

Supporting Information

Comparison of the Polymorphs of VOPO₄ as Multi-Electron Cathodes for Rechargeable Alkali-Ion Batteries

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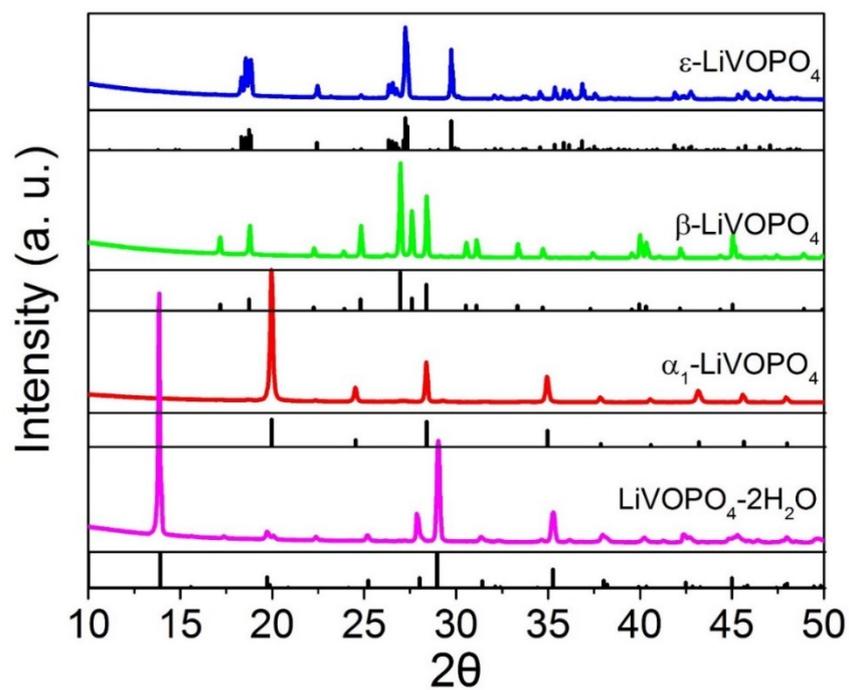


Figure S1. XRD patterns for all LiVOPO_4 polymorphs synthesized in this work.

