Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Phase Transformation, Charge Transfer, and Ionic Diffusion of $Na_4MnV(PO_4)_3$ in Sodium-Ion Batteries: A Combined First-principles and Experimental Study

Xinying Gao[a], Ruqian Lian[a], Li He[a], Qiang Fu[b,*], Sylvio Indris[b], Björn Schwarz[b], Xudong Wang[c], Gang Chen[a], Helmut Ehrenberg[b], Yingjin Wei[a,*]

[a] Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, 2699 Qianjin Street, Changchun 130012, P. R. China.

[b] Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany.

[c] Department of Materials Science and Engineering, University of Wisconsin at Madison, 1509 University Avenue, Madison, WI 53706, USA.

Corresponding authors: yjwei@jlu.edu.cn (Y.J. Wei); qiang.fu@kit.edu (Q. Fu)

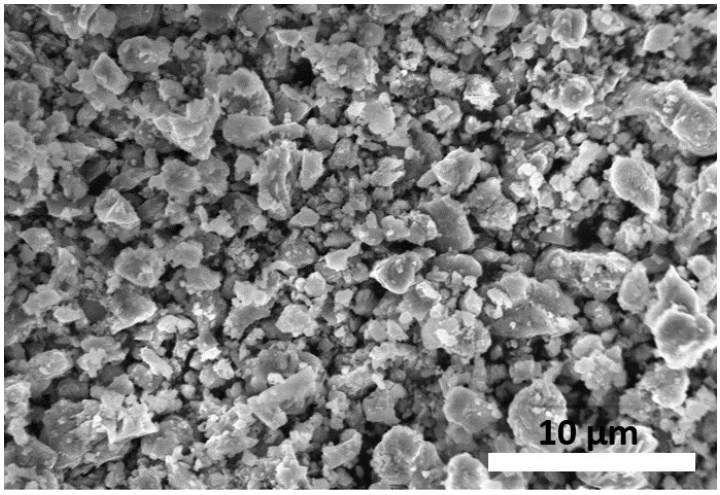

Fig. S1. SEM image of the $Na_4MnV(PO_4)_3$ material.

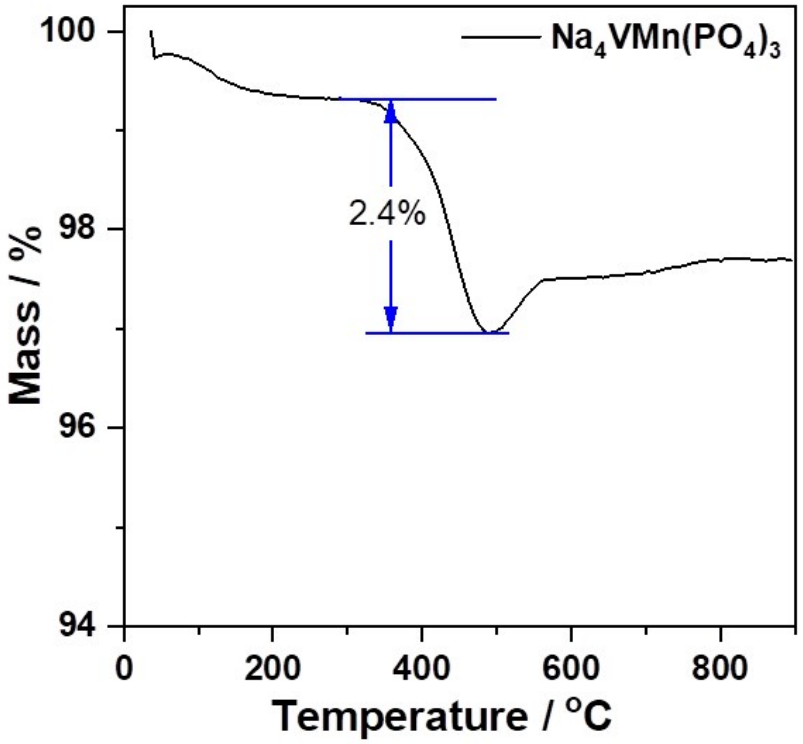

Fig. S2. TG curve of the $Na_4MnV(PO_4)_3$ material heated in O_2.

