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Topotactically synthesized TiO_2 nanowires as promising anode materials for high-performance lithium-ion batteries

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Abstract

Anatase TiO_2 nanowires (ATN) have been successfully synthesized via a topotactic chemical transformation. The as-prepared ATN have an average diameter of around 30 nm with 1-2 micrometers in length. The electrochemical properties are investigated by constant current discharge/charge measurements. When charged at a rate of 150 mA g^{-1}, the initial discharge capacity is about 400 mAh g^{-1}, a reversible capacity of 168 mAh g^{-1} was retained after 100 charge-discharge cycles,. This method is shown to be an effective and facile technique for improving the electrochemical performance for applications in rechargeable LIBs. The TiO_2 nanowire was shown to be a promising anode material for lithium-ion batteries, especially on the fast charging and discharging performance.

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Keywords: TiO_2 nanowires, electrical transport, electrochemical behavior, anode, lithium-ion batteries

1. Introduction

Currently, lithium-ion batteries (LIBs) have been become the research hot topic for various electronic devices application, such as, mobile phone and hybrid vehicles [1-3]. Among various electrode materials, TiO_2 anode materials recently received considerable attention due to their relatively high specific capacity and cycling stability compared to commercial graphite anode material [4-7]. It is well-known that superior anode materials should have two important prerequisite conditions, namely, good conductivity and idea microstructure for lithium-ion diffusion. However, TiO_2 has intrinsic poor conductivity determined by its electronic structure. Therefore, providing idea charge transfer and fast lithium-ion diffusion pathways would be highly desired.

Nowadays, one-dimensional nanomaterials, for example, nanowires, nanotubes, nanorods and nanoribbons, have been widely acceptable in the fields of LIBs application for these one-dimensional

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nanostructures would provide high specific capacity and enhanced cyclic stability [8-11]. The reason for this is mainly that this unique nanostructure has a high interfacial contact area with the electrolyte for lithium-ion adsorption and transport and better accommodation of strain caused by volume change. Therefore, designing and fabricating TiO_2 nanowire gave us the opportunity to obtain the high-performance LIBs.

Herein, we report the synthesis of TiO_2 nanowires by a typical topochemical synthesis route. This topotactic growth will provide an effective and versatile route to controlled fabrication of nanostructured oxides with optimizable properties. The electrochemical performance of the TiO_2 nanotubes as anode in Li-ion batteries will be presented.

2. Experimental section

The ATN was prepared by hydrothermal reaction of titanium powders with a NaOH aqueous solution. In a typical experiment, about 0.5 g titanium powders were dispersed in 40 mL of 5 mol/L NaOH aqueous solution. After sonication in an ultrasonic bath for 30 min, the solution was transferred to a 100 mL Teflon-lined stainless autoclave. The autoclave was maintained at 180 ℃ for 24 h and then cooled to room temperature naturally. The reaction product was washed with distilled water until a pH=7, and then treated with a solution of 0.1 mol/L HCl for 10 h, and then rinsed with deionized water several times until a pH=7. The washed samples were dried at 80 ℃ for 24 h and ATN were obtained. The electrochemical measurements were carried out according to the previously reported literature.

3. Results and discussion

The XRD pattern of the as-obtained ATN is presented in Fig. 1. The main diffraction peaks are indexed as tetragonal TiO_2 (anatase phase), which is in good agreement with TiO_2 (JCPDS, 71-1167). It should be noted that no other impurities can be observed in the as-made sample.

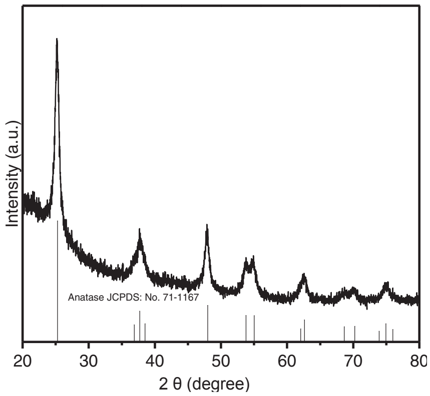

Fig. 1 XRD pattern of as-prepared ATN. The bottom bar represents anatase TiO_2, JCPDS:NO. 71-1167.

The further FESEM images of as-prepared ATN is shown in Fig. 2. It is clearly observed that the as-obtained sample is large-scale and ATN have an average diameter of around 30 nm with 1-2 micrometers in length.