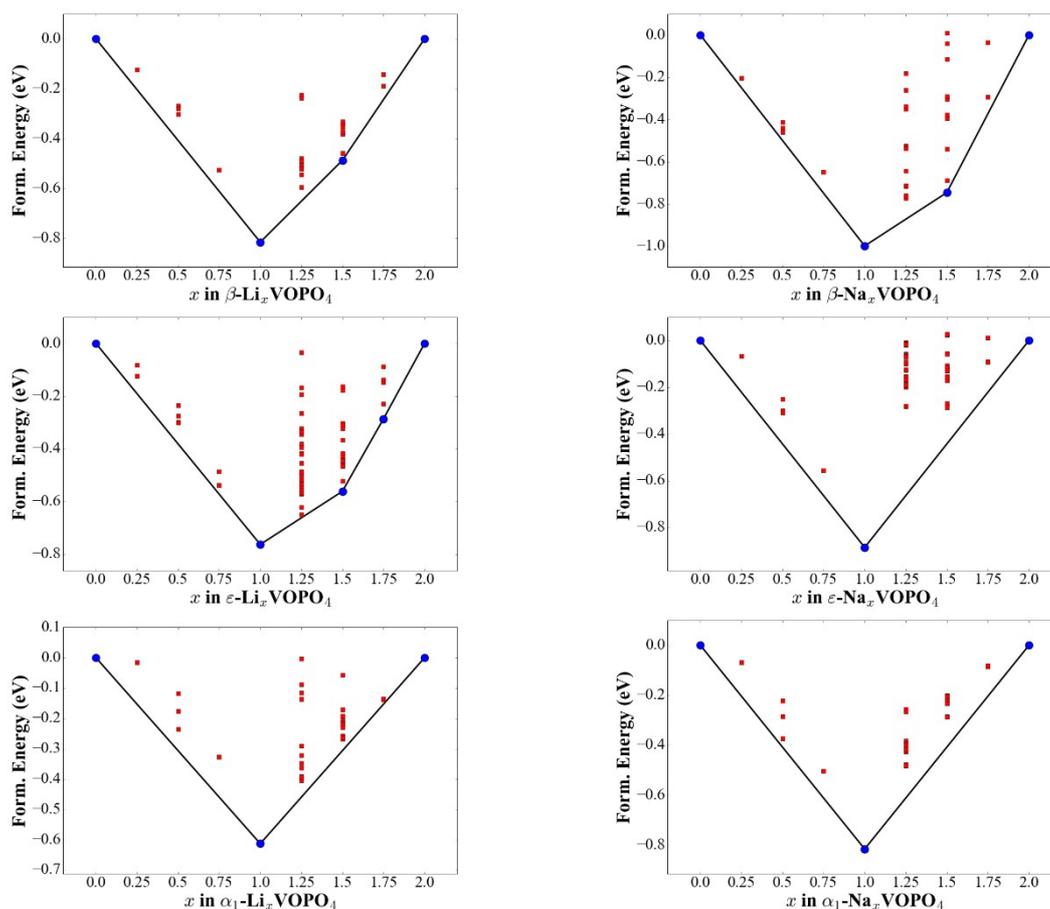


Figure S2. Pseudo-binary phase diagram for $A_x\text{VOPO}_4$ ($A=\text{Li}$ and Na) polymorphs. The red squares and blue circles denote unstable and stable structures, respectively. The black line is the convex hull.

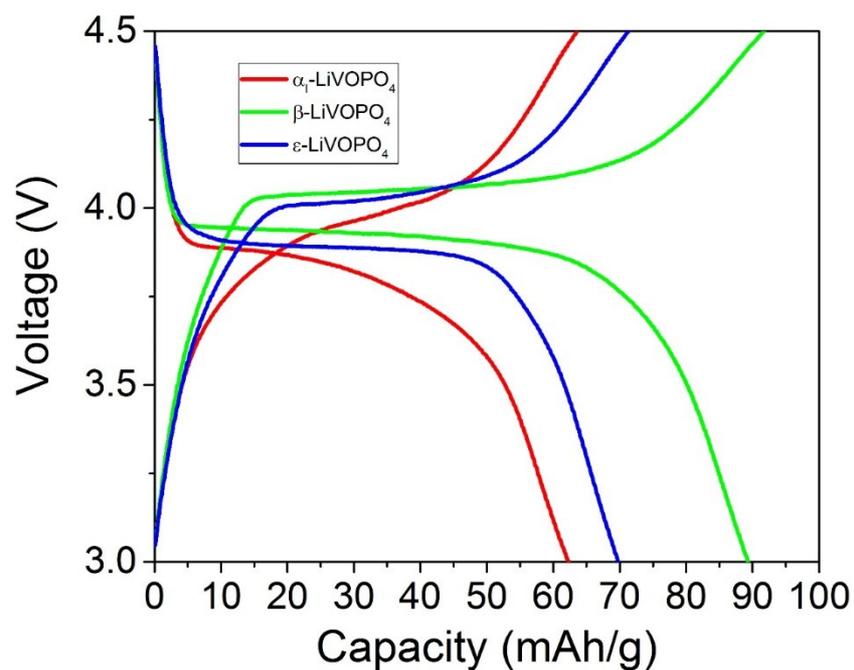


Figure S3. Galvanostatic charge-discharge curves for different LiVOPO₄ polymorphs at a charge-discharge rate of C/10.

