Supporting Information

An α-$CrPO_4$-type $NaV_3(PO_4)_3$ anode for sodium-ion batteries with excellent cycling stability and the exploration of sodium storage behavior

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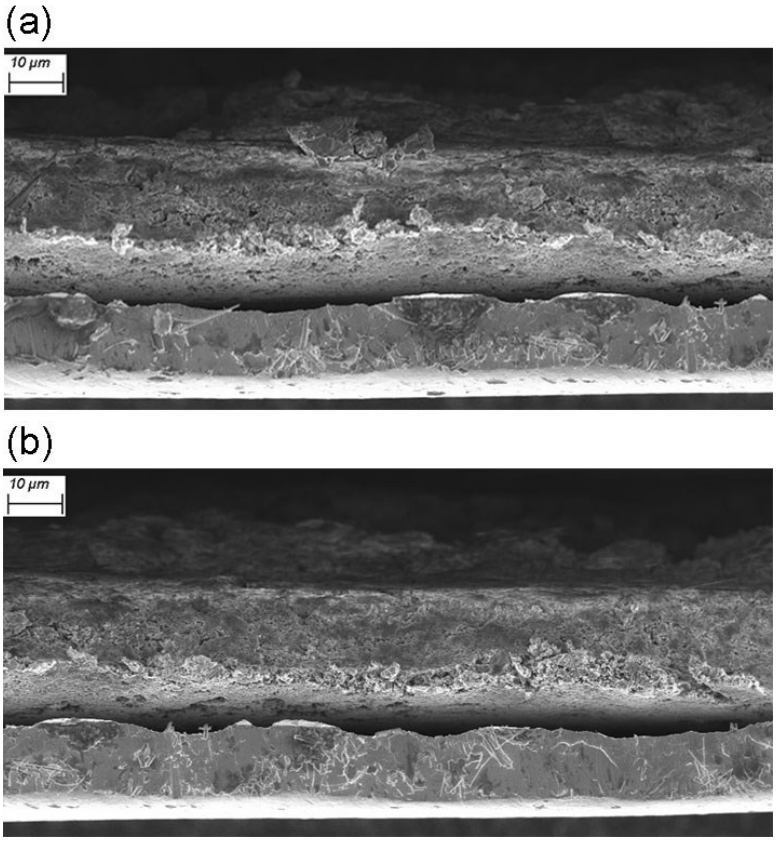

Figure S1. Cross-section SEM image of the $NaV_3(PO_4)_3$ anode before (a) and after (b) sodiation.

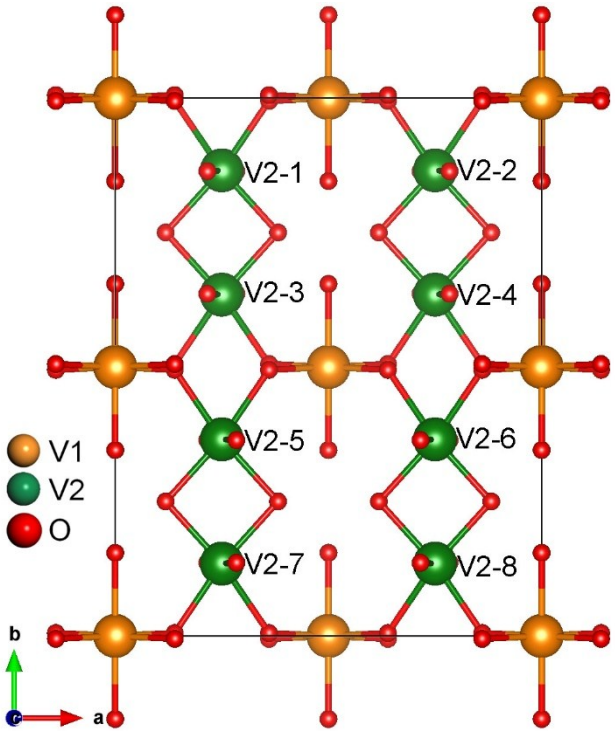

Figure S2. The distribution of V in $NaV_3(PO_4)_3$ project on (001) and the corresponding magnetization moment are shown in Table S1.

