

Supporting Information

Theoretical insights into interfacial stability and ionic transport of Li_2OHBr solid electrolyte for all-solid-state batteries

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Table S1. Calculated plateaus for the lithiation and delithiation of Li_2OHBr solid-state electrolyte.

Potential ref. to Li/Li^+ (V)	μ_{Li} ref. to Li metal (eV)	Δn_{Li} per formula	Phase equilibria
0.80	-0.80	2.00	Li_2O , LiH, LiBr
		0	$\text{Li}_4\text{H}_3\text{BrO}_3$, LiBr
3.15	-3.15	-0.67	$\text{Li}_4\text{H}_3\text{BrO}_3$, Br

3.27	-3.27	-1.67	LiH ₃ O ₂ , Br ₂ O ₃ , Br
3.96	-3.29	-2.00	Br ₂ O ₃ , H ₂ O, Br

Table S2. Predicted reaction products and reaction energies (meV/atom) between cathodes (LiCoO₂, LiMn₂O₄ and LiFePO₄) and Li₂OHBr solid-state electrolyte.

Cathodes	Li ₂ OHBr, <i>x</i>	Phase equilibria	ΔE (meV/ atom)
LiCoO ₂	-	LiCoO ₂ +Li ₂ OHBr	0
Li _{0.5} CoO ₂	0.5	LiH ₂ BrO+LiCoO ₂ +LiBr+Li ₂ CoO ₃	-8
LiMn ₂ O ₄	0.60	LiH ₂ BrO+LiBr+Mn ₃ O ₄ +Li ₂ MnO ₃	-19
	0.50	LiH ₂ BrO+LiBr+Mn ₂ O ₃ +Li ₂ MnO ₃	-17
Li _{0.5} Mn ₂ O ₄	0.75	LiMnO ₂ +LiBr+Li ₂ MnO ₃ +LiH ₂ BrO	-45
	0.733	Mn ₃ O ₄ +LiBr+Li ₂ MnO ₃ +LiH ₂ BrO	-47
	0.667	Li ₂ MnO ₃ +LiBr+LiMn ₂ O ₄ +LiH ₂ BrO	-50
	0.444	LiMn ₂ O ₄ +LiBr+Li ₅ Mn ₇ O ₁₆ +LiH ₂ BrO	-58
	0.381	MnH ₄ Br ₂ O ₂ +LiBr+Li ₅ Mn ₇ O ₁₆ +LiH ₂ BrO	-56
	0.348	MnH ₄ Br ₂ O ₂ +LiBr+Li ₅ Mn ₇ O ₁₆ +Br	-54
	0.254	MnH ₄ Br ₂ O ₂ +Mn ₂ O ₃ +Li ₅ Mn ₇ O ₁₆ +Br	-45
LiFePO ₄	0.667	Fe(OH) ₂ +LiBr+Li ₃ PO ₄	-40
	0.615	FeH ₈ Br ₂ O ₄ +FeO+LiBr+Li ₃ PO ₄	-39
Li _{0.5} FePO ₄	0.75	FeO+LiFeO ₂ +LiH ₂ BrO+LiBr+Li ₃ PO ₄	-67
	0.714	FeHO ₂ +FeO+LiH ₂ BrO+LiBr+Li ₃ PO ₄	-75
	0.677	FeH ₈ (BrO ₂) ₂ +FeO+FeHO ₂ +LiBr+Li ₃ PO ₄	-79
	0.667	FeH ₈ (BrO ₂) ₂ +Fe ₂ O ₃ +FeO+LiBr+Li ₃ PO ₄	-80
	0.60	FeH ₈ (BrO ₂) ₂ +Fe ₂ O ₃ +LiFePO ₄ +LiBr+Li ₃ PO ₄	-81
	0.49	FeH ₈ (BrO ₂) ₂ +Fe ₂ O ₃ +LiFePO ₄ +LiFeBr ₄ +Li ₃ PO ₄	-78
	0.286	LiFePHO ₅ +LiFePO ₄ +LiFeBr ₄ +Li ₃ PO ₄	-60
	0.222	LiFePHO ₅ +LiFePO ₄ +LiFeBr ₄ +Li ₃ Fe ₂ (PO ₄) ₃	-53