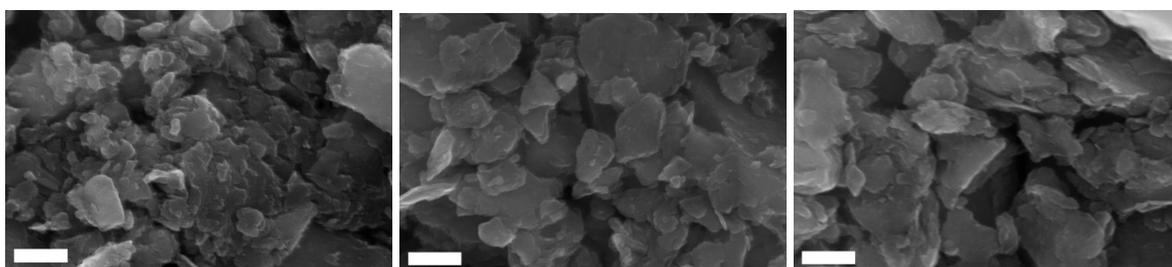


Figure S4. SEM images of (left to right) β -, ϵ -, and α_1 -LiVOPO₄ after ball-milling. Scale bars are 200 nm.

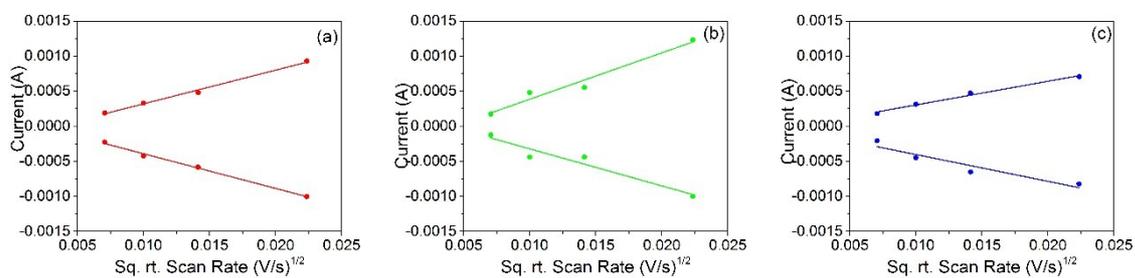
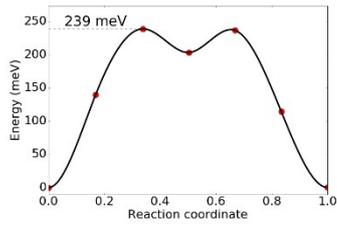
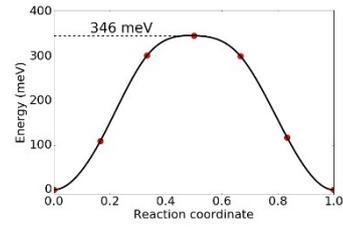


Figure S5. Current vs $v^{1/2}$ plots for the high-voltage transformation in (a) α_1 -, (b) β -, and (c) ϵ -LiVOPO₄.