Table S1 Eight kinds of initial and calculated magnetic moment distributions for different valence states of V2 (8g sites) in $NaV_3(PO_4)_3$. The magnetization moment of V1 (4a sites, V^{3+}) is listed as a reference and the calculations are performed in the unit cell. The energy for the non-magnetic structure is -530.575 eV. (U-J=4.2 eV)

Mag.	V1	V2-1	V2-2	V2-3	V2-4	V2-5	V2-6	V2-7	V2-8	Energy (eV)
1-Initial	2	3	2	2	3	3	2	2	3	
1-Calc.	2.032	2.866	2.025	2.025	2.866	2.866	2.025	2.025	2.866	-557.210
2-Initial	2	2	3	3	2	2	3	3	2	
2-Calc.	2.032	2.025	2.865	2.865	2.025	2.025	2.865	2.865	2.025	-557.209
3-Initial	2	2	2	3	3	3	3	2	2	
3-Calc.	2.037	2.470	2.468	2.478	2.476	2.476	2.478	2.468	2.470	-556.466
4-Initial	2	3	3	2	2	2	2	3	3	
4-Calc.	2.037	2.469	2.468	2.479	2.477	2.477	2.479	2.468	2.469	-556.466
5-Initial	2	2	2	3	3	2	2	3	3	
5-Calc.	2.035	2.867	2.866	2.022	2.022	2.866	2.867	2.022	2.022	-557.241
6-Initial	2	3	3	2	2	3	3	2	2	
6-Calc.	2.035	2.867	2.866	2.022	2.022	2.866	2.867	2.022	2.022	-557.329
7-Initial	2	2	3	3	2	3	2	2	3	
7-Calc.	2.037	2.508	2.438	2.440	2.506	2.438	2.508	2.506	2.440	-556.467
8-Initial	2	3	2	2	3	2	3	3	2	
8-Calc.	2.037	2.460	2.486	2.488	2.459	2.486	2.460	2.459	2.488	-556.466

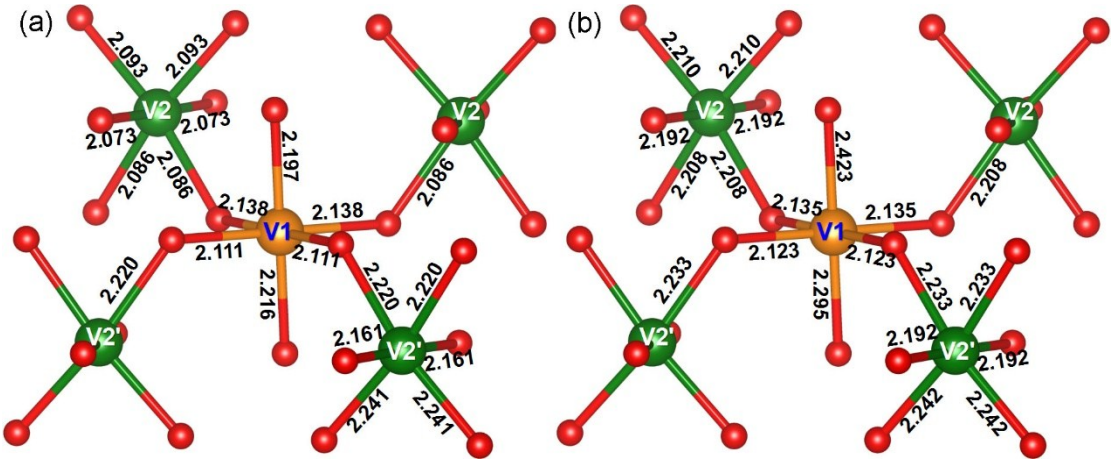

Figure S3. Local distribution and atomic positions around different V in (a) $Na_2V_3(PO_4)_3$ and (b) $Na_3V_3(PO_4)_3$ obtained from GGA+U calculations.

