



Room-temperature pre-reduction of spinning solution for the synthesis of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanofibers as high-performance cathode materials for Na-ion batteries

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ABSTRACT

The continuous and uniform $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanofibers are successfully synthesized through room-temperature pre-reduction with oxalic acid assisting electrospinning method for the first time. With the reduction and chelation of oxalic acid in the spinning solution, the V^{5+} can be reduced to V^{3+} , and the viscosity and conductivity of the solution are well modified, so that the precursor and the final product nanofibers have more uniform, surface-smooth morphologies without spindle-like protrusions. The sample shows the well-crystallized rhombohedral $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ phase and excellent electrochemical performances. The initial discharge specific capacity of the sample at 0.05C reaches up to 114.0 mAh g^{-1} and still remains 78.1 mAh g^{-1} at 10C rate. The capacity retention after 100 cycles at 0.05C still holds 97.0%, and the coulombic efficiency is always close to 100%. The causes that the $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanofibers exhibit good rate performances, cyclic ability and structural reversibility can be mostly ascribed to the perfect nanofibers. The uniform and smooth $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanofiber consists of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanoparticles uniformly embed in the perfect 1D carbon nanowire, which builds up a continuous network with highly efficient electronic and ionic channels, thus the impressive properties can be realized.

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1. Introduction

In the foreseeable future, the development of high-performance energy storage devices is an indispensable link in the use of renewable energy. With the increase in the demand for energy storage, and the problem of lithium resource shortage is increasingly obvious, sodium-ion battery is expected to become a prospective substitute [1–3]. Sodium-ion batteries have gained extensive attention due to their low cost and relatively high abundance of sodium in the earth's crust [4,5]. However, the working voltage of Na-ion batteries is generally lower than that of Li-ion batteries ($E_{\text{Na}/\text{Na}^+}^0 = -2.71 \text{ V}$, $E_{\text{Li}/\text{Li}^+}^0 = -3.04 \text{ V}$ vs. S.H.E.), and the radius of sodium ion (1.02 \AA) is larger than that of lithium ion (0.76 \AA). Therefore, considerable attention has been paid to find suitable electrode materials with sufficiently large interstitial space to accommodate sodium ions and to enable rapid and reversible ion insertion and extraction.

Actually, many materials have been studied as active materials for cathodes, including layered structure oxides [6,7], phosphates [8–10], fluorophosphates [11–13], pyrophosphates [14–16], etc. Among them, the charge and discharge platform of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ at around 3.4 V (vs. Na/Na^+), is comparatively high. NASICON-type $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ owns fast channels for Na-ion embedding and de-embedding, which is derived from the skeleton of the three-dimensional structure consisting of $[\text{VO}_6]$ octahedron and $[\text{PO}_4]$ tetrahedron [17–20]. Thus, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ with relatively high ionic conductivity and good structural stability is expected to be a promising cathode material for Na-ion batteries. Despite the above advantages, the intrinsic low electronic conductivity of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ limits its excellent electrochemical performance. Generally speaking, the electrochemical properties of the cathode materials can be notably enhanced by coating electronically conductive materials (typically carbon) [21–24]. In addition, reducing the particle sizes of the materials can effectively shorten the migration paths for electrons and sodium ions [22,25]. Thus, for the material itself, nanocrystallization is one of important methods to improve the rate performance. Nowadays, because of its simplicity, convenience

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and environmental friendliness, electrostatic spinning as a versatile way to obtain nano-sized materials has been widely recognized. Significantly different from other methods (solid state method [26,27], sol-gel method [17,28] and soft template method [29], etc.), network-like nanowires can be directly collected by using electrospinning. Nanoparticles can be encapsulated *in-situ* by a one-dimensional carbon shell, increasing conductivity and reducing structural damage during the charge and discharge processes. Moreover, a conductive network structure can be built up with the one-dimensional nanofibers, which will provide fast channels for ions transport of electrode materials. This method has been successfully applied in the preparation of lithium-ion battery materials such as LiFePO_4 [30], $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [31,32], $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [33], and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [34,35], resulting in effectively improved electrochemical properties.

Recently, it has been reported that nano-sized $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite can also be synthesized by electrospinning method. For example, Liu et al. [36] prepared short nanofibers $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ by electrospinning method combined with two-step calcination. Although the nanofiber composite exhibits good cycling stability at high current rates, the specific capacities are not ideal (71 mAh g^{-1} at 5C for pure $\text{Na}_3\text{V}_2(\text{PO}_4)_3$). Kajiyama et al. [37] synthesized oriented nanoparticles $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ confined in a one-dimensional carbon sheath through an electrospinning method. The $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanowires are longer than those reported by Liu [36], but the nanowires with large variations in diameter show unsatisfactory capacity and cycle performance at high currents. Li et al. [38,39] utilized electrospinning to obtain $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite with improved electrochemical performances, but the composite morphology cannot maintain intact nanofibers after heat treatment substituted by willow branches shaped nanofibers or smooth-faced nanorods. Based on above results, it is obvious that the continuous and intact nanofiber morphology cannot be well maintained after calcination, and the properties of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, especially high rate capability, need further improvement. However, morphological control is a key point to improve electrochemical properties of electrode materials, and the morphology of electrospun nanofibers can be significantly affected by the compositions and properties of the spinning solution. The effects of the composition and properties of the spinning solution are mainly reflected in the corresponding viscosity and conductivity, which have significant impacts on the nanofiber morphology [38–41]. Thus, in order to obtain uniform and continuous $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanofibers with excellent performances, the balance point of solution viscosity and conductivity should be controlled.

