Electrospun Na$_3$V$_2$(PO$_4$)$_3$/C nanofibers as self-standing cathode material for high performance sodium ion batteries

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Abstract

This work focuses on the preparation of a 3D flexible Na$_3$V$_2$(PO$_4$)$_3$/C fiber membrane, as self-standing cathode for Na-ion batteries, via a facile and simple electrospinning method, is followed by a hot-pressing process. A series of heat treatment temperatures are studied in detail, it is found that the temperature of the thermal process is a key parameter for controlling the structural organization of the material, as well as the size and dispersion of Na$_3$V$_2$(PO$_4$)$_3$ nanoparticles on the carbon surface. Hence, Na$_3$V$_2$(PO$_4$)$_3$ nanoparticles, with a size of 40 nm and highly disperse on the carbon nanofibers, are obtained after calcination at 800 °C. In addition, this sample (Na$_3$V$_2$(PO$_4$)$_3$/C Nanofiber-800) exhibits the best electrochemical performances among all the samples. For instance, it displays a considerably high initial discharge capacity of 109, 84, 77, and 71 mA h g$^{-1}$ at a current density of 0.1, 10, 20, and 30 C, respectively. Moreover, the Na$_3$V$_2$(PO$_4$)$_3$/C Nanofiber-800 shows notable cycle stability with about 95.3% capacity retention of its initial capacity after 1000 cycles at 2 C. These high performances is attributed to the unique nanofiber structure and uniform distribution of Na$_3$V$_2$(PO$_4$)$_3$ nanoparticles in the highly conductive carbon matrix.

1. Introduction

Nowadays, lithium-ion batteries (LIBs) are considered as the main power source that responds to the growing demand of energy storage devices [1–4]. However, the limited lithium resources restrict the development and application of LIBs to large-scale energy storage. Rechargeable sodium-ion batteries (SIBs) are an attractive alternative owing to their low cost, wide availability of sodium resources, and similar properties with Li[5–8]. However, because of the larger Na$^+$ ionic radius (0.76 Å for Li$^+$ versus 1.02 Å for Na$^+$), it is proved to be a crucial obstacle to affect Na$^+$ diffusing, resulting in poor cyclability and rate capability and has limited the practical application of SIBs. Thus, it is very important to develop new kinds of electrode materials for Na ions with broad pathways and robust structure to overcome this unsatisfactory performance imposed by the large ionic radius of sodium [9]. It is acknowledged that the cathode materials play a key role in high-performance SIBs. Hence, the reports on cathode materials, such as Na$_x$MnO$_2$ [10], NaFeF$_3$ [11], NaCrO$_2$ [12], NaMPO$_4$ [13, 14], Na$_{0.75}$Co$_{0.25}$Mn$_{0.65}$Fe$_{0.35}$Ni$_{0.15}$O$_2$ [15], V$_2$O$_5$ [16], used for sodium ion batteries is continuously growing. Among these, Na$_3$V$_2$(PO$_4$)$_3$(NVP), a NASICON-structure with open three dimensional framework, has an excellent ionic conductivity and good thermal stability, allowing it to be used as a suitable cathode material for sodium ion battery systems [17]. In addition, NVP as a cathode material, has two flat voltage plateaus at 3.4 and 1.6 V versus Na$^+$/Na and a theoretical capacity of 117 mA h g$^{-1}$ based on the $\text{V}^{3+}/\text{V}^{2+}$ redox reaction. Therefore, all these advantages make NVP a promising cathode material for SIBs.
Unfortunately, similar to Li$_3$V$_2$(PO$_4$)$_3$[18–20], NVP has relatively low electronic conductivity that limits its electrochemical performance. These problems are overcome, by applying various strategies, such as controlling the particle size [21, 22], coating the Na$_3$V$_2$(PO$_4$)$_3$ with conductive materials [23, 24], or doping with metal ions [25]. Among them, the carbon coating is an effective way for enhancing the capability and cycle stability of NVP, but the traditional carbon-coating technology cannot completely prevent the particle agglomeration or growth that can have a strong influence on the (de)insertion process and electrochemical behavior. Therefore, the growing of nanoparticles on one-dimensional (1D) carbon nanofibers is considered as a feasible method to eliminate this disadvantage during desodiation and sodiation processes. To the best of our knowledge, electrospinning technique is a novel strategy to fabricate various one dimensional (1D) nanostructure composites. These structures significantly improve the ionic and electronic transport, prevent particles agglomeration or particle growth, and are recognized as the most suitable architectures for applications in energy storage systems [26–29]. For example, Liu et al synthesized Na$_3$V$_2$(PO$_4$)$_3$ nanofibers using a simple electrospinning method as cathode materials for SIBs [30]. These nanofibers exhibit a capacity of 101 and 20 mA h g$^{-1}$ at 0.1 and 20 C, respectively. Moreover, they demonstrated that the interconnected 1D nanofibers formed an unique 3D network structure that leads to a good rate capability. Li et al further optimized the Na$_3$V$_2$(PO$_4$)$_3$/C nanofibers morphology, whose budding willow branches-like shape ensures an excellent cycle stability (a capacity of 107.2 mA h g$^{-1}$ was obtained at 0.2 C after 125 cycles) of the nanofibers [31]. These advantages are mainly attributed to carbon nanofibers, which can improve the electric conductivity of Na$_3$V$_2$(PO$_4$)$_3$ and provide a shorter and more efficient electron transport for sodium ions. The electrodes used for SIBs are prepared by mixing the active materials with polymer binders and conductive agents. However, the presence of binders reduces the overall volumetric/gravimetric energy density and influences the cycle stability [32, 33].

