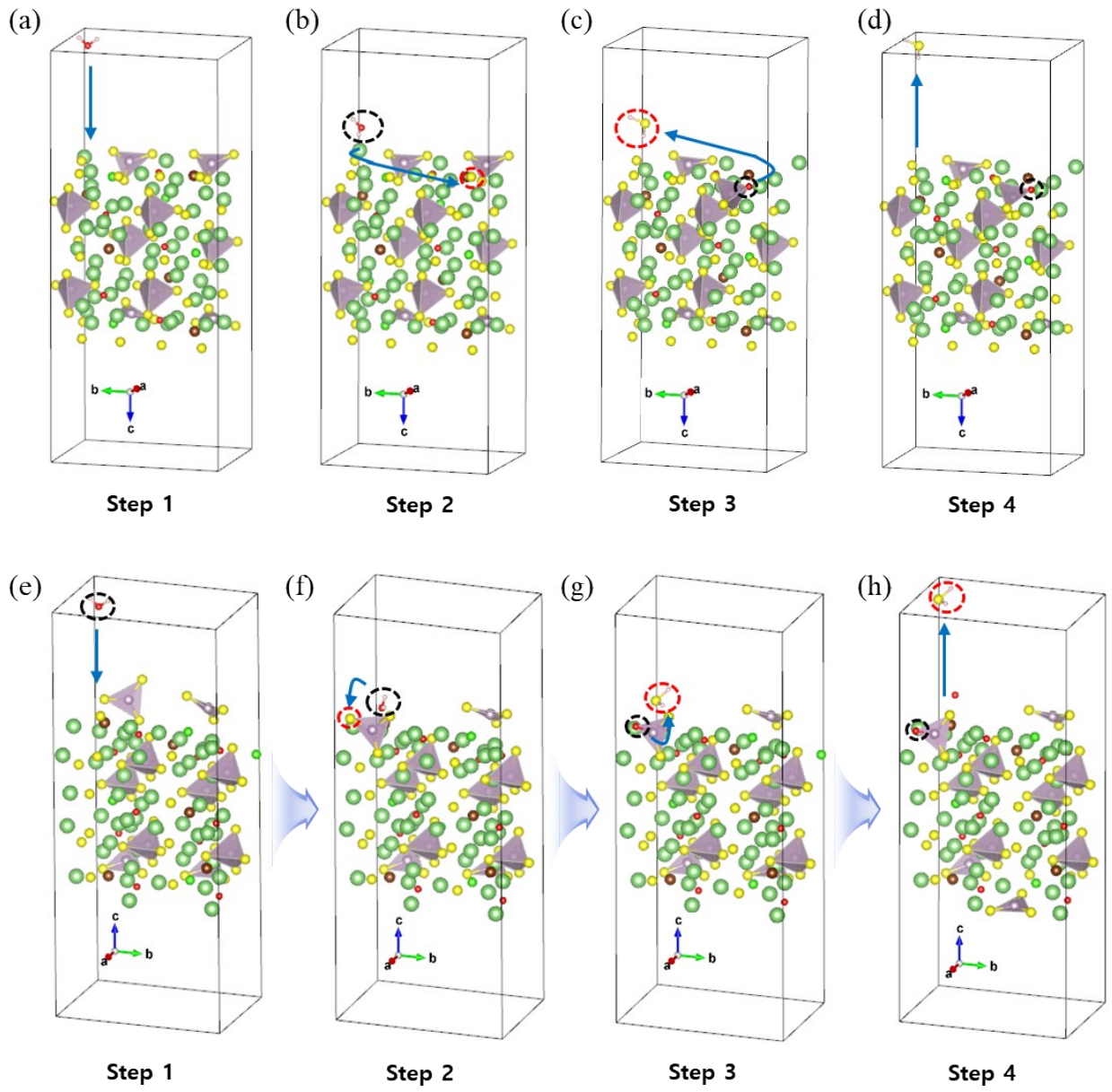

Fig. S6 Atomic structures of (a-d) $Li_6POS_{4.5}Br_{0.5}Cl_{0.5}$ and (e-h) $Li_6POS_5Br_{0.5}Cl_{0.5}$ of reaction steps from H_2O to H_2S