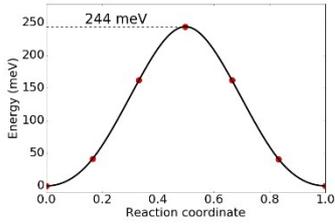


A → B

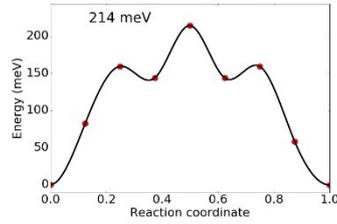


A → B

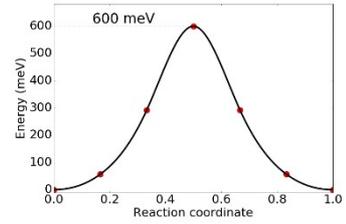
ϵ -LiVOPO₄ + v_{Li}⁺



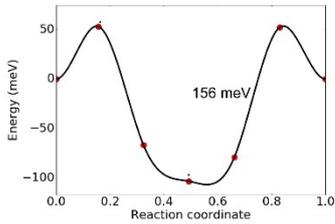
A → B



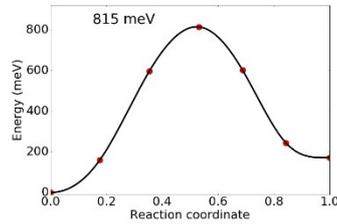
B → C



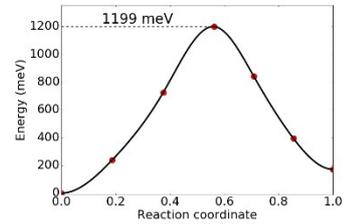
D → E



E → F

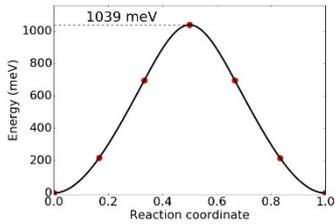


A → G

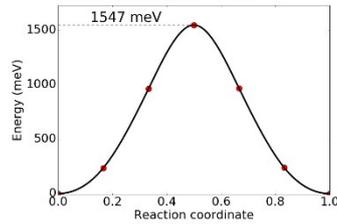


A → H

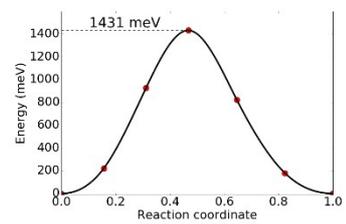
ϵ -NaVOPO₄ + v_{Na}⁺



A → B

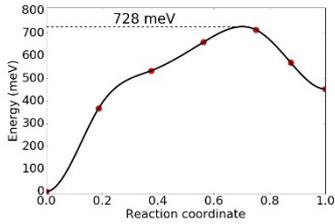


B → C

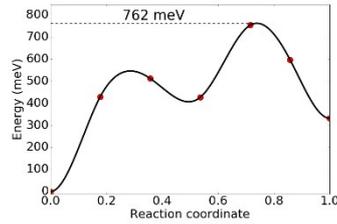