In a previous work reported by our group [34], 3D flexible Na$_3$V$_2$(PO$_4$)$_3$/C fiber membrane was prepared by electrospinning method, followed by a hot-press process to protect the structure of Na$_3$V$_2$(PO$_4$)$_3$/C composite fiber membrane. Furthermore, it was noticed that the different temperatures (i.e., 700, 800, and 900 °C) used for the hot-press step had an impact on the final morphology and structure of NVP/carbon nanofibers. Herein, investigating these flexible fiber membranes resulted from the hot-press process at various temperatures (i.e., NVP/CNF-700, NVP/CNF-800, and NVP/CNF-900) is continued by focusing on their structure and performance. Then, these flexible membranes can be directly used as working electrodes. The results revealed that the NVP/CNF-800 composite membrane exhibits the highest electrochemical performance.

2. Experimental

2.1. Materials synthesis

The Na$_3$V$_2$(PO$_4$)$_3$/C nanofibers were prepared through an electrospinning technique followed by a heat treatment (hot-press). The procedure of the preparation of electrospun precursor is as follows. Four mmol ammonium vanadate (NH$_4$VO$_3$), 8 mmol oxalic acid (H$_2$C$_2$O$_4$), 6 mmol dihydrogen phosphate (NaH$_2$PO$_4$) were successively dissolved in 10 ml distilled water at room temperature to form a uniform blue solution (solution A). Separately, 3 g polyvinyl alcohol (PVA) was dissolved into 20 ml deionized water and vigorously stirred at 65 °C for 4 h (solution B). Then, the solution A was slowly added to the solution B, and the mixture was further stirred for another 4 h to obtain the final spinning solution. The resulting solution was transferred to a 30 ml plastic syringe equipped with a 21-gauge blunt needle. A voltage of 28 kV was applied on the needle relative to a drum collector positioned at about 10 cm from the tip of the needle, and the ejection rate of electrospinning was 0.3 ml h$^{-1}$. After electrospinning, the as-collected fiber membrane was horizontally tiled on an alumina ceramic plate and pressed by another alumina ceramic plate (0.6 mm in thickness). The assembly was then stabilized at 350 °C for 5 h and calcined (carbonized) at different temperatures (i.e., 700, 800, and 900 °C) with a heating rate of 3 °C min$^{-1}$ for 8 h in Ar atmosphere. The resulted Na$_3$V$_2$(PO$_4$)$_3$/C nanofibers were denoted as NVP/CNF-700, NVP/CNF-800, and NVP/CNF-900, respectively.

