Electronic Supporting Information (ESI)

New Low-Voltage Plateau of Na₃V₂(PO₄)₃ Anode for Na-Ion Batteries

Zelang Jian,ᵃ ‡Yang Sun,ᵇ ‡Yong-Sheng Huᵇ,* and Xiulei Jiᵃ,*

ᵃ Department of Chemistry, Oregon State University, Corvallis, OR, USA, 97331-4003, United States. E-mail: David.Ji@oregonstate.edu
ᵇ Key Laboratory for Renewable Energy, Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China. Email: yshu@aphy.iphy.ac.cn

‡ Z. Jian and Y. Sun contributed equally to this work.

Experimental Section

Spin-polarized calculations were performed using the Vienna Ab initio Simulation Package (VASP)¹ 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 literature⁵, the effective U value of V ions was set to 4.0 eV. The supercell consisting of two Na₃V₂(PO₄)₃ 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⁻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 Na₃V₂(PO₄)₃ composite was synthesized by mixing stoichiometric amounts of NaH₂PO₄ (Aldrich, 99.6%) and V₂O₃ (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 Na₃V₂(PO₄)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 Na₃V₂(PO₄)₃/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.
The electrodes were prepared with Na$_3$V$_2$(PO$_4$)$_3$/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 °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$_3$V$_2$(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$_1$V$_2$(PO$_4$)$_3$ and b. Na$_3$V$_2$(PO$_4$)$_3$
Table S1. Crystallographic data of the Na$_3$V$_2$(PO$_4$)$_3$ at room temperature.

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

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.

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

Reference: