Supporting Information

New 4V-class and zero-strain cathode material for Na ion batteries

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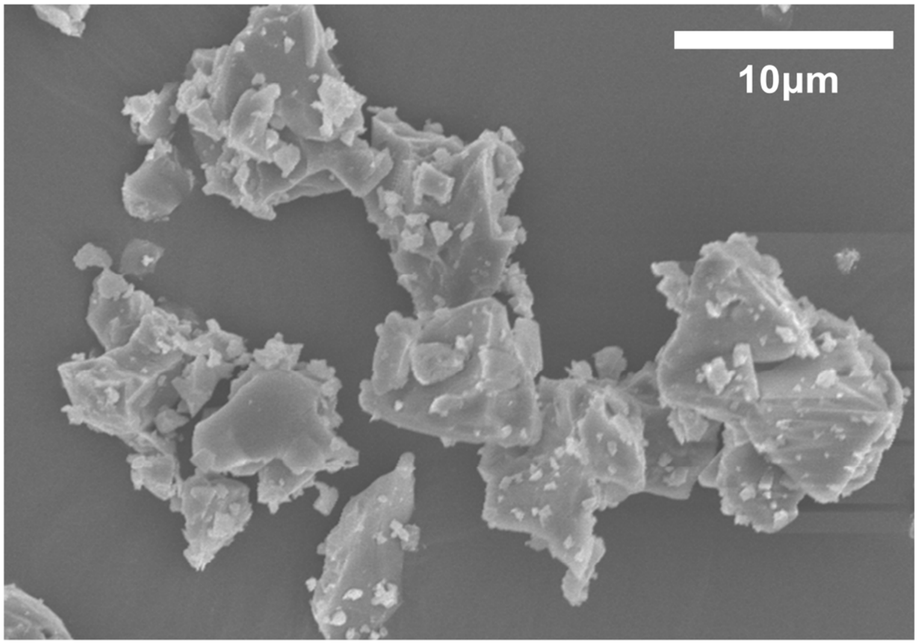
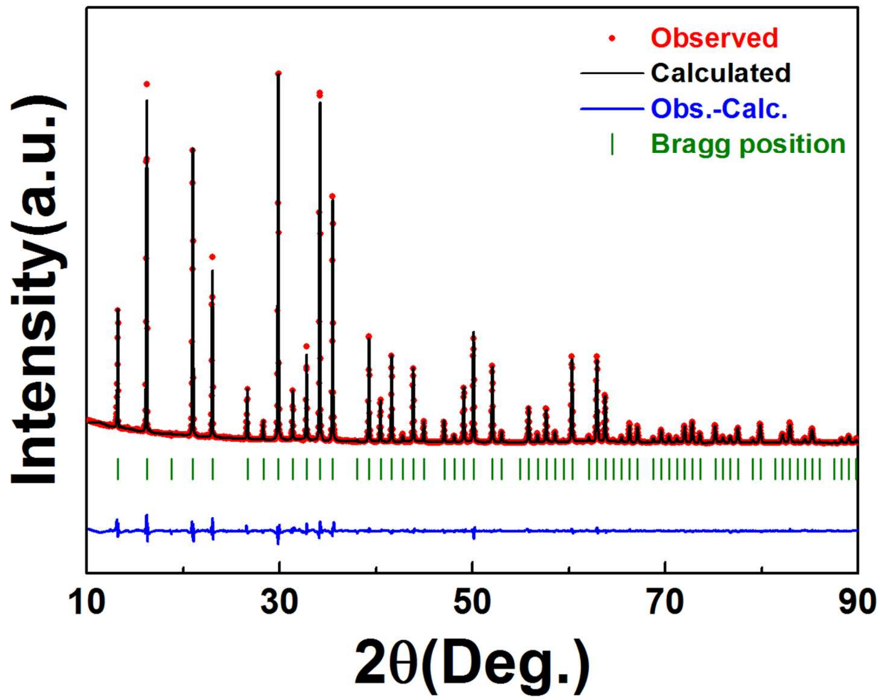
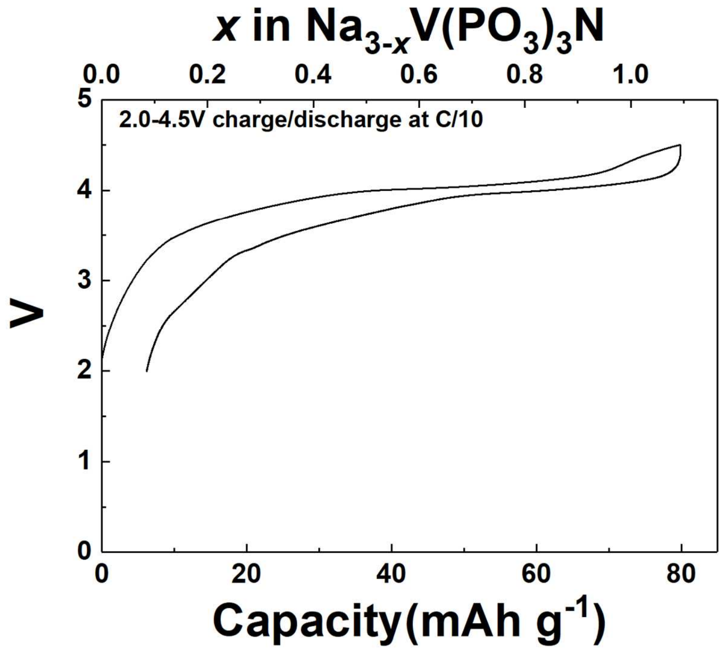