2.2. Physico-chemical characterization

The crystallinity of NVP/CNF samples was analyzed by x-ray diffraction on a Bruker D8 Advance diffractometer with a Cu Kα radiation in the range from 10 to 70° (2θ) and a step size of 0.02°. The morphology and microstructure were characterized by field-emission SEM (Hitachi Su-70) and TEM (JEOL, JEM-2100). The carbon content and graphitization degree of the composite fiber membranes were measured by a VarioEL III elemental analyzer (Elementar, Germany) and a Renishaw inVia Raman spectrometer. The x-ray photoelectron spectroscopy (XPS) were performed with a K-Alpha+.
2.3. Electrochemical measurements

The Na$_3$V$_2$(PO$_4$)$_3$/C composite fiber membranes were directly pressed as self-standing working electrodes and dried at 80 °C under vacuum for 12 h. The reference electrode was sodium metal, and the separator was a glass fiber. The electrochemical performance was assessed by using a CR2016 coin-cell placed in a glove box filled with argon. The electrolyte solution was an anhydrous propylene carbonate containing 1 M NaClO$_4$ and 5 vol % fluoroethylene carbonate, the active mass loading of each electrode was 1.0-2.0 mg cm$^{-2}$. The charge-discharge tests were performed on an automatic battery tester system (Neware, China) and using a voltage range from 2.8 to 4.0 V using. Cyclic voltammetry (CV) tests were performed in the potential range of 2.5–4.0 V (versus Na$^+$/Na, 0.2 mV s$^{-1}$). The electrochemical impedance spectra (frequency range of $10^5$–$10^{-2}$ Hz) and CV tests were conducted on a Solartron Analytical instrument. All the electrochemical measurements were carried out at 298 K.

3. Results and discussion

The crystal structures of the three samples were investigated by XRD, as shown in figure 1 (a). The diffraction peaks displayed by the patterns of all the three samples reveal a typical NASICON structure crystallized in the space group R$ar{3}$c (a = 8.724 Å, c = 21.764 Å) [35, 36]. In addition, the intensity of diffraction peaks of the NVP/CNF samples gradually increases as the temperature increases from 700 to 900 °C.

To identify the structural characteristics of the carbon fiber formed on the surface of NVP particles, Raman spectroscopy was used. Figure 1 (b) shows the Raman spectra of all three samples, i.e., NVP/CNF-700, NVP/CNF-800, and NVP/CNF-900. All spectra exhibit two prominent peaks corresponding to the D (1358 cm$^{-1}$) and G (1598 cm$^{-1}$) bands of carbon. The I$_D$/I$_G$ intensity ratio is usually used to assess the graphitization degree of carbon [37]. The I$_D$/I$_G$ values obtained for the three samples are 0.98, 0.86, and 0.78 for NVP/CNF-700, NVP/CNF-800, and NVP/CNF-900, respectively, suggesting that the carbon fibers in all samples is partially graphitized and the graphitization process increases with temperature. Furthermore, the carbon content measured on a carbon–sulfur analyzer is 21.6%, 14.2%, and 7.3% in NVP/CNF-700, NVP/CNF-800, and NVP/CNF-900, respectively.
XPS measurement was further conducted to investigate the chemical composition and oxidation states of NVP/CNF-800 (figure 1(c)), this sample only consisted of five elemental signals (Na, V, O, P and C) are detected in the survey spectrum. Figure 1(d) shows the binding energy of V $2p_{1/2}$ and V $2p_{3/2}$ at 524.2 and 517.1 eV, respectively. There is no higher binding energy peak near 519–520 eV, meaning that V$^{5+}$ from NH$_4$VO$_3$ precursor is successfully reduced to V$^{3+}$ [38–40].

