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Phase Transformation, Ionic Diffusion, and Charge Transfer Mechanisms of $KVOPO_4$ in Potassium Ion Batteries: First-principles Calculations

Ruqian Lian[a], Dashuai Wang[a], Xing Ming[b], Rongyu Zhang[c], Yingjin Wei[a,*], Jianrui Feng[a], Xing Meng[a], Gang Chen[a]

[a] Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, Changchun 130012, China.

[b] College of Science, Guilin University of Technology, Guilin 541004, China.

[c] College of New Energy, Bohai University, Jinzhou 121000, China.

[*] Corresponding author

Email: yjwei@jlu.edu.cn (Y. J. Wei); Tel: 86-431-85155126

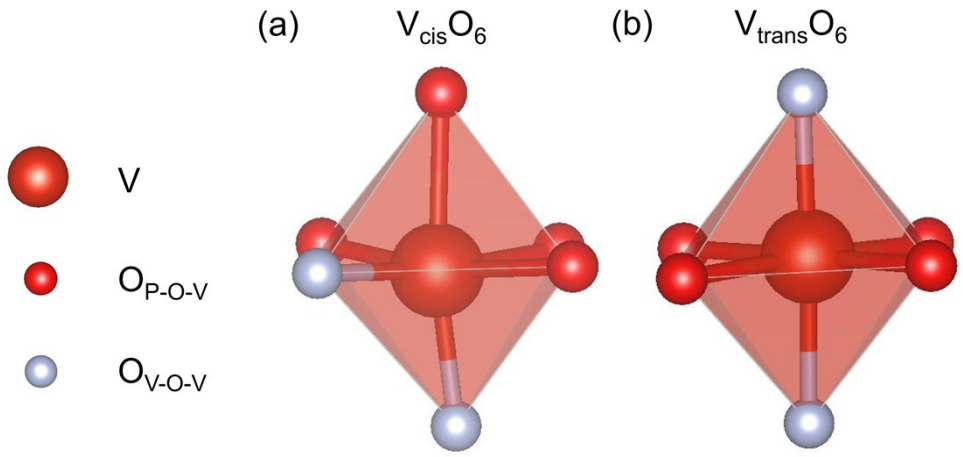

Figure S1. Schematic diagram of $V_{cis}O_6$ and $V_{trans}O_6$. $O_{P\text{-}O\text{-}V}$ is corner-shared O that connects VO_6 octahedra and PO_4 tetrahedra, $O_{V\text{-}O\text{-}V}$ is corner-shared O that connects two VO_6 octahedra.

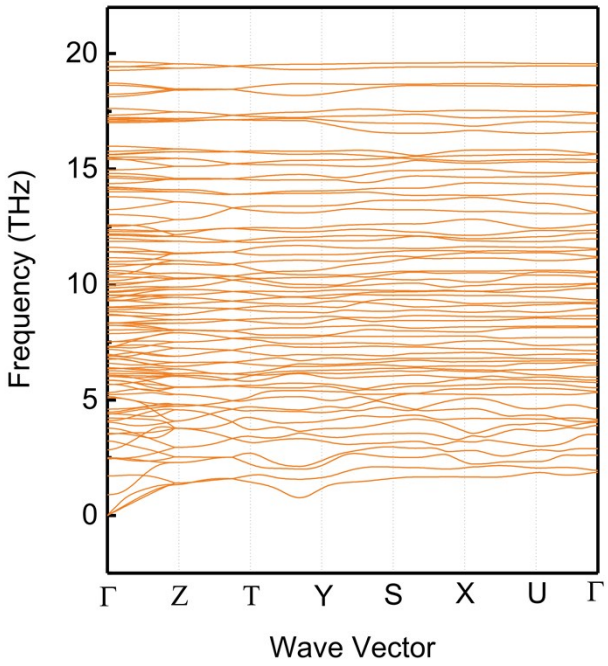

Figure S2. Calculated phonon band structures for $VOPO_4$.

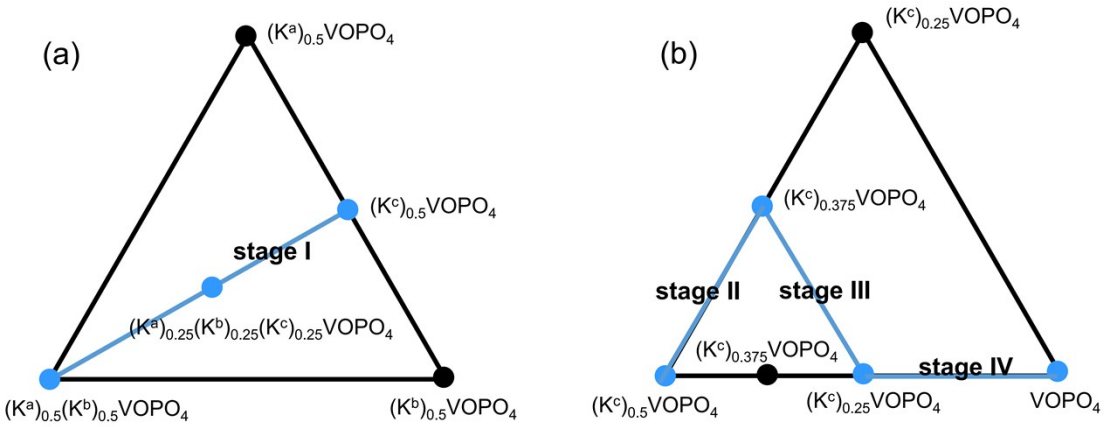

Figure. S3. Phase diagrams for (a) stage I and (b) stage II ~ IV. Blue circles represent the stable phase of K_xVOPO_4 during K extraction, and black circles represent metastable phases with relatively higher energy.