B → D

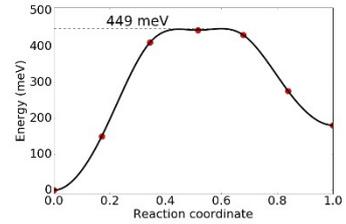
α ₁-LiVOPO₄ + v_{Li}⁺



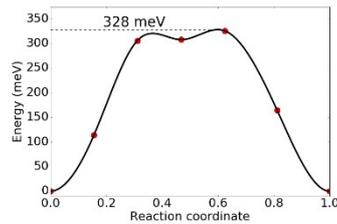
A → B



A → C

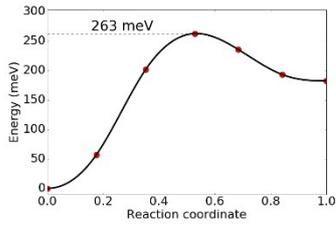


A → D

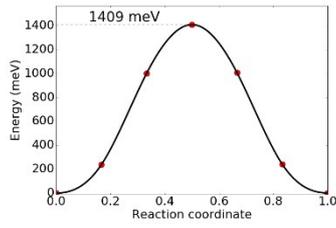


A → E

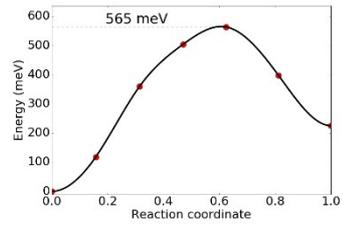
α ₁-NaVOPO₄ + v_{Na}⁺



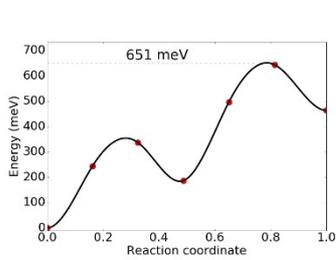
A → B



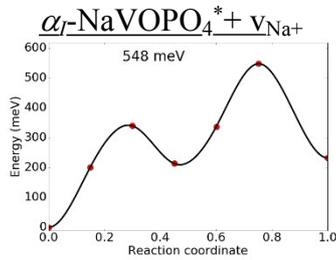
A → C



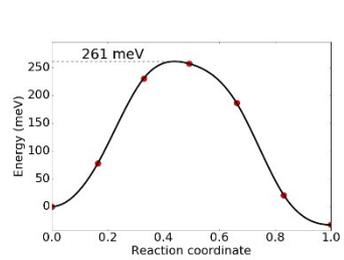
A → D



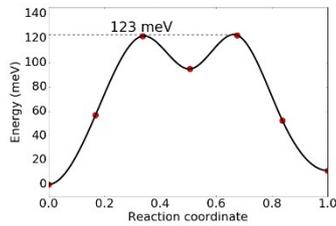
A → B



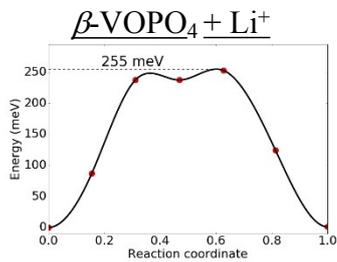
A → C



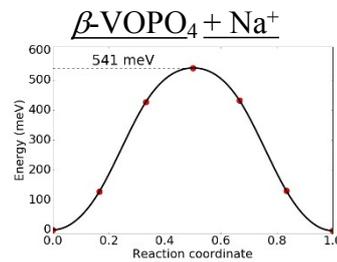