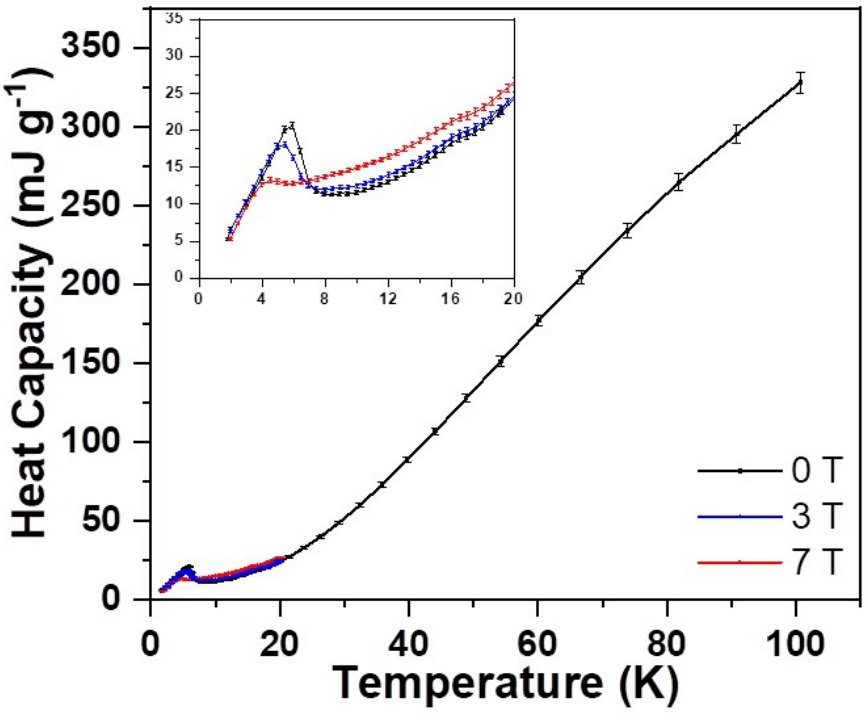

Fig. S3. Heat capacity curve of the $Na_4MnV(PO_4)_3$ material.

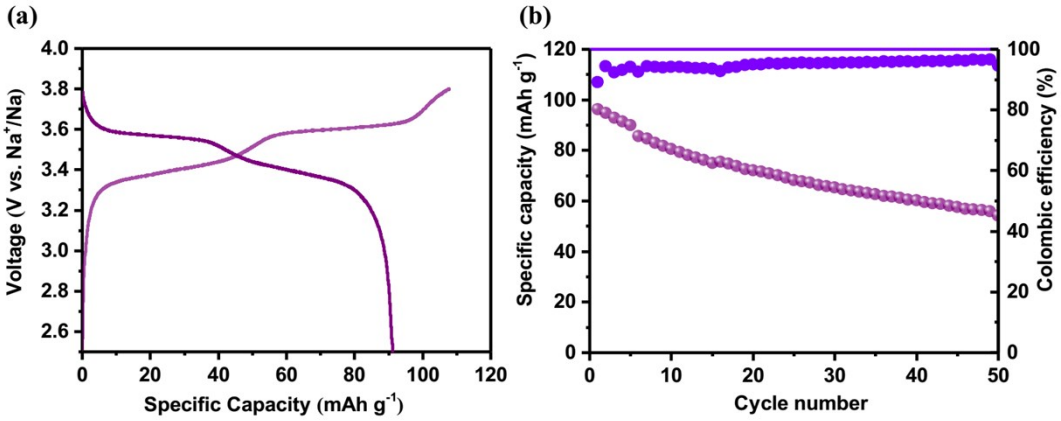

Fig. S4. The charge-discharge profiles and cycling performance of $Na_4MnV(PO_4)_3$ at the current density of 3 $mA \cdot g^{-1}$ (a-b, respectively).