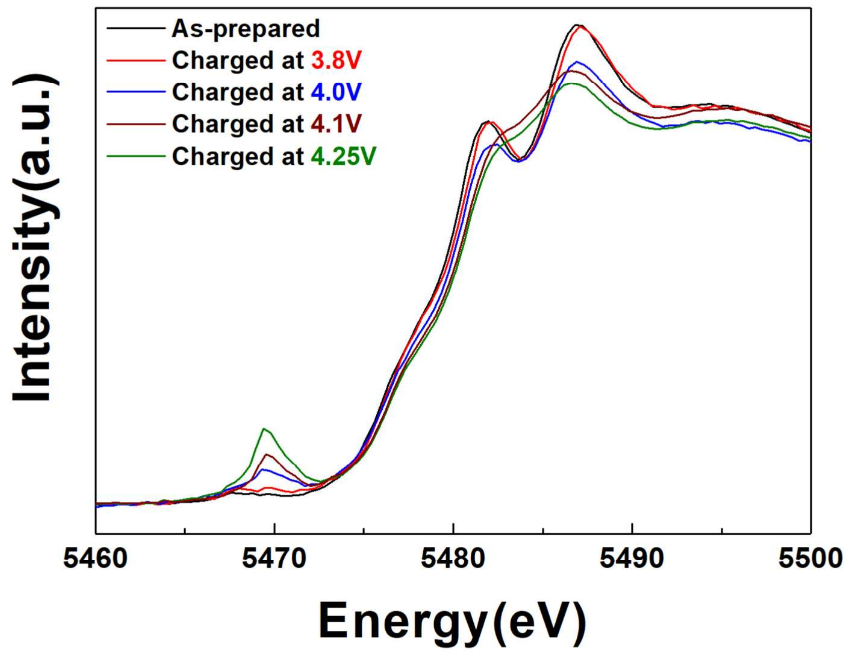
Supporting Figure S1 SEM image of $Na_3V(PO_3)_3N$.



