

Full paper

TiNb₂O₇ hollow nanofiber anode with superior electrochemical performance in rechargeable lithium ion batteries



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ABSTRACT

Hollow microstructure always exhibits some special properties in the field of electrochemistry. Here, this study reports the rational design and preparation of TiNb₂O₇ nanofibers with one dimensional hollow structure via co-electrospinning. The as-electrospun TiNb₂O₇ hollow nanofibers show high intercalation potential, low charge-charge resistance and fast electrochemical kinetics. The electrochemical results exhibit that the TiNb₂O₇ hollow nanofibers deliver a reversible capacity of 210.1 mAh g⁻¹ after 150 cycles at a current rate of 0.4 C, and 158.4 mAh g⁻¹ after 900 cycles even at a current rate of 10 C with an outstanding capacity retention of 80.6%. The excellent electrochemical performance of nanofibers can be related to the unique morphology of hollow structure. Furthermore, the lithium ions storage mechanism of TiNb₂O₇ hollow nanofibers is also systematically analyzed, which is related to one two-phase coexistence and two solid-solution processes during the whole charge-discharge cycle. In addition, it is also demonstrated by in situ and ex situ observations that TiNb₂O₇ hollow nanofibers have outstanding structural stability and electrochemical reversibility. Therefore, the TiNb₂O₇ hollow nanofibers can be applied as an alternative promising electrode material for the next rechargeable lithium ions batteries.

1. Introduction

Rechargeable lithium ion batteries (LIBs) for electrochemical energy storage embody several principals of green chemistry. Therefore, efforts have been devoted to explore appropriate electrode materials with the properties of good safety, low toxicity, long cycling life and high specific capacity which will provide technologies toward a sustainable future. Graphite that has been an excellent anode material is the main anode material in traditional commercial LIBs owing to its low cost, structural stability and good specific capacity [1]. However, the application of graphite is confined to its poor rate performance and low operating potential plateau of about 0.1 V (versus Li/Li⁺), which may lead to the formation of the solid electrolyte interface (SEI) film even the problem of the risk for lithium plating [1–4]. To solve this problem, many alternative insertion hosts such as TiO₂ [4–8], LiCrTiO₄ [9–11] and Li₄Ti₅O₁₂ [12–14] have been proposed and developed so far. Among multitudinous alternative materials, spinel Li₄Ti₅O₁₂ has drawn great attention due to its availability, good thermal stability and structure stability during the cycling process. As compared to the graphite, spinel Li₄Ti₅O₁₂ can perfectly avoid the formation of the SEI

film because of its high operating potential plateau at approximately 1.5 V [11–13]. Unfortunately, the poor electronic conductivity and low specific capacity of Li₄Ti₅O₁₂ have limited its application [11]. TiO₂, including anatase, rutile and TiO₂-B, is also one of the most famous metal oxide-based intercalation anodes for LIBs due to its availability and low toxicity. However, TiO₂ shows the poor high-rate properties and cyclability [6–8]. As a consequence, exploring some new anode materials is a constant task for battery researchers and material chemists because of the increasing requirements for high power density and large energy density of LIBs.

Recently, the pseudo-binary system TiO₂-Nb₂O₅ such as TiO₂-Nb₂O₅ (TiNb₂O₇) [1,15–37], 2TiO₂-Nb₂O₅ (Ti₂Nb₂O₉) [38], TiO₂-3Nb₂O₅ (TiNb₆O₁₇) [39,40], 2TiO₂-5Nb₂O₅ (Ti₂Nb₁₀O₂₉) [41–44], and TiO₂-12Nb₂O₅ (TiNb₂₄O₆₂) [45] has been the research interest of many battery researchers. Among the pseudo-binary system TiO₂-Nb₂O₅, TiNb₂O₇ has been considered as a promising anode candidate to replace spinel Li₄Ti₅O₁₂ due to its multiple redox couples of Ti⁴⁺/Ti³⁺, Nb⁵⁺/Nb⁴⁺ and Nb⁴⁺/Nb³⁺ [1,15–37], and it shows the similar electrochemical behavior to TiO₂-B [8]. On the base of these multiple redox couples, the TiNb₂O₇ material can deliver a high

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theoretical capacity of 387.6 mAh g^{-1} , which is close to the theoretical capacity for the traditional graphite anode material and surpasses that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [20] and TiO_2 [4–8]. However, TiNb_2O_7 prepared by traditional solid state method usually requires high temperature above 1000°C and possesses low surface area, which leads to the unsatisfactory electrochemical performance [17,20,35]. Hence, researchers have tried various methods to prepare TiNb_2O_7 with a smaller size like nanostructure in order to conquer these barriers. Jo et al. reported a block copolymer assisted self-assembly method to prepare ordered mesoporous TiNb_2O_7 [18]. Park et al. reported a solvothermal reaction to obtain porous TiNb_2O_7 microspheres [21]. Though these methods (including hydrothermal method, solvothermal method, electrospinning and so on) can prepare nanomaterials successfully, electrospinning can be an inexpensive, simple and versatile way to generate nanofibers [46–48]. In addition, nanofibers with a small size can improve the capacity and cyclability effectively due to its short Li^+ insertion/extraction distance, facile strain relaxation and large surface [46–49]. Furthermore, nanofibers can also keep away from the self-aggregation of nanoparticles to some degree [46], so that nanofibers have appeared to be interesting among battery researchers and material chemists.

