3.0 V High Energy Density Symmetric Sodium-Ion Battery: $Na_4V_2(PO_4)_3 || Na_3V_2(PO_4)_3$

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Supporting Information

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ABSTRACT: Symmetric sodium-ion batteries (SIBs) are considered as promising candidates for large-scale energy storage owing to the simplified manufacture and wide abundance of sodium resources. However, most symmetric SIBs suffer from suppressed energy density. Here, a superior congeneric $Na_4V_2(PO_4)_3$ anode is synthesized via electrochemical preintercalation, and a high energy density symmetric SIB $(Na_3V_2(PO_4)_3)$ as a cathode and $Na_4V_2(PO_4)_3$ as an anode) based on the deepened redox couple of V^{4+}/V^{2+} is built for the first time. When measured in half cell, both electrodes show stabilized electrochemical performance (over 3000 cycles). The symmetric SIBs exhibit an output voltage of 3.0



V and a cell-level energy density of 138 W h kg⁻¹. Furthermore, the sodium storage mechanism under the expanded measurement range of 0.01-3.9 V is disclosed through an in situ X-ray diffraction technique.

KEYWORDS: sodium-ion battery, symmetric cell, 3.0 V, high energy density, $Na_3V_3(PO_4)_3$

INTRODUCTION

With the continuous depletion of fossil energy, the whole worldwide energy demand could be provided by renewable energy sources in the near future, such as solar, wind, and tide. Nevertheless, this green energy cannot be sufficiently used without proper storage.² For large-scale energy storage applications, the most important objective is achieving the superior performance, security, and acceptable cost.³⁻⁶ As the most likely option in the field of large-scale electrochemical energy storage systems, sodium-ion batteries (SIBs) receive great attention because of the wide abundance and low cost of sodium resources, although their energy density is usually lower than that of lithium-ion batteries.⁷⁻¹⁸ Generally, symmetric systems have simplified manufacture and better compatibility compared with asymmetric systems, which can make the symmetric SIBs more capable in the matter of cost advantages for large-scale energy storage systems.^{19,20} In addition, security in large-scale applications is vital. Among the current electrode materials, Na superionic conductor (NASICON)-type materials are considered as one of the safest electrode materials because of their intercalation reaction and great structural stability.²¹ To sum up, considering the security and cost performance, symmetric SIBs with NASICON-type electrodes are considered as promising candidates for large-scale energy storage.

However, a lot of current efforts related to SIBs directed at large-scale applications have used the too complicated process for good performance, and their costs are far from meeting the need of large-scale manufactures.²² On the other hand, symmetric SIBs suffer from suppressed energy density owing to their low chemical potential, which immensely limited their applications.² Thus, developing a high-energy NASICONrelated symmetric SIBs with an inexpensive method could be a promising solution.

As the typical representative of NASICON-type materials, $Na_3V_2(PO_4)_3$ (NVP) has been greatly investigated for the symmetric SIB owing to its natural multistep redox reaction.^{10,21,23,24} Its unique structure provides a three-dimensional framework that is known for facile Na⁺ ion migration.^{25,26} Taking advantage of the voltage difference between the two plateaus at around 3.3 and 1.6 V, Yamaki and co-workers first reported NVP-based symmetric SIBs in 2010.² Afterward, Passerini et al.¹⁰ and Yu et al.²³ introduced symmetric SIBs based on NVP bipolar electrodes with modified processes, delivering an output voltage of 1.7 V and connected

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Figure 1. (a) XRD pattern, (b) HRTEM image, and (c) SAED image of NVP/C. (d) Schematic diagram of the preintercalation process.

with an energy density of ~70 W h kg⁻¹.^{19,28–30} Nevertheless, this insufficient performance is inadequate for practical largescale applications, and the total potentialities of NVP have not been fully developed. As the anode, NVP could provide a deeper redox reaction (till fully reducing to V²⁺), a higher specific capacity (90 mA h g⁻¹), and a lower redox potential (0.3 V) compared to the traditional cognition.^{31,32} Owing to the lack of a suitable way to be utilized in symmetric SIBs, this optimized redox reaction has not been applied although it could provide superior electrochemical performances. The structural transition and sodium-ion storage mechanism also need to be deeply investigated.

