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Supporting Information For

Phase Stability and Its Impact on the Electrochemical Performance of $VOPO_4$ and $LiVOPO_4$

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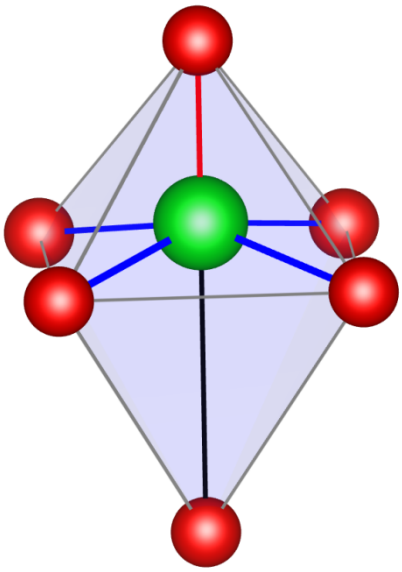

Figure S1. Schematic of typical bonding in VO_6 octahedra. Red: short V=O bond (typically ~1.55-1.75 Å); blue: V-O bond with distances typically around 1.85-1.95 Å; black: long V…O bond (typically 2.20-3.00 Å)

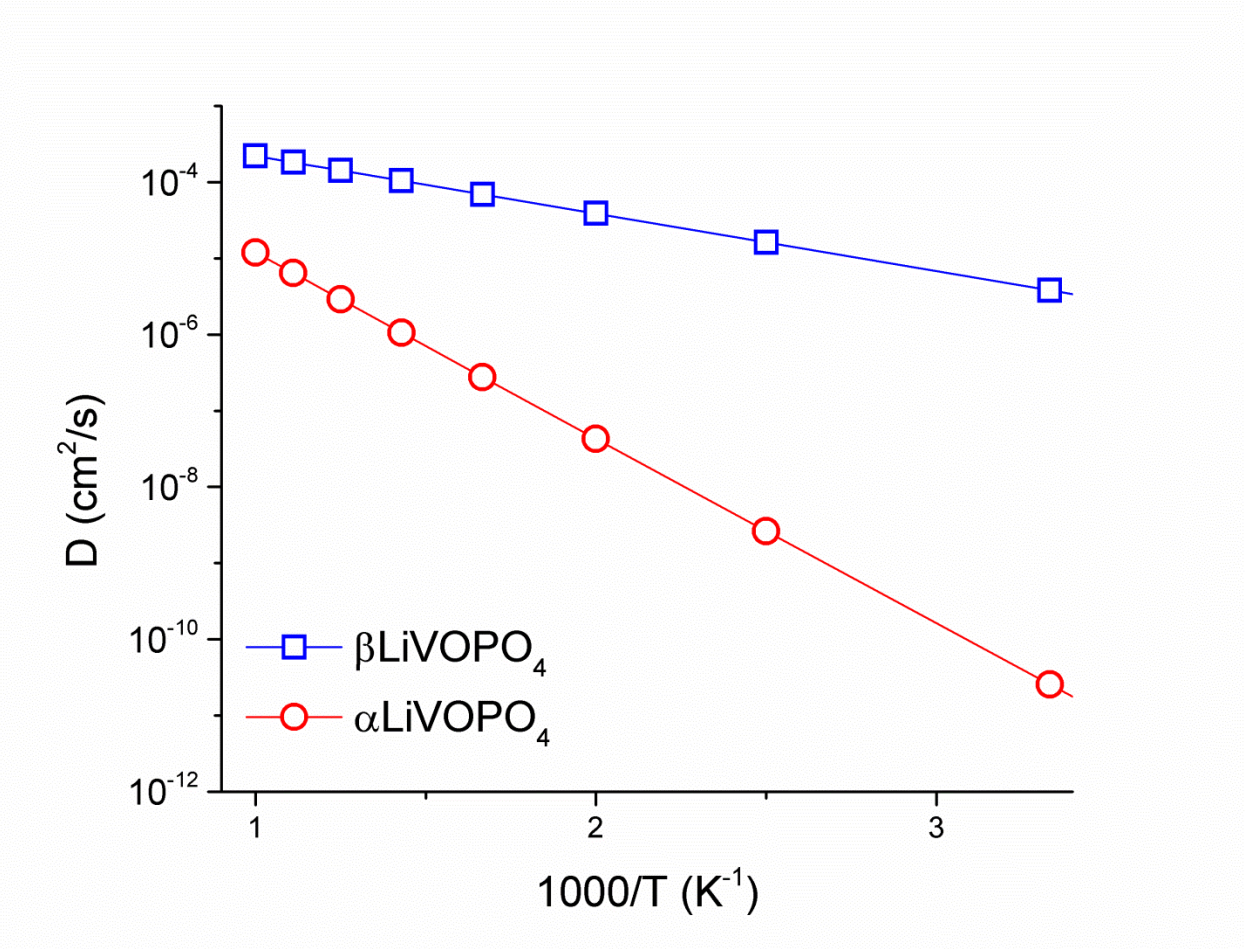

Figure S2. Calculated net Li diffusivity in $\beta LiVOPO_4$ and $\alpha LiVOPO_4$ as a function of temperature.