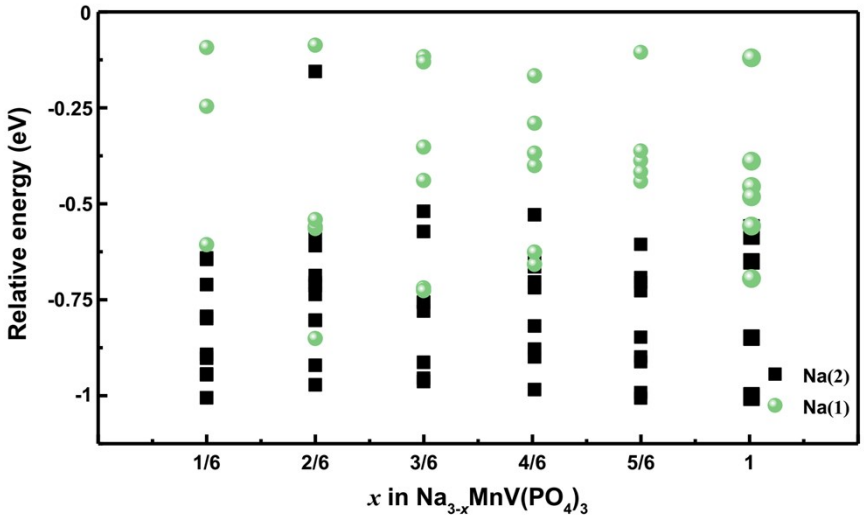

Fig. S5. Calculated relative energies of $Na_{3-x}MnV(PO_4)_3$ in different structural forms: $Na(1)Na(2)_{2-x}MnV(PO_4)_3$ (black) and $Na(1)_{1-x}Na(2)_2MnV(PO_4)_3$ (green).

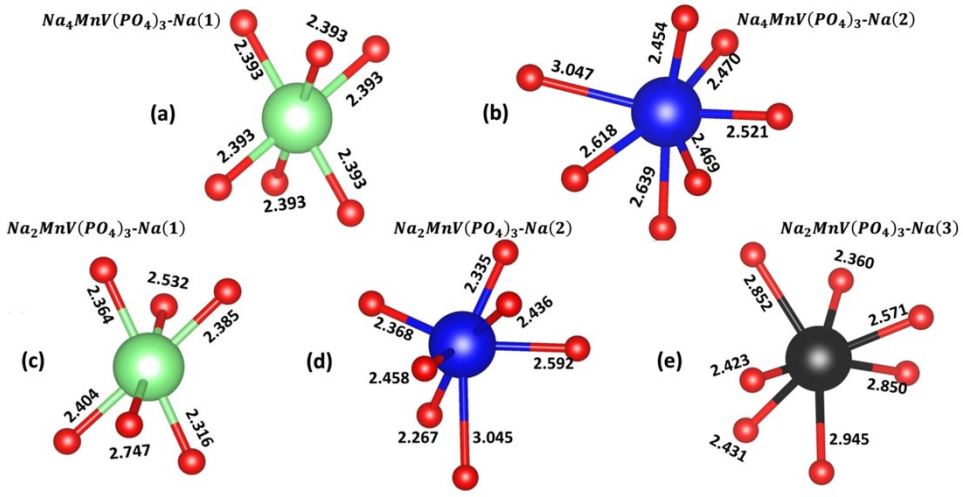

Fig. S6. Bond lengths of Na–O. Na(1) and Na(2) in $Na_4MnV(PO_4)_3$ (a-b, respectively). Na(1), Na(2), and Na(3) in $Na_2MnV(PO_4)_3$ (c–e, respectively).