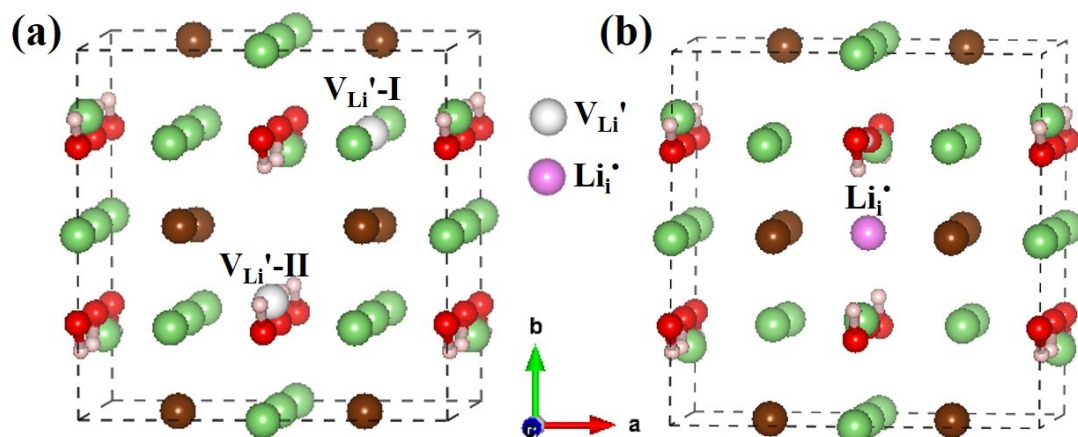


Figure S1. Possible defect configurations of the Li_2OHBr in (a) single lithium vacancy (V_{Li}') and (b) single lithium interstitial (Li_i').

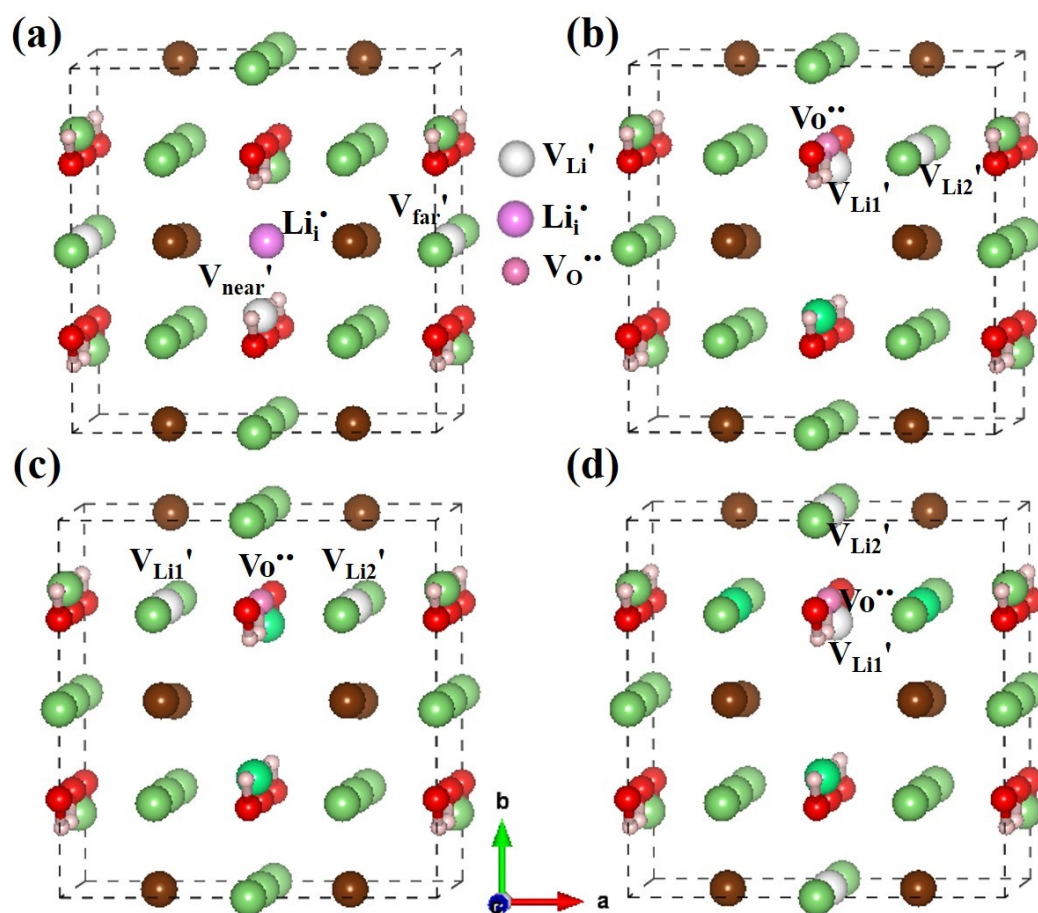


Figure S2. Possible defect configurations of the Li_2OHBr in (a) Frenkel defect pair ($V_{\text{Li}}' - \text{Li}_i'$). (b)-(d) show the adjacent, separated-1 and separated-2 Li_2O Schottky defect pair ($2V_{\text{Li}}' - V_{\text{O}}''$),