Although the preparation of TiNb_2O_7 nanofibers using electrospinning technique has been reported [28–33], less work has been done to investigate the electrochemical properties of TiNb_2O_7 hollow nanofibers and a comparison of lithium storage performance between TiNb_2O_7 hollow nanofibers (denoted as HTNO) and TiNb_2O_7 nanofibers (denoted as TNO). More importantly, hollow nanofibers exhibit larger surface area than nanofibers. Herein, we report a facile coelectrospinning method to synthesize HTNO. By comparing the electrochemical performance of TNO anode material, HTNO shows a higher reversible specific capacity. Additionally, to realize the lithium ions storage mechanism of HTNO upon cycling, an in-situ XRD technique is also used in this work.

2. Experimental section

2.1. Synthesis of materials

One-dimensional TiNb_2O_7 hollow nanofibers were fabricated by one-step dual-nozzle coaxial coelectrospinning followed by calcinations, as described in a previous study [50]. The synthesis route is schematically depicted in Fig. 1. For the preparation of the outer sol solution, the carrier polymer solution based on poly(vinylpyrrolidone) (1.80 g; M_w : 1,300,000; Aladdin) dissolved in ethanol (5 mL) and N,N -dimethylformamide (1 mL) was mixed with a solution containing titanium(IV) butoxide (0.65 g, Aladdin), niobium(V) ethoxide (1.51 g, Aldrich), ethanol (3 mL) and N,N -dimethylformamide (1 mL), and acetic acid (4 mL) at room temperature. Then, the yellow outer sol

solution was obtained. In a similar way, poly(acrylonitrile) (1.40 g; M_w : 150,000; Aladdin) was dissolved in N,N -dimethylformamide (10 mL) with vigorous stirring for 24 h to prepare the colorless inner sol solution. For comparison, the TiNb_2O_7 nanofibers were also prepared by co-electrospinning followed with calcinations. The preparation of the outer sol solution was described as mention above. The inner sol solution was replaced by the aforementioned the outer sol solution.

The co-electrospinning setup is shown in Fig. 1. Two precursor solutions were loaded into two separate syringes, respectively. One syringe was connected to the inner needle (0.7 mm in diameter) and the other syringe was connected to the outer needle (1.4 mm in diameter) of the concentric nozzles. The flow rates of the inner and outer solutions were 0.2 and 0.6 mL h^{-1} , respectively. Electrospinning experiments were performed with a distance of approximately 15 cm between the needle tip and the round stainless steel collector. A voltage of 15 kV was applied to the needle tip and the round stainless steel collector.

The as-collected precursor fibers were calcined in air at 800°C at a heating rate of 3°C min^{-1} for 9 h in order to remove the carrier polymer and obtain the TiNb_2O_7 hollow nanofibers and TiNb_2O_7 nanofibers.

2.2. Materials characterization

Material morphology was collected with a Hitachi SU-70 scanning electron microscope (SEM). High-resolution transmission electron microscopy (HRTEM) images were recorded by using a JEOL JEM-2010 microscope. The crystal structure was characterized by X-ray diffraction (XRD) (Bruker D8 Focus), using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). In-situ XRD measurements were also characterized by using the aforementioned XRD equipment. The in-situ cell for XRD observation was described in previous reports [51,52]. The slurry was directly cast on the metallic Be disk.

2.3. Electrochemical measurements

The electrochemical performance was evaluated in the CR2032 type coin cells with lithium foil as the anode. The working electrodes were fabricated by mixing the active materials, carbon black and poly(vinylidene difluoride) binder, at a weight ratio of 8:1:1. The slurry made by using N -methyl pyrrolidone as the solvent was uniformly cast onto a copper foil. Then, the electrodes were dried in a vacuum oven at 100°C for 24 h. The mass loading of active materials was about 1.5 mg cm^{-2} . All the coin cells were assembled in an argon-filled glove box. Glass fibers from Whatman were used as separators. The electrolyte used was a 1 mol L^{-1} LiPF_6 in ethylene carbonate/dimethyl carbonate (at a volume ratio of 1:1) solution.

Charge-discharge behaviors were tested on a LANHE CT2001A

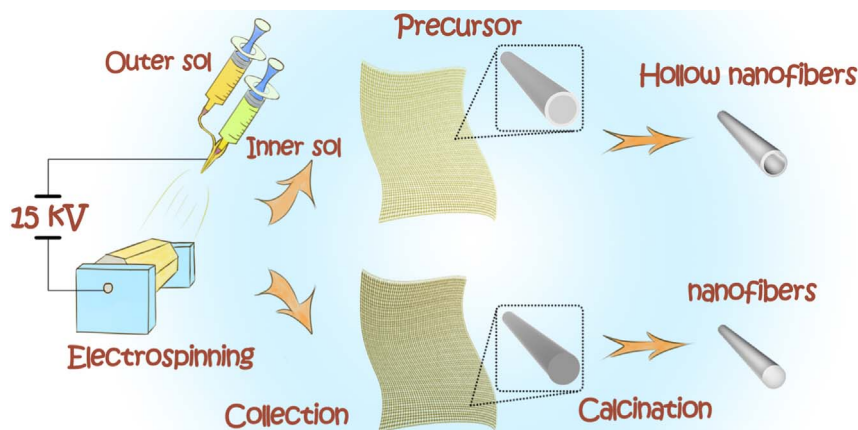


Fig. 1. Schematic illustration of the preparation and formation of hollow TiNb_2O_7 nanofibers (denoted as HTNO) and TiNb_2O_7 nanofibers (denoted as TNO).

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