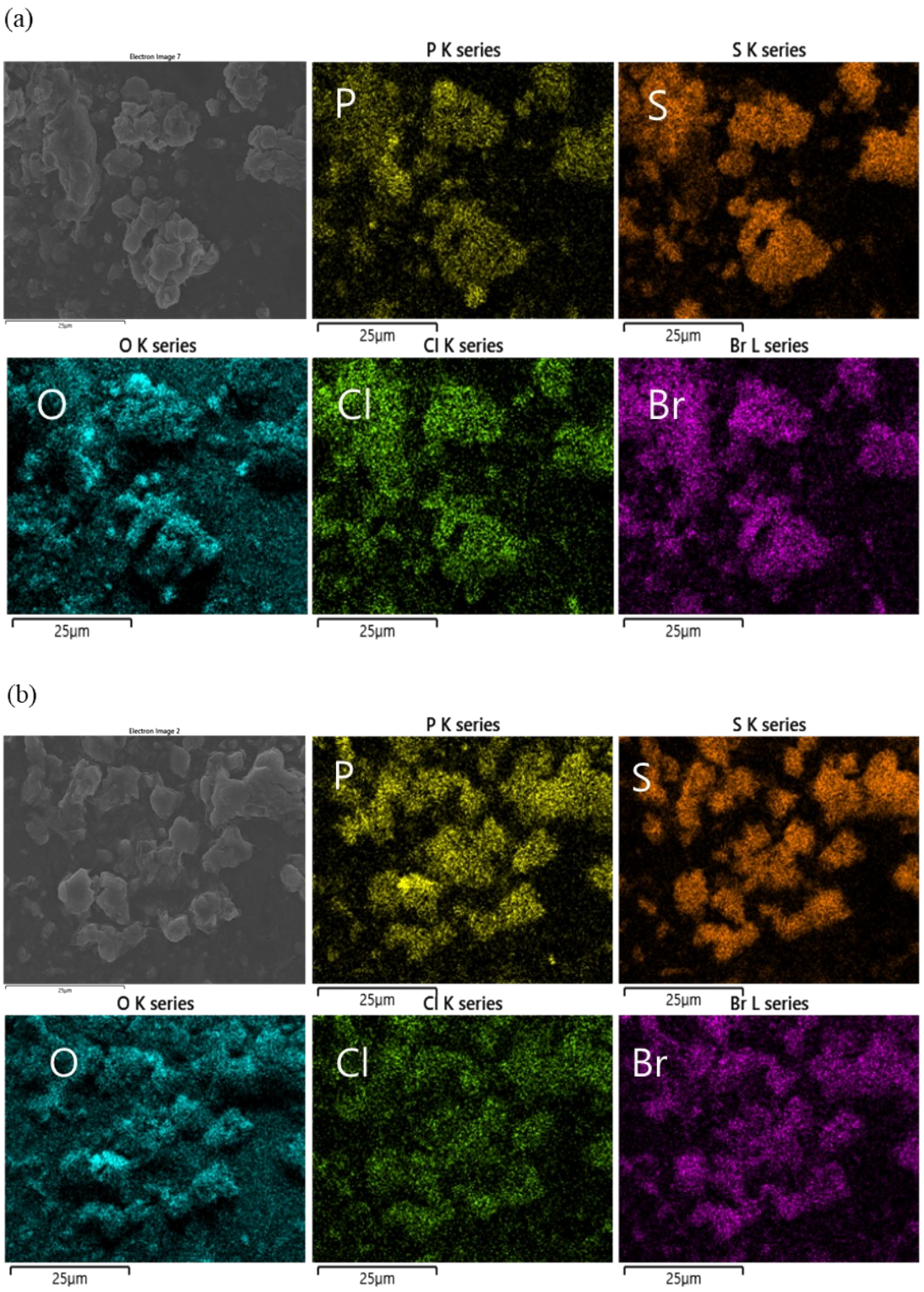

Fig. S7 Morphology and distributions of constituents in (a) $Li_6PS_5Br_{0.5}Cl_{0.5}$ and (b) $Li_6PO_{0.5}S_{4.5}Br_{0.5}Cl_{0.5}$.

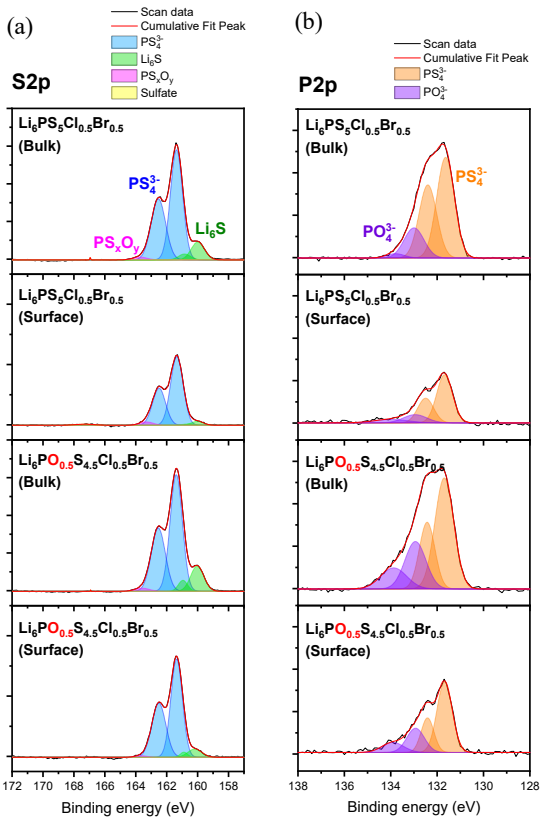

Fig. S8 (a)S2p and (b)P2p XPS spectra of $Li_6PS_5Br_{0.5}Cl_{0.5}$ and $Li_6PO_{0.5}S_{4.5}Br_{0.5}Cl_{0.5}$ solid electrolytes after exposure to dry air.