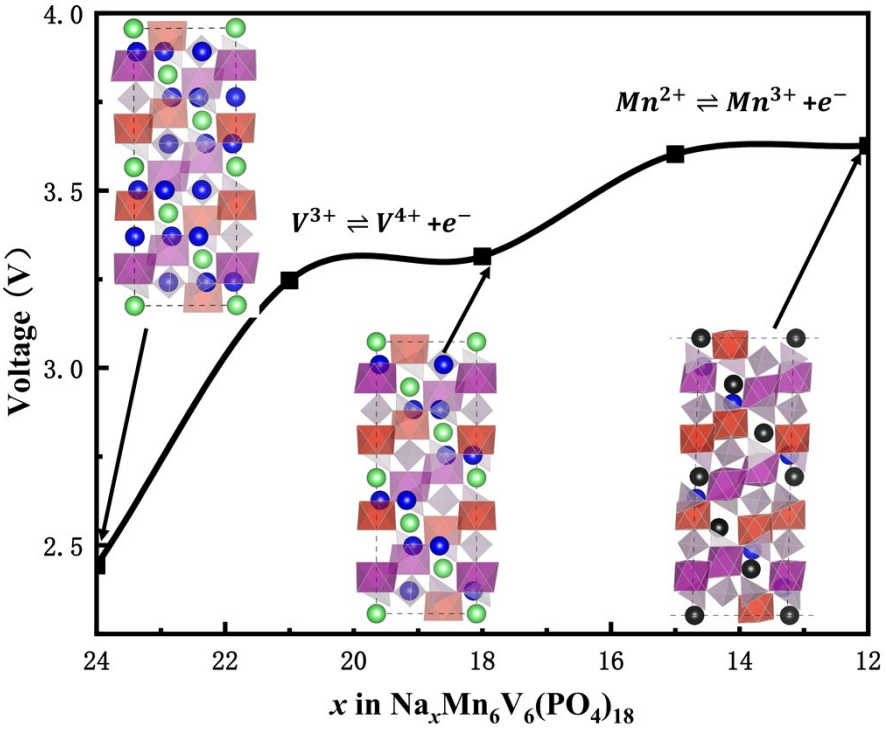

Fig. S7. Calculated voltage profile of $Na_4MnV(PO_4)_3$.