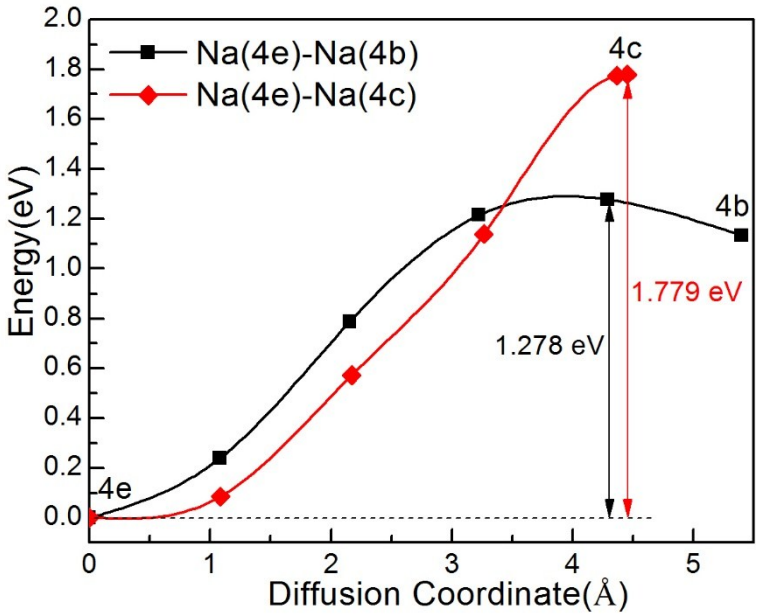

Figure S4. The energy barriers for two Na^+ in one channel diffusion from 4e sites to 4b (or 4c) sites in $NaV_3(PO_4)_3$ at the same time.