A → D



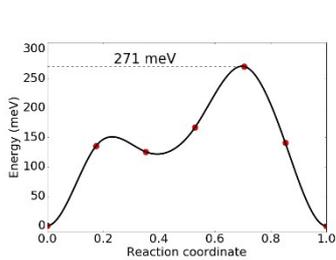
A → E



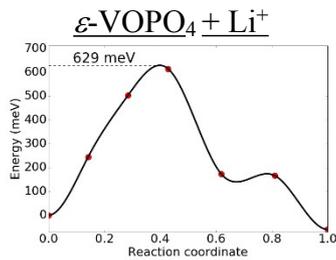
A → B



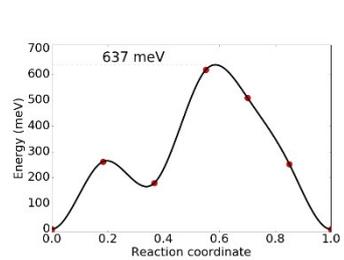
A → B



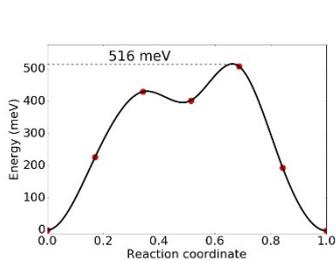
A → B



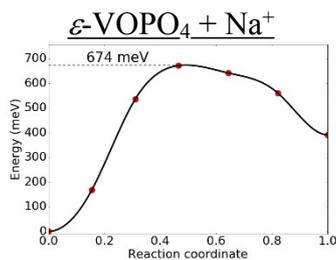
A → B



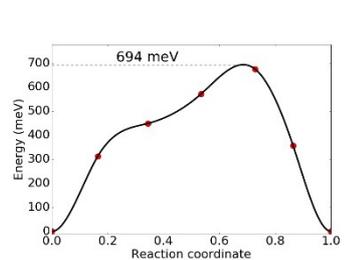
A → D



A → B



A → C



A → D

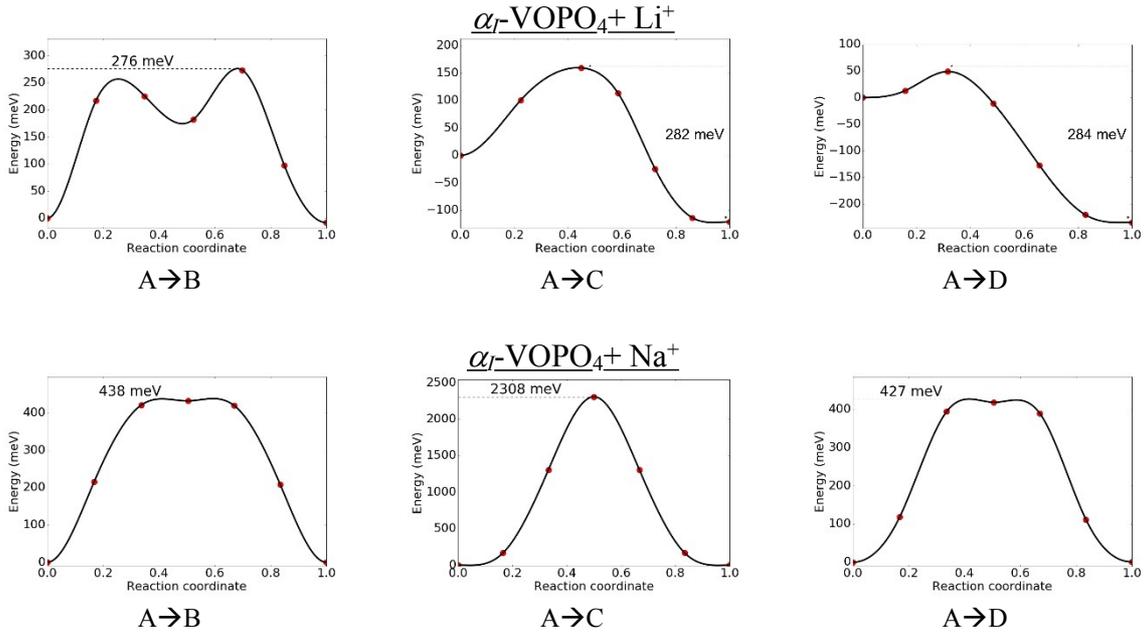
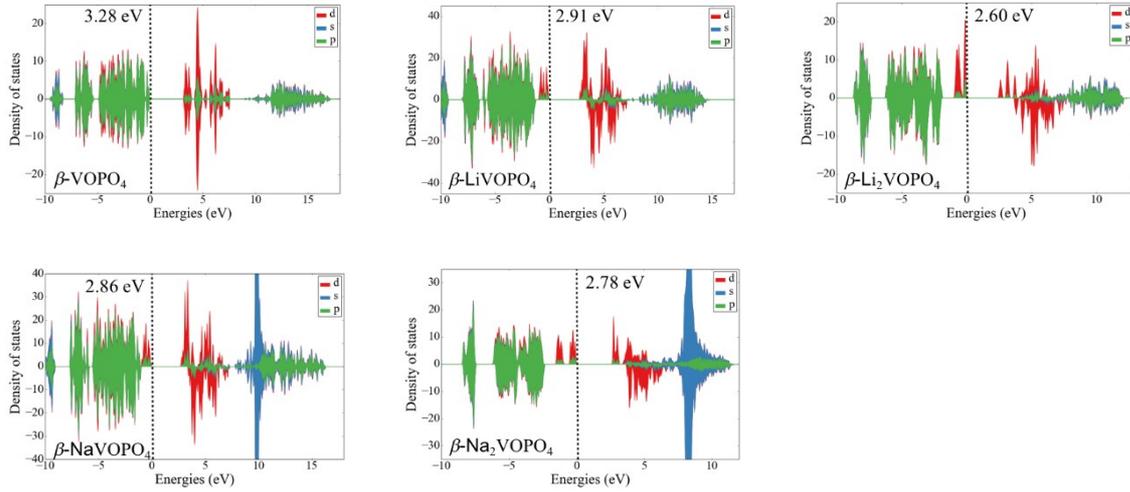


Figure S6. Calculated CI-NEB migration barriers in $A_x\text{VOPO}_4$ polymorphs ($A=\text{Li}$ and Na ; $x=0$ and 1). The labels are associated with those in Table S1.