Herein, we propose a high-performance SIB by using $Na_3V_2(PO_4)_3$ as a cathode and $Na_4V_2(PO_4)_3$ as an anode for the first time. The monocrystalline NVP with carbon decoration (NVP/C) is synthesized as the target material. The congenetic $Na_4V_2(PO_4)_3$ anode is obtained through the preintercalation method. Both electrodes exhibit the outstanding cycling stability and rate performance when utilized as a cathode or an anode for SIBs. The symmetric SIBs based on the above redesign are fabricated for the first time, and electrochemical tests clearly demonstrate an output voltage of 3.0 V and a high cell-level energy density of 138 W h kg⁻¹ compared to the previous NVP-based symmetric SIBs of 1.7 V and ~70 W h kg⁻¹. Furthermore, the structural transition and the sodium storage mechanism are investigated through an in situ X-ray diffraction (XRD) technique.

EXPERIMENTAL SECTION

Synthesis of NVP/C materials. All of the chemicals were of analytical grade and purchased from the Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). First, V₂O₅ (1 mmol), H₂C₂O₄·2H₂O (3 mmol), glucose (1 mmol), and NaH₂PO₄ (3 mmol) were added into 15 mL of deionized water under stirring for 1 h at 80 °C. Then, Nmethylpyrrolidone (50 mL) was added into the above solution and kept stirring for another 15 min. After that, the uniform precursor was obtained by drying at 80 °C in an electronic oven. In the end, the NVP/C electrode materials were obtained from the precursor via preheating at 400 °C for 4 h, followed by annealing at 750 °C for 8 h in Ar/H₂ (95:5) atmosphere with a heating rate of 5 °C min⁻¹. For comparison, a series of experiments with different annealing temperatures were carried out to find the optimal recipe (NVP/Cannealing temperature). Preintercalation was carried out by an electrochemical process with coin cells in argon gas at room temperature.

Characterization. The morphology was characterized by using a field emission scanning electron microscopy (SEM, JEOL JSM-7100F) at an acceleration voltage of 15 kV. The crystal structure was performed using a D8 ADVANCE X-ray diffractometer (Cu K α radiation). The transmission electron microscopy (TEM) images and the selected-area electron diffraction (SAED) patterns were collected using a TEM (Titan G2 60-300, FEI). Raman spectra were obtained using a Renishaw INVIA micro-Raman spectroscopy system. The pore structure and surface area were measured using a Tristar II 3020 instrument by nitrogen adsorption at 77 K. Carbon content analysis was determined by a Vario EL cube CHNSO elemental analyzer.

Electrochemical Measurements. The electrochemical performances were evaluated by assembling 2016 coin cells in a glovebox filled with argon gas. The electrodes were made by mixing active materials acetylene black and polyvinylidene fluoride at a weight ratio of 7:2:1, and N-methylpyrrolidone as a solvent. Then, the slurry was spread onto an aluminum foil and dried at 70 °C for at least 10 h. The electrolyte was 1 M NaClO4 in ethyl carbonate and dimethyl carbonate with a mass ratio of 1:1, and 5% fluoroethylene carbonate was used as an additive. A Whatman glass microfiber filter (Grade GF/ F) was used as the separator. The mass loadings of the active material were 1.8-2.5 and 1.5-2 mg cm⁻² for the anode and the cathode, respectively. The symmetric battery system balance was achieved by controlling the electrode capacity ratio of anode and cathode to 1.2. The battery was aged for 6 h before testing to ensure infiltration of the electrolyte. The cell-level energy density was calculated based on the masses of the cathode and anode. The cyclic voltammetry (CV) curves were obtained with an electrochemical workstation (CHI1000D). Galvanostatic charge/discharge measurements were cycled at a multichannel battery testing system (LAND CT2001A). The electrochemical impedance spectroscopy (EIS) was performed by an electrochemical workstation (Autolab PGSTAT302N, frequency range: 0.1 to 10^5 Hz).

RESULTS AND DISCUSSION

The phase characterization of NVP/C was verified by using a powder XRD (Figure 1a). All diffraction peaks are fully consistent with the NVP ($R\bar{3}c$ space group, JCPDS card no. 00-053-0018), corresponding well with the previously reported literature.^{33–35} This NVP has a NASICON framework of the [PO₄] tetrahedral units sharing corners with the [VO₆] octahedron units; the sodium atoms are located in the voids/ channels of the framework (Figure S1).²⁴ The peak intensity of NVP/C-650 is lower than that of NVP/C-750 (Figure 1a). This result indicates that the crystallinity of NVP/C-650 is lower than that of NVP/C-850 owing to over high annealing temperature.²⁵ The high-resolution TEM (HRTEM)



Figure 2. Cycling performances of NVP/C-650, NVP/C-750, and NVP/C-850 at the current density of 40 mA g^{-1} under the voltage windows of (a) 0.01–1.2 and (b) 2.5–3.9 V.



