Ultra-long BiNbO$_4$ nanowires with hierarchical architecture exhibiting reversible lithium storage

Guangxia Tang[1], Haojie Zhu[1], Haoxiang Yu, Xing Cheng, Runtian Zheng, Tingting Liu, Jundong Zhang, Miao Shui, Jie Shu[*]

Faculty of Materials Science and Chemical Engineering, Ningbo University, No. 818 Fenghua Road, Jiangbei District, Ningbo 315211, Zhejiang Province, People's Republic of China

ABSTRACT

With the development of science and technology, lithium ion batteries have become a representative of modern high-performance batteries due to their excellent performance. In this work, BiNbO$_4$ with the nanowire morphology is fabricated by a simple electrospinning method on a stainless steel mesh cage collector. Here, we demonstrate that the BiNbO$_4$ nanowires display a reversible capacity of 165 mAh g^{-1} and remarkable cycling stability at a current density of 50 mA g^{-1}. When cycled at 700 mA g^{-1}, BiNbO$_4$ nanowires can maintain the capacity retention of 60% after 700 cycles, revealing better cycling properties than other Bi-based anode materials. In addition, in-situ X-ray diffraction analysis suggests that BiNbO$_4$ nanowires have good electrochemical reversibility. BiNbO$_4$ is transformed into Bi nanocrystallites and Li$_3$NbO$_4$ during the first discharge process. With the continuation of the discharge, active Bi nanocrystallites react with lithium ions to form Li$_3$Bi alloys. This is a reversible process that provides reversible capacity as the reaction proceeds.

1. Introduction

Thanks to the rapid development of electric vehicle technology, mobile communication technology and aerospace technology, as well as the requirements of a low-carbon economy, lithium ion batteries with high capacity and good cyclability have attracted great attention [1–5]. Among rechargeable batteries, lithium ion batteries belong to a kind of environmentally friendly energy storage devices with high specific capacity. In addition, the average output voltage is about 3.6 V, which is three times the average output voltage of Ni-Cd and Ni-MH batteries. It is these advantages that contribute to the widespread use of lithium ion batteries in various fields. The development of lithium ion batteries depends mainly on the choice of anode materials [6–8]. In the past, due to the great cycling performance and moderate price, graphite as a common commercial anode material satisfies quite a few requirements for use in commercial lithium ion batteries [9]. Nevertheless, there are still many problems in the application of graphite, such as the impurities in graphite which may cause the occurrence of side reactions and the failure of capacity [10–14]. Therefore, to meet the growing demand of the energy storage systems, people must develop anode materials with good performance.

In the published reports, a great number of studies have shown that transition metal oxides (TMOs) can be used as effective alternatives to conventional graphite anodes [15]. Some TMOs typically have theoretical capacities of over 600 mAh g^{-1}, which provide large storage capacities compared to traditional graphite anodes. Such as TiO$_2$, Co$_3$O$_4$ and Fe$_2$O$_3$, all have higher lithium ion storage capacity [16–22]. However, their poor conductivity severely limits electron transport and results in a series of problems such as rapid capacity decay and poor rate capability. To better solve these problems, scientists have found that binary metal oxides and ternary metal oxides have good performance in all aspects and can be used as possible anode materials [23–25]. So far, many materials have been proposed and developed, such as LiCrTiO$_4$ [26–28], TiNb$_2$O$_7$ [29, 30] and LiNbO$_3$ [31]. Through extensive research on these multiple oxides, we have found that BiNbO$_4$ nanowires exhibit excellent electrochemical performance as anode materials.