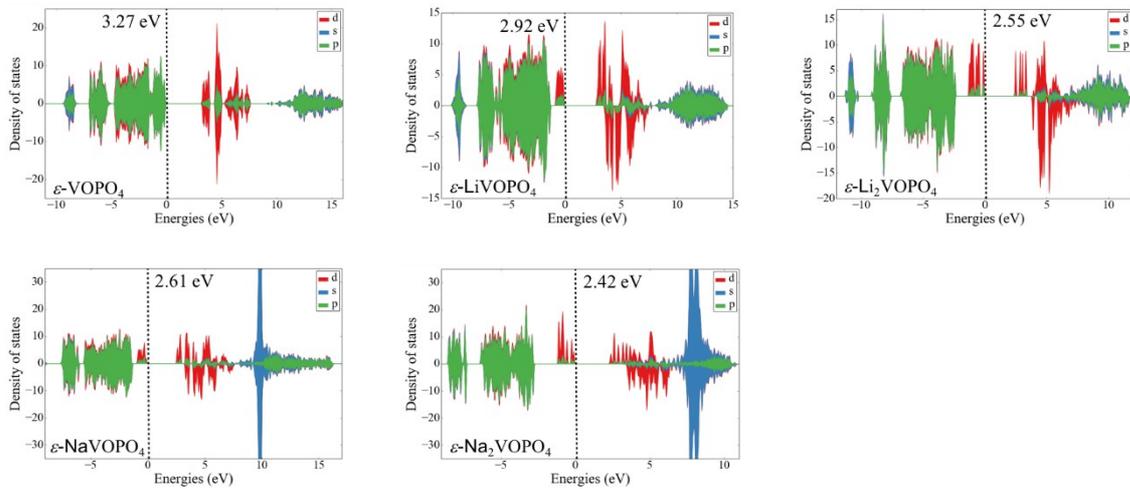
Table S1. The CI-NEB migration barriers and the associated local environment information in $A_x\text{VOPO}_4$. A^* stands for the alkali-ion in the transition state of a migration path. The minimum distances from A^* to oxygen, vanadium and phosphorus are abbreviated as Min $A^*\text{-O}$, Min $A^*\text{-V}$ and Min $A^*\text{-P}$, respectively.

$A_x\text{VOPO}_4$ ($x = 0, 1$)	Path	Barrier (meV)	Min $A^*\text{-O}$ (Å)	Min $A^*\text{-V}$ (Å)	Min $A^*\text{-P}$ (Å)
$\beta\text{-LiVOPO}_4 + v_{\text{Li}^+}$	$A \rightarrow B$	239	1.869	2.887	2.635
$\beta\text{-VOPO}_4 + \text{Li}^+$	$A \rightarrow B$	255	1.878	2.993	2.629
$\varepsilon\text{-LiVOPO}_4 + v_{\text{Li}^+}$	$A \rightarrow B$	244	1.826	2.874	3.076
	$B \rightarrow C$	214	1.998	2.571	3.239
	$D \rightarrow E$	600	1.803	2.593	3.063
	$E \rightarrow F$	156	1.876	2.968	2.883
	$A \rightarrow G$	815	1.899	2.819	2.441
	$A \rightarrow H$	1199	1.931	3.415	2.295
$\varepsilon\text{-VOPO}_4 + \text{Li}^+$	$A \rightarrow B$	271	1.853	2.870	2.703
	$A \rightarrow C$	637	1.945	2.672	2.563
	$A \rightarrow D$	629	1.803	2.619	2.226
$\alpha_T\text{-LiVOPO}_4 + v_{\text{Li}^+}$	$A \rightarrow B$	728	1.868	2.969	2.555
	$A \rightarrow C$	762	1.856	2.943	2.484
	$A \rightarrow D$	449	1.827	3.060	2.468
	$A \rightarrow E$	328	1.802	3.176	2.473
$\alpha_T\text{-VOPO}_4 + \text{Li}^+$	$A \rightarrow B$	276	1.856	3.119	2.619
	$A \rightarrow C$	282	1.856	3.105	2.623
	$A \rightarrow D$	284	1.855	3.095	2.629
$\beta\text{-NaVOPO}_4 + v_{\text{Na}^+}$	$A \rightarrow B$	346	2.111	3.211	2.699
$\beta\text{-VOPO}_4 + \text{Na}^+$	$A \rightarrow B$	541	2.131	3.117	2.683