Figure 3. CV curves of (a) anode and (b) cathode at a scan rate of 0.1 mV s^{-1} under the voltage windows of 0.01-1.2 and 2.5-3.9 V, respectively. Cycling performance of (c) anode and (d) cathode under a current density of 40 mA g⁻¹. Rate performance of (e) anode and (f) cathode.

image shows the amorphous carbon layer of NVP/C, and the thickness of the carbon layer is around 5 nm (Figure 1b). The marked lattice fringe with a *d*-spacing of 0.44 nm corresponds to the *d*-spacing of (104) planes. The SAED patterns indicate a single crystallization character of NVP/C, which marks to the (300) and (113) planes (Figure 1c). The homogeneous distributions of Na, V, P, O, and C elements were confirmed through energy-dispersive spectrometry (EDS) element mapping (Figure S2). The carbon content of the NVP/C sample is 8%, which was determined by the CHNSO elemental analyzer.

Raman spectroscopy is a powerful technique to characterize the carbon phase of NVP/C. The spectrum (Figure S3) shows two characteristic bands located at 1343 cm⁻¹ (D-band) and 1597 cm⁻¹ (G-band).³⁶ The spectral parameters are achieved by curve fitting in the Gaussian numerical simulation.³⁷ The ratio of I_{D1}/I_G is calculated to be 3.02, which indicates that the carbon layer exists as amorphous carbon.³⁸ The surface area and pore structure of NVP/C were measured by the nitrogen isothermal adsorption technique (Figure S4). The surface area of NVP/C is 54.2 m² g⁻¹, and the pore size distribution curve



Figure 4. (a) Schematic diagram of the $Na_4V_2(PO_4)_3||Na_3V_2(PO_4)_3$ symmetric SIBs. (b) Voltage profiles of NVP/C half cells and full cells (formula: the cell-level capacity of the battery was calculated based on masses of both the cathode and anode). (c) Electrochemical impedance spectra of the full cell after different cycles and the corresponding fitted equivalent circuit model. (d) Typical voltage profiles of our work and traditional NVP-based symmetric full cell. (e) Cycling performance of symmetric full cells under a current density of 40 mA g⁻¹. (f) Cell-level capacity, discharge voltage, and energy density of the recently published symmetric SIBs ($Na_{0.66}Ni_{0.17}Co_{0.17}Ti_{0.66}O_2$,⁴⁷ $Na_{0.6}Cr_{0.6}Ti_{0.4}O_2$,⁴⁸ $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$,²¹ $Na_{3}V_2(PO_4)_3$,^{20,23,28} $Na_{2.55}V_6O_{16}$,⁴⁹ $Na_2V_6O_{16}$,⁵⁰ $Na_3MnTi(PO_4)_3$,²⁹ and $NiFe_2O_4$,⁵¹).

(Figure S4 inset) displays that the pore sizes are mainly below 25 nm. Prior to the measurement, the anode underwent an electrochemical route to form the sodiated phase $(Na_4V_2(PO_4)_3)$ and the stable solid electrolyte interface (SEI) (Figure 1d). We employed a galvanostatic discharge/ charge cycle with coin cell upon 1.2 V to achieve the electrochemical preintercalation (Figure S5), and Figure S6 indicates the formation of the SEI after the electrochemical measurement. In fact, the electrochemical preintercalation strategy presented here is a proper way to reveal the nature of the material. More easily scalable solvothermal routes for preintercalation may be more achievable in industry, which should be further developed.³⁹

The electrochemical performances of the prepared material as an anode or a cathode with coin cells for SIBs were checked in the voltage windows of 0.01-1.2 and 2.5-3.9 V, respectively. NVP/C-750 delivers the highest initial discharge capacities of 105 and 110 mA h g^{-1} as an anode and a cathode, respectively (Figure 2a,b), compared to those of NVP/C-650 (75 and 88 mA h g^{-1}) and NVP/C-850 (82 and 97 mA h g^{-1}). This is owing to the low crystallinity of NVP/C-650 and the impurity of NVP/C-850, which lead to the instability of the crystal, especially during the mass of Na⁺ ion insertion.^{21,25,40} Two pairs of redox peaks at around 0.3 V (anode) and 3.3 V (cathode) are observed within CV curves (Figure 3a,b), corresponding to the redox couples of $V^{3+/2+}/V^{2+}$ and $V^{4+}/$ V^{3+} , respectively.^{31,41} The long-term cycling stabilities of NVP/ C-750 were tested with the galvanostatic charge-discharge measurement at 40 mA g^{-1} (Figure 3c,d). The capacities of NVP/C-750 maintain 84 and 93 mA h g⁻¹ after 3000 cycles, corresponding to the capacity retention of 81 and 84% as an anode and a cathode, respectively. NVP/C also displays excellent rate performances (Figure 3e,f). When the current