Considering the above factors, this paper proposes, for the first time, room-temperature pre-reduction of the spinning solution to modify the nanofiber morphology and to enhance the material performances. Room-temperature pre-reduction for solid phase preparation of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ has been demonstrated to provide excellent electrochemical performance at low cost [42–44]. As the universal vanadium source of raw materials is pentavalent (NH_4VO_3 used herein), vanadium should be reduced to trivalent before the $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ crystallization, meanwhile, polyoxovanadate structure formed in the precursor nanofibers must be broken during the synthesis process of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, leading to the limit in the $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ crystallization. Thus, an organic acid addition (oxalic acid) is selected as a reductant, complexing agent and carbon source to pre-reduce and adjust the spinning solution. At room temperature, pentavalent vanadium ion can be reduced by oxalic acid before electrospinning. Furthermore, the roles of oxalic acid in the spinning process are discussed in detail, containing the effects on the spinning solution viscosity and conductivity, the nanofiber morphology and the electrochemical performances. With the additive oxalic acid, smooth, continuous and uniform $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$

nanofibers can be successfully synthesized, and superior rate capability and cycling ability are achieved.

2. Experimental

2.1. Synthesis of materials

The $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanofibers were prepared by electrospinning method after pre-reduction of spinning solution at room temperature. The raw materials were analytical grade without any further purification. The preparation processes are as follows: firstly, oxalic acid was dissolved in deionized water to obtain a homogeneous solution (0.15 mol L^{-1} , 30 mL) at room temperature. Then, NaH_2PO_4 and NH_4VO_3 (stoichiometric ratio = 3: 2) were added to the oxalic acid solution. A green solution was obtained after continuously stirring at 70°C for 2 h, denoted Solution I. Polyvinylpyrrolidone (PVP K90, MW = 1,300,000) was dissolved in deionized water and stirred at room temperature for 2 h. The PVP solution (1.5 g mL^{-1} , 30 mL) was designated as Solution II. Solution I was slowly poured into solution II and then vigorously stirred for 2 h to ensure uniformity of the final spinning solution. After the above steps, the spinning process is carried out as shown in Fig. 1. The spinning solution was injected into a 5 mL plastic syringe with a stainless steel needle. The inner diameter of the stainless steel needle was 0.6 mm and the rate of the injection was 0.05 mL min^{-1} . There was a voltage difference of 12 kV between the spinning liquid ejection port and the aluminum foil collector at a distance of 25 cm. The precursor fibers were collected and then dried in air at 120°C for 12 h. Then the dried fibers were heated up to 800°C in a tube furnace with a ramp rate of $2.5^\circ\text{C min}^{-1}$ and held for 10 h in Ar atmosphere. After cooling to room temperature, $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite nanowires were removed from the tube furnace. In contrast, a yellow spinning solution without oxalic acid addition was prepared. Electrospinning and heat treatment were then carried out under the same conditions.

2.2. Characterization

The viscosities of the spinning solutions were characterized at 25°C by a viscometer (LICHEN, NDJ-8S). The electrical conductivities of the spinning solutions were measured at 25°C using a conductivity meter (YUEPING, DDS-307). The crystallographic information of the $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ material was determined by X-ray diffraction (XRD, Rigaku, ultima VI) with Cu $K\alpha$ radiation. The scanning electron microscopy (SEM, Hitachi SU5000) with energy dispersive spectrometer (EDS) was carried out for morphology analysis. And the HRTEM images was obtained by high resolution transmission electron microscopy (HRTEM, FEI, Tecnai G2 F20). The chemical state of the precursor was analyzed using X-ray photoelectron spectroscopy (XPS) (ESCALAB 250 XI). The carbon concentrations were analyzed by C-S analysis (Eltar, Germany).

2.3. Electrochemical measurements

The cathode electrode was fabricated with the active material, acetylene black and binder poly (vinylidene fluoride) in a weight ratio of 8:1:1 by using N-methylpyrrolidone (NMP) solvent with an aluminum foil as a current collector. The typical positive loading density is 2.5 mg cm^{-2} . The CR2025 coin-type cell was assembled in an argon-filled globe box using the electrode dried in vacuum for 12 h at 120°C , a metallic sodium foil as a counter and a glass fiber (Whatman GF/A) as a separator. NaClO_4 (1 M) dissolved in propylene carbonate (PC) and FEC (1:0.05 in volume) was used as the electrolyte. The galvanostatic charge and discharge were characterized on a LAND instrument at room temperature ($\sim 25^\circ\text{C}$). The

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