In this paper, BiNbO$_4$ precursor is prepared by electrospinning method. The precursor is calcined in the muffle furnace at 800 °C for 12 h to get the BiNbO$_4$ nanowires. The obtained one-dimensional BiNbO$_4$ nanowires have a large surface area and the contact area with the electrolyte increases. In particular, one-dimensional nanowire morphology shortens the ion-diffusion path and makes the reaction kinetics better [32–36]. Due to the aforementioned merits, the BiNbO$_4$

---

nanowires have a high reversible capacity of $155\,\mathrm{mAh\,g^{-1}}$ at a current density of $100\,\mathrm{mA\,g^{-1}}$. The $BiNbO_4$ nanowires also exhibit cycling stability and superior rate capability due to the large surface area and the short diffusion distance. Moreover, in-situ X-ray diffraction is also used to investigate the lithium storage mechanism of $BiNbO_4$, and it shows that the reversible capacity of $BiNbO_4$ is attributed to the alloying/dealloying reaction during the lithiation/delithiation processes.

2. Experimental section

2.1. Synthesis of materials

The raw $BiNbO_4$ sample was fabricated by a simple electrospinning way. For the preparation of the precursor solution, 2.1 g polyvinylpyrrolidone (PVP; MW: 1300000; Macklin) was dissolved in 16 mL of absolute ethanol (99.8%, Macklin) and 5 mL of deionized water for 12 h with magnetic stirring. Subsequently, bismuth nitrate pentahydrate (AR, Aladdin) and niobium oxalate (98%, Macklin) were dissolved in the above mixture, a transparent solution was obtained after constant stirring for 12 h. After that, the resulting solution was charged into two 10 mL plastic syringes with needle (dia. 21G). The solution was continuously sprayed from the tip of needle at a rate of $1\,\mathrm{mL\,h^{-1}}$ and collected by a stainless steel mesh cage at a distance of 20 cm from the tip. Finally, the collected sample was calcined at 800 °C for 12 h in the muffle furnace to obtain $BiNbO_4$ nanowires.

2.2. Material characterization

The crystal structure of the $BiNbO_4$ sample was studied using the Bruker D8 X-ray diffraction, and the scanning angle 2θ of Cu-Kα radiations (λ = 1.5406 Å) was 10° to 60°. The aforementioned device is also used in in-situ XRD measurements. Moreover, the in-situ cell for XRD observation was described in detail in previous reports [37, 38]. The surface morphology and crystal structure of $BiNbO_4$ was observed by using scanning electron microscopy (SEM, Hitachi SU-70) fitted with an energy dispersive spectrometer (EDS).

2.3. Electrochemical measurements

For the study of electrochemical properties, 80 wt% $BiNbO_4$, 10 wt % carbon black conductive additive (10–20 nm, Ningbo ShanShan) and 10 wt% polyvinylidenefluoride (PVDF-5130, Solvay) were mixed in *N*-methyl-2-pyrrolidone (NMP, Macklin) solvent, and then the resulting slurry is uniformly poured onto the current collector (copper foil) to obtain a working electrode. Then the electrode was dried at 80 °C for 24 h to remove moisture. The mass of $BiNbO_4$ is about $2\,\mathrm{mg\,cm^{-2}}$. A half-cell was prepared by using the $BiNbO_4$ electrode as a working electrode, lithium metal foil as a counter electrode, and Whatman fiber as the separator, wherein $LiPF_6$ (concentration is $1\,\mathrm{mol\,L^{-1}}$) dissolved in a mixture of dimethyl carbonate and ethylene carbonate (1:1 in volume) as an electrolyte.

The discharge/charge performance of the batteries was tested in the potential range of 1.0–3.0 V using a multi-channel LANHE CT2001A battery test instrument. Electrochemical impedance spectroscopy (EIS) analysis was performed on a CHI 660D electrochemical workstation with a frequency range of 10^{-2}–10^5 Hz. Cyclic voltammetry (CV) was tested on the CHI1000B electrochemical workstation.

3. Result and discussion

The synthesis process of $BiNbO_4$ nanowires is schematically illustrated in Fig. 1a. The bismuth niobate dispersed in PVP solution is loaded into two syringes, which are driven by separate pumps. Owing to the simultaneous operation of the two syringes, the fibers are uniformly covered on the collector during the electrospinning process. This not only helps to obtain an electrospun precursor with uniform

thickness (Fig. 1b), but also facilitates the outward extension of the electrospun fibers during the subsequent calcination. It can be seen that this study uses a hollow stainless steel mesh cage as the collector. At room temperature, the hollow collector is more conducive to the uniform evaporation of the solvent such as ethanol in the precursor fiber membrane than the traditional solid rounded roller. Then, the obtained precursors are calcined in a muffle furnace at 800 °C for 12 h and cooled down in the furnace to ambient temperature. In the calcination process, PVP and solvent in the electrospun precursors gradually decompose and volatilize to form the $BiNbO_4$ nanowires with uniform thickness (Fig. 1c).