densities return to the beginning, the capacities can reach as high as the initial capacities. The reversible capacity of the $Na_4V_2(PO_4)_3$ anode reaches up to 210 mA h g⁻¹, which was revealed by the galvanostatic intermittent titration technique (GITT, Figure S7). Prior to the measurement, the electrodes were cycled two times to ensure the accuracy. Apart from the capacity attributed to the reversible phase transition,³² the extra capacity of the $Na_4V_2(PO_4)_3$ anode could be attributed to the following reactions: carbon coating,³¹ "space charge layer",⁴² and "polymer-/gel-like film".⁴³ With increasing the current density, the capacity loss could be related to the slow kinetics of the above extra reaction. The diffusion coefficient value of $Na_4V_2(PO_4)_3$ is 1.22×10^{-12} , which is calculated based on the EIS measurement (Figure S8). Figure S9 shows the typical voltage profiles in different current densities, which shows charge-discharge plateaus at around 0.3 and 3.3 V as an anode and a cathode, respectively. For the anode, it needs to be emphasized that the above voltage plateau is more suitable compared to the well known hard carbon owing to the fact that the voltage plateau of hard carbon (0.01 V) is very close to the sodium plating voltage. It could cause safety issues since the sodium plating.

On the basis of above results, symmetric full cells were assembled by using NVP/C electrode materials. The schematic diagram of the symmetric full cell is proposed in Figure 4a. Na⁺ ions are extracted from Na₃V₂(PO₄)₃ to form NaV₂(PO₄)₃, and Na⁺ ions inset in Na₄V₂(PO₄)₃ to form Na₅V₂(PO₄)₃.^{31,34} The reactions of the cathode (I) and anode (II) in the symmetric battery can be described as follows

$$Na_{3}V_{2}(PO_{4})_{3} \leftrightarrow NaV_{2}(PO_{4})_{3} + 2e^{-} + 2Na^{+}$$
(I)

$$Na_4V_2(PO_4)_3 + e^- + Na^+ \leftrightarrow Na_5V_2(PO_4)_3$$
 (II)

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The oxidation and reduction peaks (3.2 and 2.95 V, respectively) of V^{4+}/V^{2+} can be observed from the CV curves (Figure S10). The simulated charge–discharge curves are obtained from the difference of half cells, agreeing well with the experimental results (Figure 4b). The cell-level capacity of the full cell (based on the total mass of the cathode and anode active materials) can be determined from the standard relationship as follows^{44,45}

$$C_{\text{full}} = \frac{1}{\frac{1}{C_{\text{c}}} + \frac{1}{C_{\text{c}}}} = \frac{C_{\text{a}}C_{\text{c}}}{C_{\text{a}} + C_{\text{c}}}$$

where $C_{\text{fully}} C_{\text{av}}$ and C_{c} is the specific capacities of the full cell, anode, and cathode, respectively. The resistance of the full cell was measured by the EIS (Figure 4c), the high-middle frequency semicircle stands for the charge-transfer resistance $(R_{\rm ct})$ between the electrodes and the electrolyte and the line in the low-frequency range represents the Warburg resistance (Z_w) related to the Na⁺ ion diffusion. On the basis of the fitted equivalent circuit, the R_{ct} values of the full cell after 2, 20, and 100 cycles are 174, 210, and 224 Ω , respectively. The typical voltage profiles show that our full cells deliver an output voltage plateau of 3.0 V and a cell-level capacity of 46 mA h g^{-1} (Figure 4d). In contrast, the prototype traditional NVP-based symmetric battery delivers an output voltage of 1.7 V and a cell-level capacity of 36 mA h g⁻¹. Figure S11 shows that the obtained full cell is capable of lighting the light-emitting diode bulb. The capacity retention is 87% after 100 cycles (Figure 4e). Because of the SEI building in advance, the initial Coulombic efficiency of the full cell can reach as high as 95%. The rate performance of the full cell was also measured (Figure S12). When the current density reached to 160 mA g^{-1} , the cell-level capacity of 24 mA h g^{-1} was maintained. With the current density returned back to 40 mA g⁻¹, more than 40 mA h g^{-1} cell-level capacity could be recovered. The cell-level capacities, discharge voltages, and energy densities of recently published symmetric SIBs are presented in Figure 4f. To ensure that our comparisons are under the consistent standard, the cell-level capacity and energy density of recently published symmetric SIBs have been recalculated.⁴⁶ It is clear that our work has a cell-level energy density of 138 W h kg⁻¹, which has a decent improvement compared to the previous symmetric SIBs.

