

## Electronic Supporting Information (ESI)

# New Low-Voltage Plateau of Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> Anode for Na-Ion Batteries

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## Experimental Section

Spin-polarized calculations were performed using the Vienna *Ab initio* Simulation Package (VASP)<sup>1</sup> within the projector augmented-wave approach.<sup>2</sup> Generalized gradient approximation (GGA) in the parameterization of Perdew, Burke, and Ernzerhof (PBE)<sup>3</sup> pseudopotential was used to describe the exchange–correlation potential. A Hubbard-type correction *U* was taken into account due to the strongly correlated nature of the V-3*d* electrons.<sup>4</sup> According to previous literature<sup>5</sup>, the effective *U* value of V ions was set to 4.0 eV. The supercell consisting of two Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> formula units was used through all calculations. The plane-wave cutoff was set to 520 eV. The reciprocal space *k*-point mesh interval was *ca.* 0.04 Å<sup>-1</sup>. Geometry optimizations were performed by using a conjugate gradient minimization until all the forces acting on ions were less than 0.01 eV/Å per atom.

## Characterization and measurements

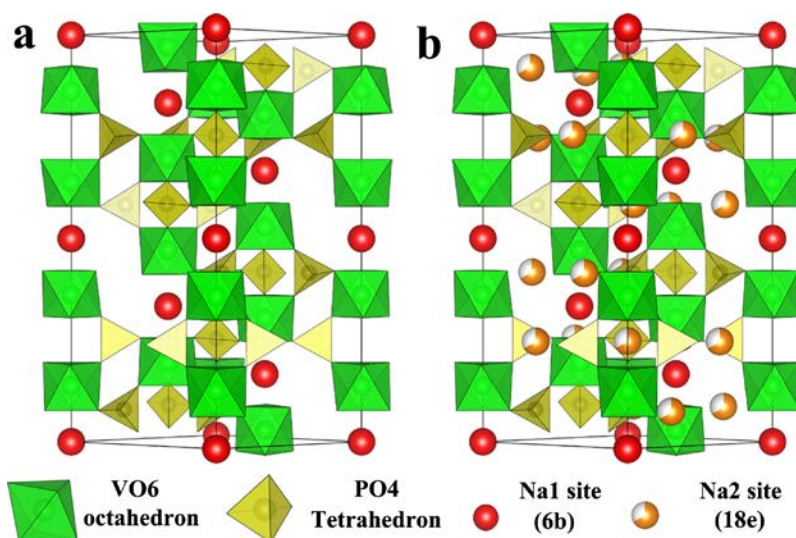
The carbon coated rhombohedral Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> composite was synthesized by mixing stoichiometric amounts of NaH<sub>2</sub>PO<sub>4</sub> (Aldrich, 99.6%) and V<sub>2</sub>O<sub>3</sub> (Aldrich, 98+%) and glucose as a carbon source. The precursors were ball milled and then calcinated at 800 °C for 12 hours. A powder X-ray diffraction (XRD) pattern of the obtained Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C was collected by using a Rigaku Ultima IV Diffractometer with Cu Kα (λ = 1.5406 Å) radiation. Scanning electron microscope (SEM) images were obtained on FEI NOVA 230 high resolution SEM. TG curve of the Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C sample was obtained using Shimadzu TGA-50 instrument under air from room temperature to 800 °C with a ramping rate of 10 °C/min. Raman spectra were obtained on a Micro Raman spectrophotometer

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(Ventuno21, JASCO).

The electrodes were prepared with  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  as active materials, carbon additives and poly(vinyl difluoride) at a weight ratio of 80: 10: 10. The slurry was cast on pure Al foil and dried at  $100\text{ }^\circ\text{C}$  in a vacuum for 10 h. The loading mass of obtained electrode is about  $3\text{ mg}/\text{cm}^2$ . The coin cells CR2032 were assembled with pure sodium foil as the counter electrode, a glass fiber as separator, and  $1\text{ M NaPF}_6$  EC: DMC (1:1) as the electrolyte in an argon filled glove box. The electrochemical measurements were performed on Hokudo Denko Charge/Discharge instruments at  $25\text{ }^\circ\text{C}$ . The Na storage tests for the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  sample were performed at a voltage range of 0.01–3 V. Cyclic voltammetry (CV) was performed on a Solartron 1253B Frequency Response Analyzer.

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Figure S1 The crystal structures of a.  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  and b.  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$

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Table S1. Crystallographic data of the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  at room temperature.