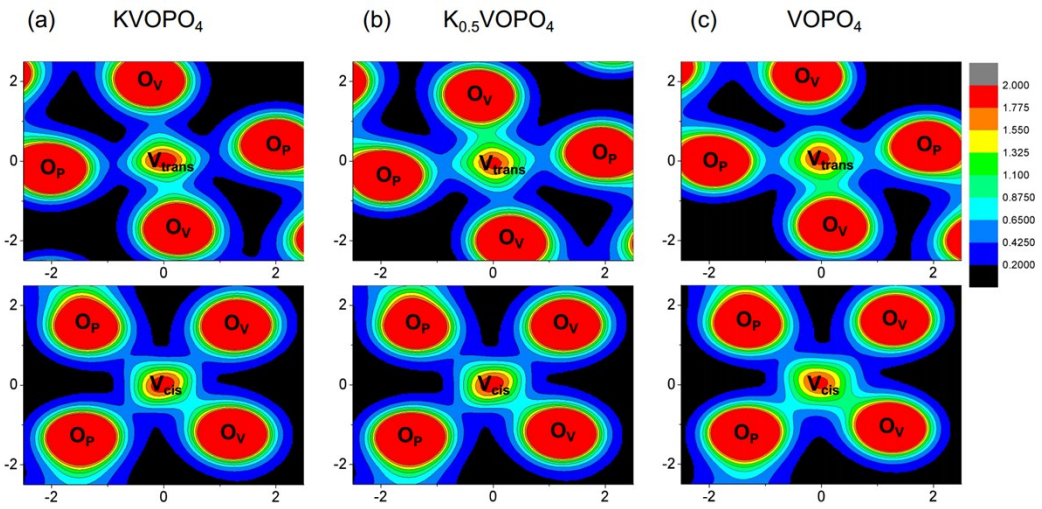

Fig. S4. Electron density distribution of V-O bonds in (a) $KVOPO_4$, (b) $K_{0.5}VOPO_4$, and (c) $VOPO_4$.

Table S1. Calculated lattice parameters and atomic positions of $KVOPO_4$

$KVOPO_4$				
a = 12.891 Å; b = 6.428 Å; c = 10.527 Å; V = 872.3 $Å^3$; $\alpha = \beta = \gamma = 90°$				
atom	Wychoff	x	y	z
O (1)	4a	0.482	0.478	0.135
O (2)	4a	0.510	0.471	0.370
O (3)	4a	0.400	0.194	0.271
O (4)	4a	0.592	0.187	0.231
O (5)	4a	0.110	0.310	0.532
O (6)	4a	0.111	0.690	0.475
O (7)	4a	0.255	0.534	0.620
O (8)	4a	0.256	0.456	0.392
O (9)	4a	0.281	0.546	0.879
O (10)	4a	0.273	0.458	0.132
K (1)	4a	0.375	0.779	0.302
K (2)	4a	0.105	0.696	0.055
P (1)	4a	0.497	0.331	0.250
P (2)	4a	0.181	0.500	0.505
V (1)	4a	0.375	0.497	0
V (2)	4a	0.247	0.267	0.244

Table S2. Energies of three $K_{1-x}VOPO_4$ ($0 \leq x \leq 1.0$) configurations, corresponding to Figure 3

Concentration	E_a (eV/f.u.)	E_b (eV/ f.u.)	E_c (eV/ f.u.)
$x = 0$		$E_{KVOPO4} = -457.46$	
$x = 0.125$	-451.92	/	-452.11
$x = 0.25$	-446.30	/	-446.73
$x = 0.375$	-441.10	/	-441.18
$x = 0.5$	-435.45	-435.31	-435.62
$x = 0.625$	-429.84	-429.57	-429.85
$x = 0.75$	-424.01	-423.70	-424.00
$x = 0.875$	-418.07	-417.98	-417.97
$x = 1$		$E_{VOPO4} = -412.24$	

Table S3. Calculated lattice parameters and atomic positions of $K_{0.5}VOPO_4$

$K_{0.5}VOPO_4$				
A = 12.667 Å; b = 6.315 Å; c = 10.467 Å; V = 837.3 $Å^3$; α = β = γ = 90°				
atom	Wychoff	x	y	z
O (1)	4a	0.488	0.487	0.136
O (2)	4a	0.510	0.466	0.376
O (3)	4a	0.398	0.194	0.263
O (4)	4a	0.594	0.188	0.230
O (5)	4a	0.114	0.325	0.528
O (6)	4a	0.114	0.709	0.471
O (7)	4a	0.264	0.562	0.607
O (8)	4a	0.256	0.474	0.377
O (9)	4a	0.282	0.559	0.869
O (10)	4a	0.277	0.471	0.120
K (1)	4a	0.403	0.842	0.442
P (1)	4a	0.497	0.338	0.253
P (2)	4a	0.185	0.516	0.496
V (1)	4a	0.375	0.518	0.010
V (2)	4a	0.245	0.250	0.251

Table S4. Lengths of the first- and second-shortest K-V and K-P bonds in $K_{0.5}VOPO_4$ and $K_{0.125}VOPO_4$

Length	$K_{0.5}VOPO_4$		$K_{0.125}VOPO_4$	
	K^b	K^c	K^b	K^c
$L_{K\text{-}V}$ (Å)	3.660	3.715	3.607	3.603
	3.757	3.775	3.722	3.629
$L_{K\text{-}P}$ (Å)	3.500	3.505	3.446	3.479
	3.630	3.691	3.623	3.597