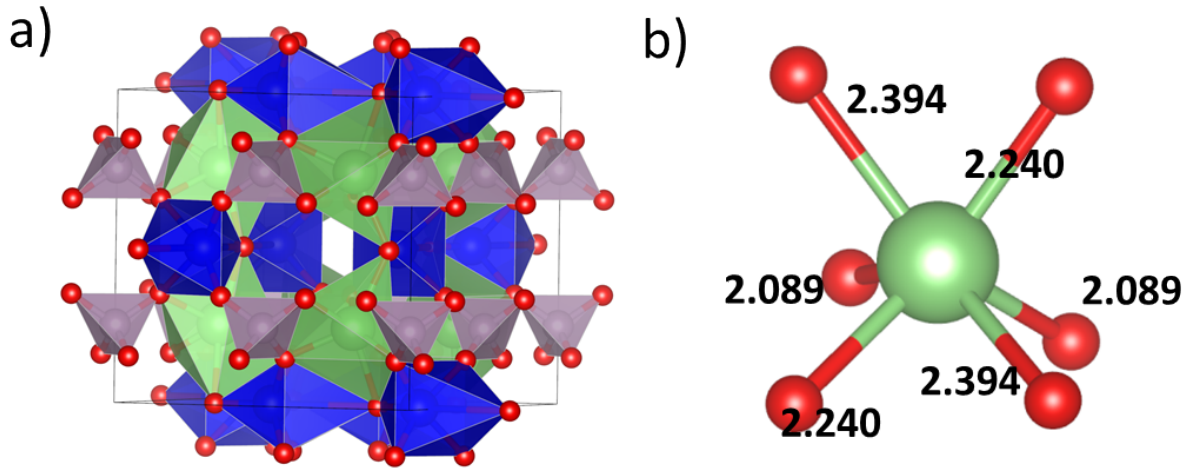

Figure S3. (a) Crystal structure of δLiVOPO$_4$. (b) Bonding environment of Li in δLiVOPO$_4$ with marked Li-O bond lengths.

Evaluate the intercalation path from $\varepsilon VOPO_4$ to $\alpha LiVOPO_4$

In order to evaluate the intercalation path from $\varepsilon VOPO_4$ to $\alpha LiVOPO_4$, we calculated the formation energy of εLi_xVOPO_4 and αLi_xVOPO_4 according to

$$E_f = E_{Li_xVOPO_4} - xE_{\alpha LiVOPO_4} - (1-x)E_{\varepsilon VOPO_4}.$$

Here $E_{Li_xVOPO_4}$, $E_{\alpha LiVOPO_4}$and $E_{\varepsilon VOPO_4}$ is the total energy of LixVOPO4, αLiVOPO4 and εVOPO4, respectively.

The values of x are chosen as x=0.03125, 0.125, 0.25 and 0.5 for εLi_xVOPO_4, and x=0.96875, 0.875, 0.75 and 0.5 for αLi_xVOPO_4

For x=0.03125(0.96875), we used 2x2x2 supercell corresponding to a formula of $(Li_{32})V_{32}O_{32}P_{32}O_{128}$. One Li atom was added or removed to give a composition $Li_1V_{32}O_{32}P_{32}O_{128}$ or $Li_{31}V_{32}O_{32}P_{32}O_{128}$ for εLi_xVOPO_4 and αLi_xVOPO_4, respectively.

For x=0.125(0.875) and 0.25(0.75), 2x1x1, 1x2x1 and 1x1x2 supercells were used, all corresponding to a formula of $(Li_8)V_8O_8P_8O_{32}$. Li atoms were added or removed to give a composition of $Li_1V_8O_8P_8O_{32}$ and $Li_2V_8O_8P_8O_{32}$ for εLi_xVOPO_4, $Li_7V_8O_8P_8O_{32}$ and $Li_6V_8O_8P_8O_{32}$ for αLi_xVOPO_4, respectively. All symmetrically distinct Li/vacancy ordering in the three supercells are included in our calculation.

For x=0.5, we and pick up several symmetrically distinct configurations in 2x1x1, 1x2x1 and 1x1x2 supercells to calculate the formation energy of $Li_4V_8O_8P_8O_{32}$. Although it is possible that more complicated long range super-structure might exist and be ignored by our searching, the calculated results still explicitly cover a large range of possible configurations and should be able to provide instructive insight about the reaction path.

Table S1. Relative energies of VOPO4 and LiVOPO4 calculated with different U values.

phase	$VOPO_4$			$LiVOPO_4$		
	U=3	U=3.5	U=4	U=3	U=3.5	U=4
α_I	123	148	136	484	381	352
α_{II}	53	48	30	974	936	884
β	0	0	0	72	87	86
ε	44	34	56	138	151	136
α	56	59	71	0	0	0
δ	50	46	46	309	320	324