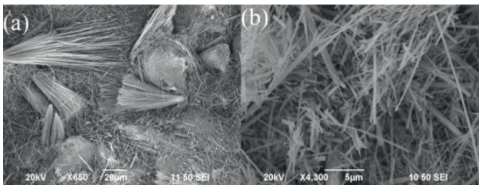

Fig. 2 FESEM images of as-prepared TiO_2 nanowires at different magnifications. (a) low magnification; (b) high magnification.

The detailed the structural analysis of the as-prepared ATN was revealed by TEM and HRTEM characterizations. As shown in Fig. 3 (a), the microscopy of the nanowires is consisted with the results of the FESEM image as shown in Fig. 2. The lattice interplanar spacing has been determined to be 0.35 nm, corresponding to the (101) plane of anatase TiO_2 (Fig. 3 (b)), which further confirms the XRD result. Fig. 3(d) indicated schematically the growth direction of the ATN.

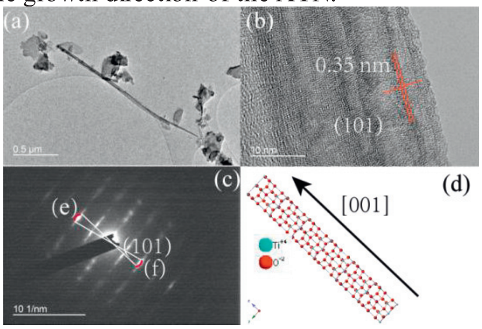

Fig. 3 TEM images of as-prepared ATN. (a) low magnification, (b) HRTEM image and its corresponding SAED. (d) a schematical crystal structure picture of ATN.

Lithium-storage properties of the as-prepared ATN were investigated by Cyclic voltammograms (CV). Fig. 4 shows the CV curves of the electrode made of the ATN at a scan rate of 0.2 mV s^{-1} in the potential range of 1–3 V. In the first cycle, there is a sharp reduction peak at 1.7 V in the cathodic process, which can be assigned to the lithium inserting process of TiO_2 crystal lattice. An obvious oxidation peak was observed at 2.1 V in the anodic scan, corresponding to the lithium extraction from the Li_xTiO_2. The potential gap of 0.4 V indicated good kinetics of fast charge transfer and lithium-ion diffusion during the charge-discharge process.

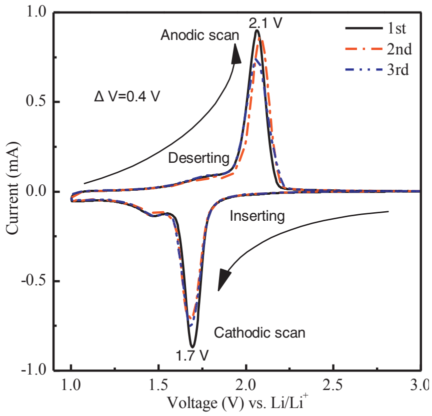

Fig. 4 Cyclic voltammograms of an as-prepared ATN recorded at a scan of 0.2 mV S^{-1}. Voltage range: 1.0 -2.5 V.

Fig. 5 displays the high reversibility of the underlying electrochemical reactions over many charge-discharge cycles. When charged at a rate of 150 mAg^{-1}, the initial discharge capacity is about 400 mAh g^{-1}, a reversible capacity of 168 mAh g^{-1} was retained after 100 charge-discharge cycles, which is comparable to the previously reported experimental results.

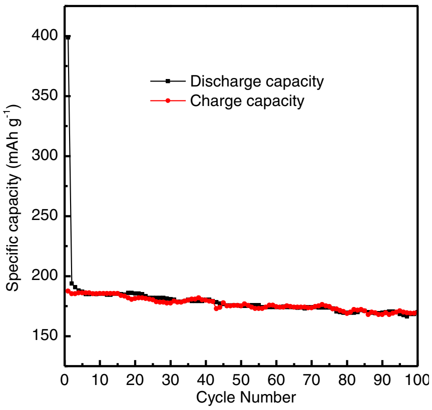

Fig. 5 Charge-discharge cycling measurements for the ATN electrode at a current rate of 150 mA g^{-1}.

4. Conclusions

In summary, we have prepared TiO_2 nanowires via a topochemical synthesis and demonstrated their superior electrochemical properties. The superior electrochemical properties may be attributed to the unique one-dimensional nanowires structure that provides efficient and rapid pathway for ion and electron transport as well as very short solid-state diffusion length.

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Biography

Dr. Hai Wang has been working on the research and development of renewable energy resources, includingsolar energy, and energy-saving devices in China. He has published over 20 conference and journal papers.