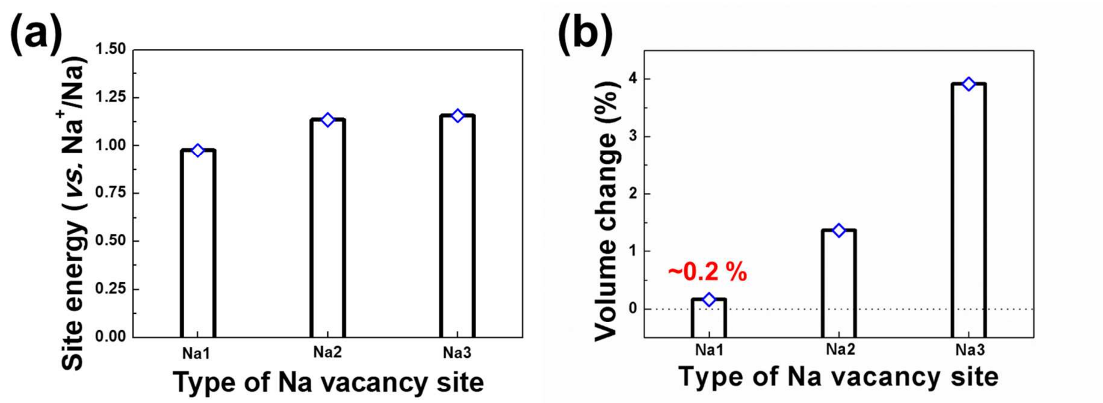
Supporting Figure S2 Refined XRD pattern of $Na_3V(PO_3)_3N$ (R_p = 7.52%, R_I = 8.53%, R_F = 7.39%, χ^2 = 8.78%).



Supporting Figure S3 Charge/discharge curve of $Na_3V(PO_3)_3N$ from 2.0-4.5V at C/10



Supporting Figure S4 *Ex-situ* XANES spectra of $Na_{3-x}V(PO_3)_3N$ samples with various Na amounts in the structure



Supporting Figure S5 (a) Site energy of a single Na vacancy from $Na_3V(PO_3)_3N$ plotted as a type of Na site. (b) Volume change of the $Na_3V(PO_3)_3N$ structure upon the removal of all Na ions in each Na site.

Atom	Multiplicity	x	y	z	B_{iso}	Occupancy
P1	12	0.3327(5)	0.0826(4)	0.2444(5)	0.95(6)	1
V1	4	0.0798(3)	-0.0798(3)	0.4202(3)	0.2(13)	1
Na1	4	0.0094(6)	0.0094(6)	0.0094(6)	1.56(10)	0.989(7)
Na2	4	0.3901(8)	0.3901(8)	0.3901(8)	1.56(10)	0.997(3)
Na3	4	0.7022(7)	0.2022(7)	0.2978(7)	1.56(10)	0.998(2)
O1	12	0.2693(4)	-0.0261(4)	0.3488(4)	1.03(5)	1
O2	12	0.3711(4)	0.0009(4)	0.1112(4)	0.92(4)	1
O3	12	0.4506(3)	0.1671(4)	0.3065(4)	1.19(5)	1
N1	4	0.1956(3)	0.1956(3)	0.1956(3)	0.88(5)	1

a = 9.44905(7) Å

Supporting Table T1 Atomic information of $Na_3V(PO_3)_3N$.

	$Na_3V(PO_3)_3N$	$Na_2V(PO_3)_3N$
Na1-O_6 (Å)	2.60 (3), 2.52 (3)	2.80 (3), 2.58 (3)
V-O_6 (Å)	2.04 (6)	1.96 (6)

Supporting Table T2 Na1-O and V-O Bond lengths of $Na_3V(PO_3)_3N$ and $Na_2V(PO_3)_3N$.

	$Na_3V(PO_3)_3N$ (x, y, z) (Å)	$Na_2V(PO_3)_3N$ (x, y, z) (Å)	Displacement (x, y, z) (Å)
V1	(0.761, 8.832, 4.035)	(0.796, 8.802, 4.003)	(0.035, -0.030, -0.032)
V2	(4.035, 0.761, 8.832)	(4.003, 0.796, 8.802)	(-0.032, 0.035, -0.030)
V3	(8.832, 4.035, 0.761)	(8.802, 4.003, 0.796)	(-0.030, -0.032, 0.035)
V4	(5.557, 5.557, 5.557)	(5.594, 5.594, 5.594)	(0.038, 0.038, 0.038)

Supporting Table T3 Cartesian coordinates of four V ions in the unit cell of $Na_3V(PO_3)_3N$ and $Na_2V(PO_3)_3N$. The displacements vectors of V ions upon desodiation is also tabulated. Due to the symmetry of $Na_3V(PO_3)_3N$ and desodiated $Na_2V(PO_3)_3N$, the direction of V ion movement cancels out each other, resulting in the negligible vector sum of net V ion displacements.