The starting materials of ammonium metavanadate, sodium acetate and phosphate acid, polyvinyl alcohol (PVA) and H$_2$O was electrospun to form a film, and then the fibrous film is carbonized at different temperatures (700, 800, and 900 °C) in an Ar atmosphere to obtain the special 3D conductive networks (figure 2). In the above preparation, PVA is used as a carbon source to release carbon dioxide to generate voids. Figure S1 is available online at stacks.iop.org/MRX/7/025508/mmedia shows the photos of the as-spun fiber membrane and calcined self-standing Na$_3$V$_2$(PO$_4$)$_3$/C electrode for Na-ion batteries, prepared by adopting an unique hot-press process to protect the structure of Na$_3$V$_2$(PO$_4$)$_3$/C composite fiber membrane during calcination. Figure S1(d) shows the photo of the free-standing and flexible NVP/CNF-800 electrode. The obtained films can be cut into small round pieces directly and tested as self-standing working electrodes for SIBs. Such self-standing electrodes simplify not only the cell packing process, but also improves the electrochemical performance of SIBs by eliminating inactive ingredients, such as binders and current collectors. The strategy and design are simple, effective, and versatile. This type of flexible electrodes can be used in industrial scale-up production. Figure S2 illustrates the SEM images of as-spun NVP/PVA fiber. It can be seen that the as-spun sample consists of 1D fibers with diameter of ~350 nm and a smooth surface. The effect of the calcination temperature on the morphology and crystallinity of the resulted composite materials was investigated.

The representative SEM images of Na$_3$V$_2$(PO$_4$)$_3$/C nanorods (NVP/CNF) are shown in figures 2(a)–(f), a 3D network structure is formed by the cross-linking of 1D fibers. This spatial organization of the fibers facilitates the continuous electronic transmission channels, resulting in an improved rate performance. The sample calcined at 800 °C consists of cross-linked nanofibers with rough surface and relatively uniform size distribution with a diameter range of 200-300 nm (figures 2(c)–(d)). The carbonized fibers (figures 2(e)–(f)) obtained by calcination at 900 °C, display a lower diameter (the size decreased by 150 nm), the roughness of the surface is more obvious while the interconnected network is still maintained compared with the as-electrospun fibers. The roughness of the surface is explained by the transformation of some needle-like fibers (figures 2(a)–(b)) into spherical particles attached to the surface, as a result of removing of small molecules. In addition, at higher temperatures, such as 900 °C, the fibers become very fragile and cannot prevent the aggregation of NVP nanoparticles during the calcination process.

![Figure 2. Schematic illustration of the synthesis process of Na$_3$V$_2$(PO$_4$)$_3$ nanorods by electrospinning and SEM images of NVP/carbon fibers after annealing at 700 °C(a), (b), 800 °C(c), (d), and 900 °C(e), (f), respectively.](image-url)
TEM images of the NVP/CNF-800 taken at different magnifications are displayed in (figures 3(a)–(c)). It can be seen that the fibers are uniformly covered by nanoparticles of approximately 40 nm. The HRTEM image shown in figure 3(d) confirms the crystallinity of the nanoparticles observed by SEM and TEM. Moreover, the interplanar spacing of 0.31 nm corresponds to the (024) diffraction plane of NASICON structured Na$_3$V$_2$(PO$_4$)$_3$, which confirms the formation of NVP nanoparticles on the surface of carbon nanofibers.

The initial charge/discharge curves of all NVP/CNF samples current density of 0.1 C in the voltage range of 2.8–4.0 V (versus Na$^+$/Na) are shown in figure 4(a). All as prepared materials exhibit a voltage plateau at ~3.4 V that corresponded to a V$^{4+}$/V$^{3+}$ redox reaction [41, 42]. The designed NVPC-800 delivers the highest initial charge capacity and Coulombic efficiency of and 94%, by comparison, the initial discharge capacities of NVP/CNF-700, NVP/CNF-800, NVP/CNF-900 are 91 and 63 mA h g$^{-1}$, respectively, these results suggest that the available annealing temperature have a crucial effect on the electrochemical properties.