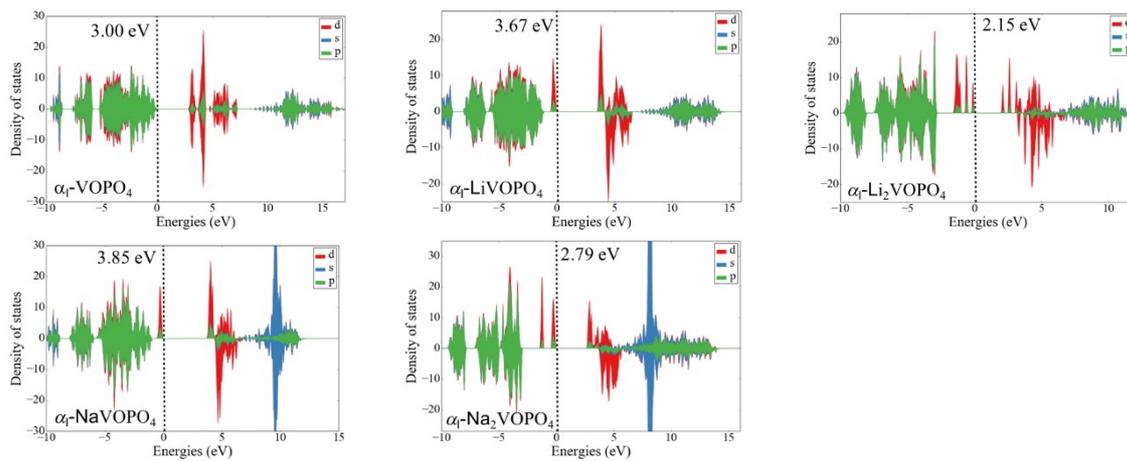
ε -NaVOPO ₄ + v _{Na+}	A→B	1039	2.013	2.938	3.156
	B→C	1547	1.999	2.720	3.140
	B→D	1431	2.056	3.314	2.512
ε -VOPO ₄ + Na ⁺	A→B	516	2.062	3.051	2.922
	A→C	674	2.155	2.981	2.648
	A→D	694	2.156	3.233	2.648
α_T -NaVOPO ₄ + v _{Na+}	A→B	263	2.166	3.523	2.988
	A→C	1409	2.045	2.560	4.023
	A→D	565	2.152	3.217	2.865
α_T -NaVOPO ₄ * + v _{Na+}	A→B	651	2.198	3.030	2.818
	A→C	548	2.195	3.004	2.762
	A→D	261	2.163	3.312	2.819
	A→E	123	3.637	2.176	2.940
α_T -VOPO ₄ + Na ⁺	A→B	438	2.176	3.754	2.744
	A→C	2308	1.889	2.257	3.886
	A→D	427	2.112	3.430	2.743



(a) β -A_xVOPO₄



(b) ε -A_xVOPO₄



(c) α_1 - A_x VOPO₄

Figure S7. Calculated hybrid HSE density of states of A_x VOPO₄ polymorphs (A=Li and Na; $x=0, 1, 2$). The computed band gaps are also labeled in the each of the sub-figures.