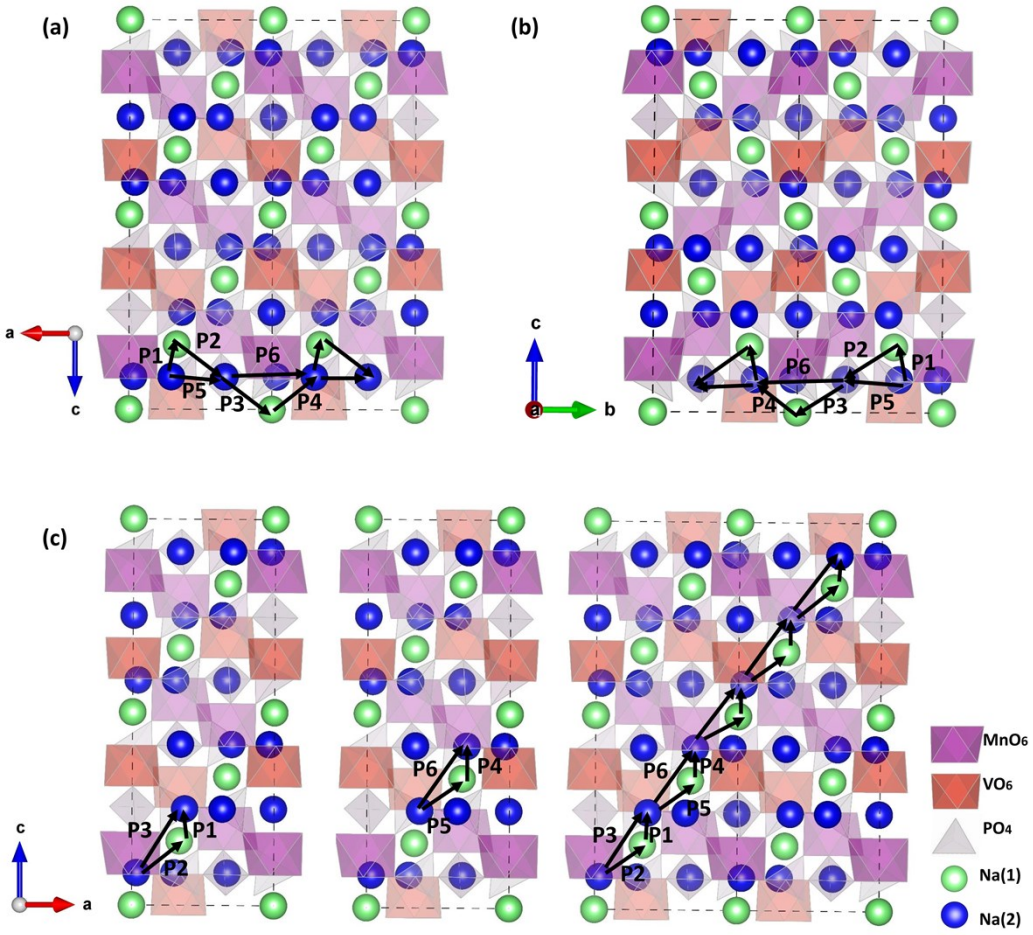

Fig. S8. Possible migration pathways for Na^+ in $Na_4MnV(PO_4)_3$ viewed from the [100], and [010] directions (a–b, respectively). (c) Schematic representation of possible Na^+ migration pathways in the $Na_4MnV(PO_4)_3$ framework from the view of [001] planes and spiral 1D diffusion pathway along the c-axis.

Table S1. Structural parameters of the $Na_4MnV(PO_4)_3$ material based on the Rietveld refinement results.

Space group: *R*-3*c*		Z=6			
a=8.9398(2) Å; *c*= 21.5317(7) Å;		*V*=1490.26(7) Å^3			
Atom	Wyckoff site	*X*	*Y*	*Z*	Occupancy
O(1)	36f	0.1918(6)	-0.0193(6)	0.1933(2)	1
O(2)	36f	0.1881(5)	0.1761(5)	0.0848(2)	1
Mn	12c	0	0	0.1498(1)	0.5
V	12c	0	0	0.1498(1)	0.5
P	18e	0.2988(3)	0	0.25	1
Na(1)	6b	0	0	0	1
Na(2)	18e	0.6414(4)	0	0.25	0.98(1)

Table S2. Calculated relative energies of the $Na(1)Na(2)_{3-x}MnV(PO_4)_3$ and $Na(1)_{1-x}Na(2)_3MnV(PO_4)_3$ structures.

Concentration	$Na(1)_{1-x}Na(2)_3MnV(PO_4)_3$ (eV/f.u.)	$Na(1)Na(2)_{3-x}MnV(PO_4)_3$ (eV/f.u.)
x = 0	-844.46	-845.12
x = 0.5	-833.35	-834.91
x = 1.0	-820.62	-821.32

Table S3. Na^+ migration energy barriers of $Na_4MnV(PO_4)_3$ along the [100] direction.

	Diffusion direction	Activation energy (eV)
P1	Na(1) ↔ Na(2)	0.380
P2	Na(1) ↔ Na(2)	0.300
P3	Na(1) ↔ Na(2)	0.390
P4	Na(1) ↔ Na(2)	0.390
P5	Na(1) ↔ Na(2)	1.320
P6	Na(1) ↔ Na(2)	1.174

Table S4. Na^+ migration energy barriers of $Na_4MnV(PO_4)_3$ along the [010] direction.

	Diffusion direction	Activation energy (eV)
P1	Na(1) ↔ Na(2)	0.380
P2	Na(1) ↔ Na(2)	0.356
P3	Na(1) ↔ Na(2)	0.389
P4	Na(1) ↔ Na(2)	0.389
P5	Na(1) ↔ Na(2)	1.305
P6	Na(1) ↔ Na(2)	1.124

Table S5. Na^+ migration energy barriers of $Na_4MnV(PO_4)_3$ along the [001] direction.

	Diffusion direction	Activation energy (eV)
P1	Na(1) ↔ Na(2)	0.317
P2	Na(1) ↔ Na(2)	0.328
P3	Na(1) ↔ Na(2)	1.343
P4	Na(1) ↔ Na(2)	0.380
P5	Na(1) ↔ Na(2)	1.373
P6	Na(1) ↔ Na(2)	1.074