Figure 4(b) illustrates the rate performances of the NVP/CNF-700, NVP/CNF-800, and NVP/CNF-900 composite fibers, evaluated in the current density range from 0.1 to 30 C. Five cycles were performed for each current density. As a first observation, it can be noted that the NVP/CNF-800 sample shows the best rate performance compared to the NVP/CNF-700 and NVP/CNF-900 regardless of the current density. The NVP/CNF-800 delivers initial capacities of 107, 104, 93, 84, 76, 77, 75, and 71 mA h g$^{-1}$ at current density of 1, 2, 5, 10, 15, 20, 25 and 30 C, respectively. Moreover, when the current density was changed back from 30 to 0.1 C, the discharge capacity was quickly and fully recovered to the original value, indicating an excellent rate capability of the composite fiber. As a comparison, the other two electrodes (NVP/CNF-700 and NVP/CNF-900) exhibit relative inferior performance, in particular for that calcined at 900 °C. The low capability of NVP/CNF-700 might be attributed to the higher carbon content, because carbon hardly provides capacity when used as cathode of batteries and thus, a higher carbon content pulled down the capability of NVP/CNF. In addition, although the NVP/CNF-900 sample has the lowest carbon content, by combining the electrochemical performances with the morphology and microstructure of this sample (SEM and TEM results), it can be seen that the nanofiber calcined at 900 °C becomes very fragile while the NVP nanoparticles gather into large aggregates, which is not conducive to the diffusion of electrons and ions and thus exhibits the weakest electrochemical performance. On the basis of these results, it can be stated that NVP/CNF-800 has both suitable carbon content and a stable three-dimensional structure of the network, which ensure an outstanding rate performance.

Figure 4(c) shows the discharge profiles of NVP/CNF-800 at various rates, the discharge plateaus become obscure gradually with the increasing current density, but the discharge plateaus are still clearly detected even at an extremely high current rate. To evaluate the electrochemical properties of NVP/CNF cathodes in sodium ion...
batteries, the four CV curves (between 2.5-4.0 V) recorded for NVP/CNF-800 at various scanning rates (ranging from 0.1 mV s$^{-1}$ to 0.6 mV s$^{-1}$) are depicted in figure 4(d). All the four CV profiles appearing a couple of well-defined redox peaks related to the V$^{3+}$/V$^{4+}$ redox couple reaction, which corresponds to a two-phase transformation between Na$_3$V$_2$(PO$_4$)$_3$ and NaV$_2$(PO$_4$)$_3$ [43, 44]. With the increase of the scan rates, the anodic peaks shift right while the relevant cathodic peaks move to left, which indicate larger polarization at higher scan rates. The intensities of anodic and cathodic peaks increase with the incremental scanning rate. The CV profiles at scanning rates of 0.1 mV s$^{-1}$ display well-defined redox peaks at ~3.49/3.31 V, the redox peaks highly overlap and the peak separation value ($\Delta E$) is 0.18, this value corresponds to the gap between charge and discharge voltage platform, and shows a good reversibility and high Coulombic efficiency.

Hence, long-term cycling performance of NVP/CNF-800 electrode was further investigated for 1000 cycles and a constant current density of 2 C (figure 4(e)). It is noted that an outstanding cycle stability was obtained after 1000 cycles with a high capacity of 101 mA h g$^{-1}$, which represents 95.3% of the initial capacity of 106 mA h g$^{-1}$. In addition, the coulombic efficiency of NVP/CNF-800 is nearly 100% throughout the cycling test, reinforcing the idea of the excellent reversibility and cyclability.
The concentration of sodium ion, respectively. The electronic conductivities where \( R, T, F, n, A \) and \( c \) are the gas constant, absolute temperature, Faraday constant, number of electrons, density and power density of SIBs are improved. Not only can improve the conductivity of Na\(_3\)V\(_2\)O\(_7\) nanoparticles during repeated charge and discharge cycles. Furthermore, the latter inclined line in low frequency region is associated with the Warburg impedance \( Z_w \), which is related with Na\(^+\) diffusion between the NVP/CNF electrode and the electrolyte \([47, 48]\). The diffusion coefficients \( (D_{Na^+}) \) can be calculated using the following equation:

\[
D_{Na^+} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2}
\]  

(1)

Where \( R, T, F, n, A \) and \( c \) are the gas constant, absolute temperature, Faraday constant, number of electrons, concentration of sodium ion, respectively. The electronic conductivities \( (\sigma) \) is related to \( Z' \) by the following equation:

\[
Z' = R_D + R_t + \frac{\sigma}{\sqrt{\omega}}
\]  

(2)

The \( \sigma \) can be calculated from plot of \( Z' \) versus \( \omega^{-1/2} \) (figure 5(b)) and the corresponding values for NVP/CNF are listed in table S1(supporting information). The calculated Na\(^+\) ion diffusion coefficient value of electrodes are \( 1.8 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}, 2.7 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1} \) and \( 0.95 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1} \) for NVP/CNF-700, NVP/CNF-800 and NVP/CNF-900 respectively. Apparently, the NVP/CNF-800 shows the highest Na\(^+\) diffusion coefficient among all samples, illustrating a temperature of 800 °C is the best choice to generate an architecture of the composite favorable for promoting the most efficient electron/ion transport channel.