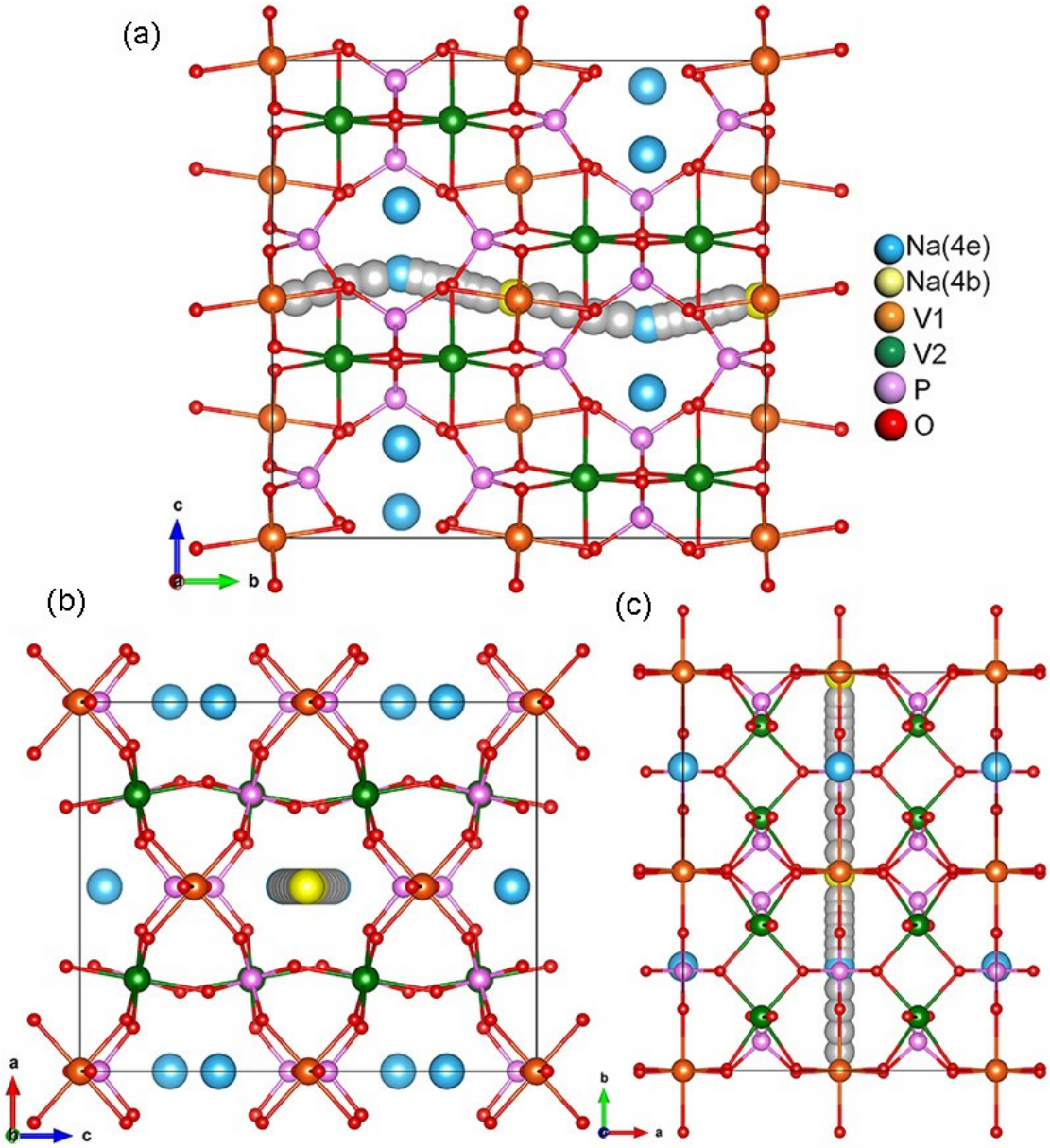

Figure S5. The Na transport trajectory in $Na_{1.125}V_3(PO_4)_3$ are along the channel in b-axis direction.

Table S2 The structural parameters of $Na_xV_3(PO_4)_3$ (x = 1, 2, 3).

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)	
$NaV_3(PO_4)_3$	10.4882	13.2133	6.4551	90	90	90	894.52	Expt.
$NaV_3(PO_4)_3$	10.6519	13.5714	6.5742	90	90	90	950.37	Calc.
$Na_2V_3(PO_4)_3$	10.8639	13.7996	6.6141	90	90	90	991.58	Calc.
$Na_3V_3(PO_4)_3$	10.9273	14.4675	6.6987	90	90	90	1059.0	Calc.

Table S3 The calculated sodium atom of $Na_xV_3(PO_4)_3$ (x = 1, 2, 3) and the corresponding Wyckoff sites (4e, 4b and 4c) coordinates. (*i.e.* the deviation of the sodium atom positions with respect to the Wyckoff sites)

	Na1 (4e)	Na2 (4b)	Na3 (4c)	
	(0.0000, 0.2500, 0.4005)	(0.0000, 0.5000, 0.5000)	(0.2500, 0.2500, 0.2500)	Wyc.
$NaV_3(PO_4)_3$	(0.0000, 0.2613, 0.3932)	——	——	Calc.
$Na_2V_3(PO_4)_3$	(0.0000, 0.2483, 0.3648)	(0.0000, 0.4862, 0.4942)	——	Calc.
$Na_3V_3(PO_4)_3$	(0.0000, 0.1779, 0.4385)	(0.0000, 0.4478, 0.4815)	(0.2500, 0.2574, 0.2500)	Calc.

Table S4 Distances (Å) between Na atoms in $Na_xV_3(PO_4)_3$ (x = 1, 2, 3).

	Na1-Na1(or 4e-4e) (b and a axis direction)		Na1-Na2 (or 4e-4b)	Na1-Na3 (or 4e-4c)	
$NaV_3(PO_4)_3$	6.730,	5.592	3.365	2.826	Expt.-Wyc.
$NaV_3(PO_4)_3$	6.929,	5.649	——	——	Calc.
$Na_2V_3(PO_4)_3$	7.128,	5.640	3.393, 3.735	——	Calc.
$Na_3V_3(PO_4)_3$	7.280,	6.019	3.372, 3.915	3.222	Calc.