To learn more about the electrochemical processes in real time, the in situ XRD technique has been utilized to investigate the sodium-ion storage mechanisms of NVP.⁵² The 2θ was recorded from 28° to 38°, a proper range that can reflect the structural transformation of NVP. At the beginning of the process, all diffraction peaks can be identified as $Na_3V_2(PO_4)_3$ with the NASICON structure. In Figure 5a, with the charging procedure, some new peaks appear and gradually strengthen. This process can be considered as the coexistence of two phase, corresponding to the voltage plateau. The diffraction peaks can be indexed to $NaV_2(PO_4)_3$ at the end of charging.³⁴ Upon the discharge to 2.7 V, the XRD pattern of $NaV_2(PO_4)_3$ completely disappears, whereas those from $Na_3V_2(PO_4)_3$ are observed. The structure transforms back to the original NVP phase at the end of discharge. A similar behavior but with the opposite trend is observed when the electrode was tested at voltage ranges of 0.01-3.0 V (Figure 5b). Upon the discharge to 1.2 V, diffraction peaks of (024) and (300) shift to smaller angles, which indicating the Na^+ ions insertion related to the *d*-space increasing. No new peaks appear or disappear, which cannot



Figure 5. In situ XRD patterns collected during the first charge– discharge of NVP/C half cell under a current density of 75 mA g⁻¹ at voltage ranges of (a) 3.0–3.9 and (b) 0.01–3.0 V with 2θ recorded from 28° to 38° [(i–iv) 0.01, 1.2, 3, and 3.9 V]. Schematic illustration of the unit cells of (c) cathode and (d) anode.

indicate the coexistence of two phases. With further discharge process, insertion of Na⁺ ions induces the disappearance of peaks of (024) and (116) and some new peaks appear. This process can also be considered as the coexistence of two phase, and the diffraction peaks can be indexed to Na₅V₂(PO₄)₃.³¹ Figure 5c,d shows the schematic illustration of the unit cells. As the cathode, there are three sodium atoms per NVP unit and two removable atoms of them located at the 18e site, occupying 2/3 of the vacancy, corresponding to the transformation of NaV₂(PO₄)₃/Na₃V₂(PO₄)₃ phases.⁵³ The third atom occupies the 6b site, which cannot be extracted from the structure. As the anode, there are five sodium atoms per unit and only one of them at the 6a site could be extracted, corresponding to the transformation of Na₄V₂(PO₄)₃/Na₅V₂(PO₄)₃ phases.⁵¹

CONCLUSIONS

In summary, the congeneric $Na_4V_2(PO_4)_3$ anode was obtained by using the preintercalation method, and the high-performance symmetric SIBs were assembled by using $Na_3V_2(PO_4)_3$ as a cathode and $Na_4V_2(PO_4)_3$ as an anode for the first time. The electrodes exhibit a stabilized electrochemical performance (over 3000 cycles) when utilized as an anode or a cathode. The full cell shows a higher output voltage of 3.0 V and a higher energy density of 138 W h kg⁻¹ than the previous symmetric SIBs of 1.7 V and ~70 W h kg⁻¹. These results introduce a kind of effective and feasible way to improve the electrochemical performance of oxidation—reduction cells. We employed the in situ XRD technique to disclose the sodium storage mechanism. This work makes the symmetric SIBs more capable in the field of large-scale energy storage applications.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b16901.

Crystal structure of NVP; EDS, Raman spectrum, and Brunauer–Emmett–Teller results of NVP/C; SEM, GITT, and EIS results of Na₄V₂(PO₄)₃; voltage profiles

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of half cell and CV curves; and rate performance of the symmetric full cell (PDF)

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Author Contributions

X.Y. and Z.Z. contributed equally to this work. L.M., W.R., and X.Y. designed the experiments. X.Y., Z.Z., and W.R. performed the experiments. L.M., Y.H., X.Y., W.R., X.Z., Q.L, Z.Z., X.W., and J.M. discussed the interpretation of results and co-wrote the paper. All authors discussed the results and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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