Atom	Type	Wyck.	X/a	Y/b	Z/c	Occ.
Na1	Na	6b	0.00000	0.00000	0.00000	0.8410
Na2	Na	18e	0.63380	0.00000	0.25000	0.7200
V	V	12c	0.00000	0.00000	0.14573	1.0000
P	P	18e	0.28760	0.00000	0.25000	1.0000
O1	O	36f	0.17650	-0.03760	0.19321	1.0000
O2	O	36f	0.19240	0.16950	0.09150	1.0000

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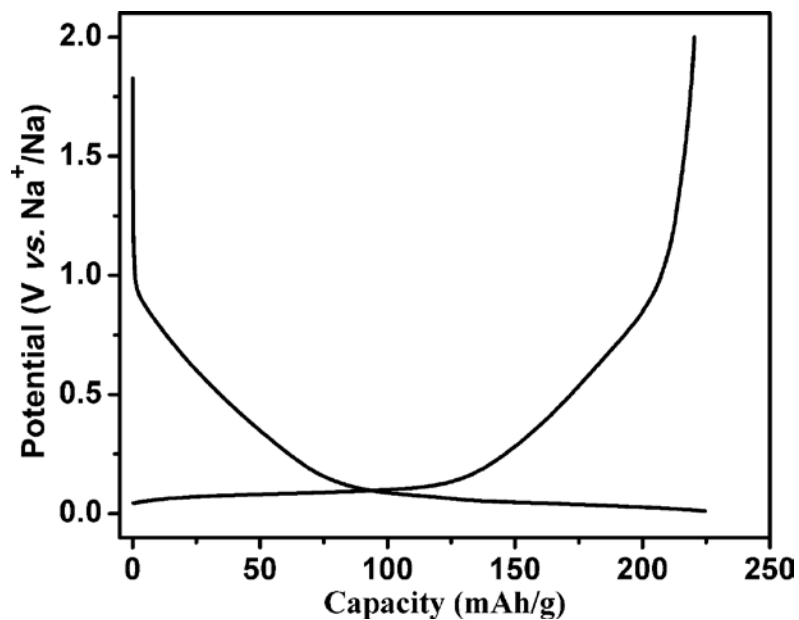


Figure S2 Typical discharge/charge profile of hard carbon.

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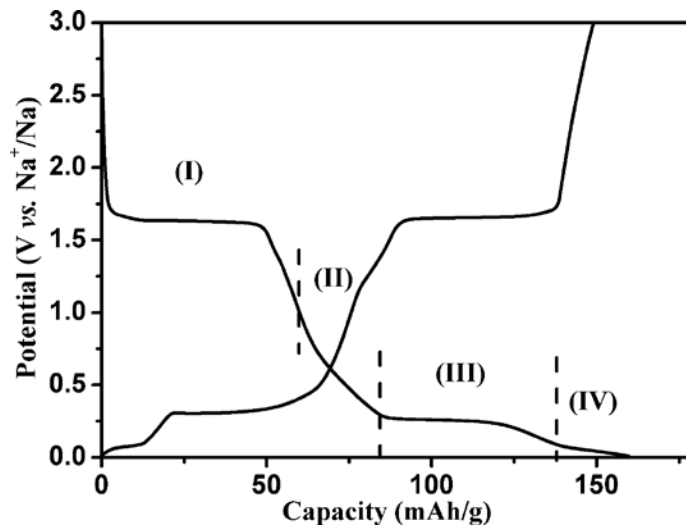


Figure S3 The divided parts for the typical discharge profile of the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  sample at the range of 0.01-3V.

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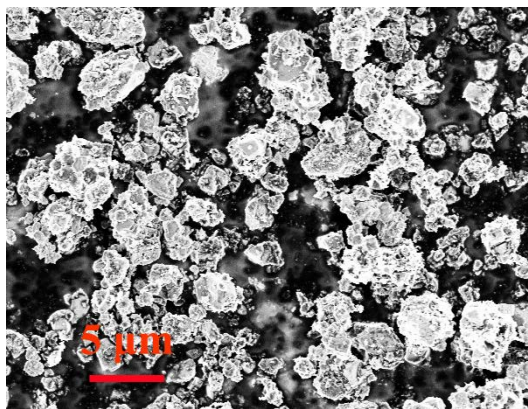


Figure S4 SEM image of the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  sample

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