The Rietveld refinement profile of $BiNbO_4$ is presented in Fig. 2a. All the reflections observed are clearly marked in the 2θ range of 10° to 60°. These diffraction reflections can be indexed to the orthorhombic system of $BiNbO_4$ using the Pnna (52) space group (JCPDS card No. 82-0348). Furthermore, there is no obvious impurity phase in the resulting sample XRD pattern. Based on the Rietveld refinement curve of $BiNbO_4$, it can be seen that the reflection intensity difference between the standard XRD curve and the experimental XRD curve of $BiNbO_4$ is small. More importantly, the lattice parameters of the sample can be obtained by using contour matching refinement. The lattice parameters of the sample (a = 5.673 Å, b = 11.714 Å and c = 4.978 Å) are very close to the standard value reported, which further indicates that the above sample is pure phase. Fig. 2b displays the crystal structure of $BiNbO_4$ in which the pink octahedrons arrange linearly on the a-axis represent $[NbO_6]$ octahedrons. At the same time, these $[NbO_6]$ octahedrons are sharing corners.

The SEM images of the precursors of $BiNbO_4$ nanowires before calcination are shown in Fig. 3a–c. It can be seen that the average diameter distribution of the precursor with the smooth surface is about 700 nm. Because the spinning nozzle is curved and unstable, these fibers are randomly arranged. Fig. 3d–f show the SEM images of $BiNbO_4$ nanowires prepared by calcining at a temperature of 800 °C for 12 h. Compared with the precursor, the outline of the calcined products is still present, but the surface morphology of the calcined products displays a palpable change. Obviously, the diameter of the calcined products is reduced to about 300 nm. Besides, after removing the PVP polymer, those nanowires show the rough surface. Fig. 3g–j display the EDS elemental mapping images of the $BiNbO_4$ nanowires. As can be seen, Bi, Nb, and O elements are uniform distributed in the mapping images, indicating the homogeneous phase of the sample.

In order to evaluate the electrochemical performance of $BiNbO_4$ nanowires, lithium foil is used as a counter electrode to evaluate its electrochemical performance between 1.0 and 3.0 V. Fig. 4a displays the CV plot for the first, second, and third cycles of the $BiNbO_4$ nanowires electrodes that are acquired at a sweep rate of $0.1\,\mathrm{mV\,s^{-1}}$ between 1.0 and 3.0 V. The solid black line represents the scan of the first cycle. The cathodic scan is performed during the first discharge (i.e., lithium ions insertion), and the cathode peak begins to appear at 2.2 V (marked "I" in the Fig. 4a). During this period, the anode materials may undergo conversion reaction in which lithium ions enter the materials and displace Bi^{3+}, then shape a new phase (Bi nanocrystallites). In the next two scans, as lithium ions continue to enter, more Bi^{3+} are separated into new phases and the potential moves to 2.1 V. Subsequently, another cathode peak begins to appear in the region of the first cycle labeled (II). The newly formed part of the Bi phase begins to undergo an alloying reaction with the continuously inserted lithium ion to form the Li_3Bi alloy. At the same time, the solid electrolyte interface (SEI) film formed by the decomposition of organic electrolyte may also have an effect on the generation of the cathode peak. Upon further discharging the cell, a significant cathode peak (III) is observed at 1.5 V (cathode scan). As can be seen from Fig. 4a, there is a relatively high current peak during the first cycle in this region, and the strong peak disappears during the second and third cycles. It indicates that there may be more than one reaction at the same time. This apparent cathode feature may be related to the irreversible partial reduction of Bi^{3+}. Meanwhile,