# New Low-Voltage Plateau of $Na_3V_2(PO_4)_3$ Anode for Na-Ion Batteries

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## Experimental Section

Spin-polarized calculations were performed using the Vienna *Ab initio* Simulation Package (VASP)[1]
15 within the projector augmented-wave approach.[2] Generalized gradient approximation (GGA) in the parameterization of Perdew, Burke, and Ernzerhof (PBE)[3] 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-$3d$ electrons.[4] According to previous literature[5], the effective U value of V ions was set to 4.0 eV. The supercell consisting of two $Na_3V_2(PO_4)_3$ formula units was used
20 through all calculations. The plane-wave cutoff was set to 520 eV. The reciprocal space *k*-point mesh interval was *ca.* 0.04 Å$^{-1}$. 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 $Na_3V_2(PO_4)_3$ composite was synthesized by mixing stoichiometric
25 amounts of $NaH_2PO_4$ (Aldrich, 99.6%) and $V_2O_3$ (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 $Na_3V_2(PO_4)_3$/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 $Na_3V_2(PO_4)_3$/C sample was
30 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

(Ventuno21, JASCO).

The electrodes were prepared with $Na_3V_2(PO_4)_3$/C as active materials, carbon additives and poly(vinyl difluoride) at a weight ratio f 80: 10: 10. The slurry was cast on pure Al foil and dried at 100 °C in a vacuum for 10 h. The loading mass of obtained electrode is about 3 $mg/cm^2$. The coin cells CR2032 were assembled with pure sodium foil as the counter electrode, a glass fiber as separator, and 1 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 °C. The Na storage tests for the $Na_3V_2(PO_4)_3$/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.
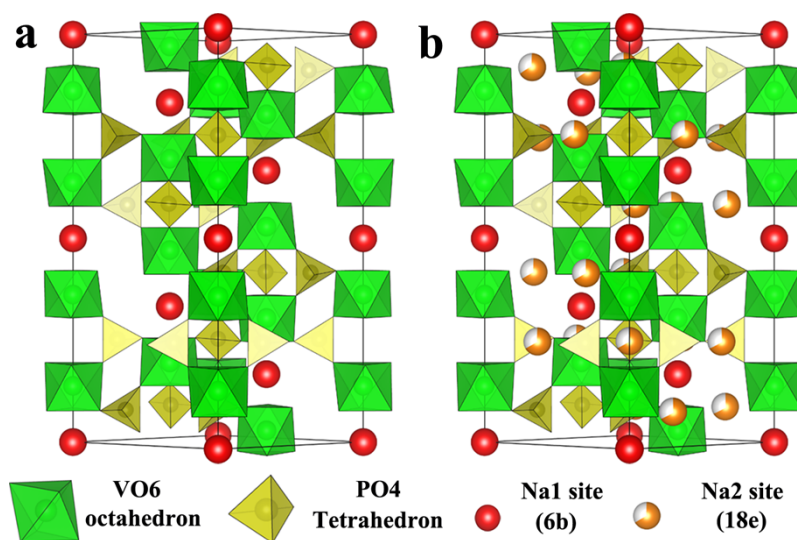


Figure S1 The crystal structures of a. $Na_1V_2(PO_4)_3$ and b. $Na_3V_2(PO_4)_3$

Table S1. Crystallographic data of the $Na_3V_2(PO_4)_3$ 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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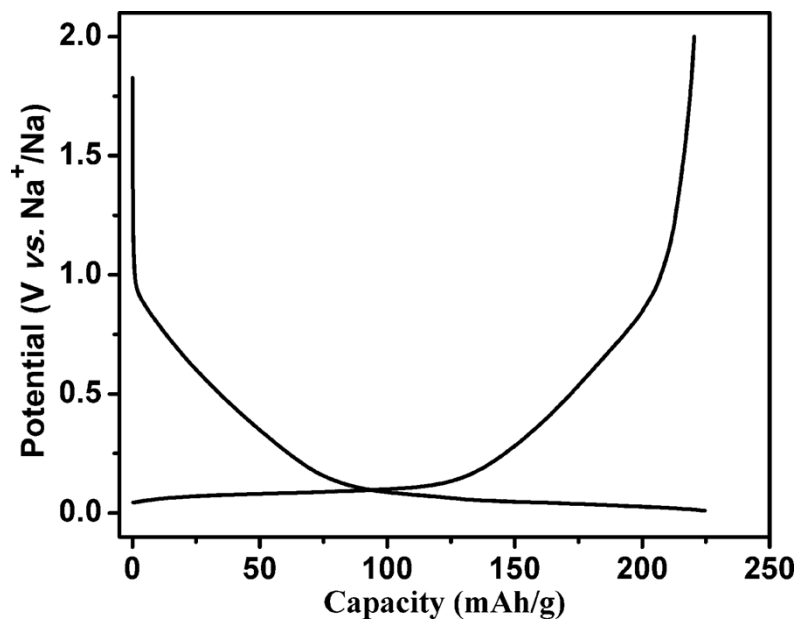


10                    Figure S2 Typical discharge/charge profile of hard carbon.
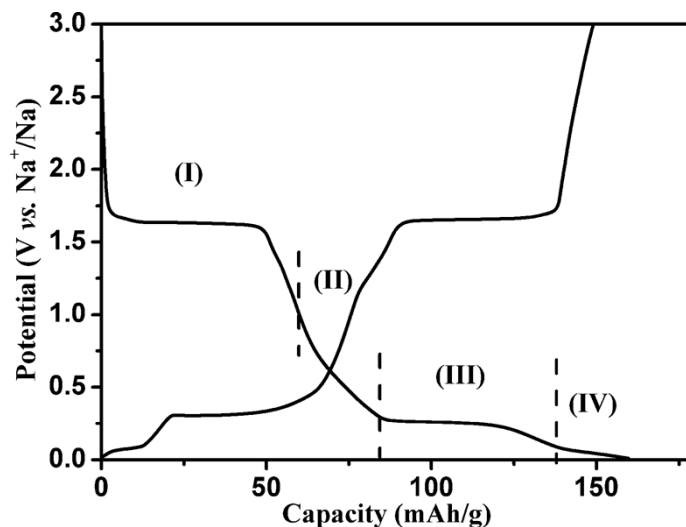
Figure S3 The devided parts for the typical discharge profile of the Na$_3$V$_2$(PO$_4$)$_3$/C sample at the range of 0.01-3V.
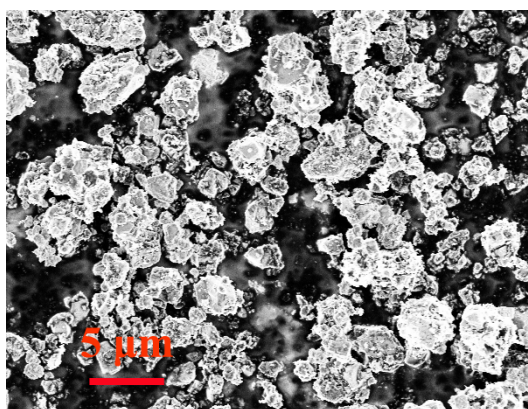
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Figure S4 SEM image of the Na$_3$V$_2$(PO$_4$)$_3$/C sample

**Reference:**

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