To investigate the kinetics of the electrode process, the electrochemical impedance spectroscopy (EIS) was carried out. The Nyquist plots and equivalent circuit of the three samples are presented in figure 5(a). All curves display a semicircle in the high frequency region and a sloping line in the low frequency region, corresponding to charge-transfer impedance \( (R_{ct}) \) and Warburg impedance \( (Z_w) \), suggesting that the electrochemical process is controlled by both charge transfer and sodium ion diffusion \([45, 46]\). Based on the fitted results of simulated equivalent circuit in table S1 (Supporting Information), the \( R_{ct} \) of the NVP/CNF-800 (110.4 \( \Omega \)) is much smaller than that of the NVP/CNF-700 (247.7 \( \Omega \)) and NVP/CNF-900 (571.5 \( \Omega \)) electrodes. These results suggest that optimizing the calcination temperature is needed to obtain the most effective charge transfer kinetics.

The morphology of NVP/CNF-800 after 1000 charge/discharge cycles at 2 C was observed by SEM. As displayed in figure 6(a), the NVP/CNF almost keeps its original structure and appearance. This result further suggesting the excellent cycling performance of the NVP/CNF-800 are attributed to its 1D nanofibers constructed 3D network structure, which significantly restrains volume expansion during successive charge/discharge processes on the structural stability. The NVP/C composite fiber membrane is schematically illustrated in figure 6(b). Such superior electrochemical performance of the NVP/CNF-800 electrode can be ascribed to the synergistic effects of 0D NVP nanoparticles, 1D CNF, and 3D interconnected CNF network. First, the resulted network provides a variety of advantages, such as a high interface between the liquid electrolyte and solid electrode, short diffusion pathway of Na\(^+\)/e\(^-\) and high conductivity along the percolating fibers. Secondly, the 3D conductive networks not only can improve the conductivity of Na\(_3\)V\(_2\)(PO\(_4\))\(_3\), but can also effectively limit the aggregation of nanoparticles during repeated charge/discharge cycles. Furthermore, such self-standing electrodes simplify the cell packing process by avoiding the use of auxiliary additives and current collectors. As a result, both energy density and power density of SIBs are improved.
4. Conclusions

In summary, 3D flexible Na$_3$V$_2$(PO$_4$)$_3$/C fiber membranes were successfully prepared by electrospinning and hot-press processes. The resulted membranes were used as self-standing cathode for Na-ion batteries. The membranes were prepared by using PVA as carbon source. Three different solids were obtained by calcination at various temperatures (e.g. 700, 800, and 900 °C). The NVP/CNF-800 showed an initial charge capacity of 109 mA h g$^{-1}$ and Coulombic efficiencies of 92% at a current density of 0.1 C. Even at an extremely high current density of 30 C, a remarkably reversible and stable capacity of 71 mA h g$^{-1}$ was noticed. In addition, the NVP/CNF-800 exhibited a noteworthy cycle stability at 2 C with 95.3% retention of its initial capacity after 1000 cycles. These outstanding results are associated with the carbon nanofibers network, which seems to play several roles, such as (i) increasing the electrolyte/electrode interface, (ii) shortening the conduction pathways, which effectively facilitates the diffusion of Na$^+$ ions, (iii) preventing the aggregation of Na$_3$V$_2$(PO$_4$)$_3$ nanoparticles while enhancing their conductivity. Furthermore, these flexible membranes can be directly used as working electrodes, without conducting additives, binders and current collectors. This way, it does not only simplify the electrode preparation process, but also improves the energy density of SIBs. Our results suggest that 3D flexible Na$_3$V$_2$(PO$_4$)$_3$/C fiber membranes are promising electrode materials for sodium-ion cells.

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