Journal of Power Sources 313 (2016) 189–197

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Elaborately prepared hierarchical structure titanium dioxide for remarkable performance in lithium storage

Qinghua Tian [a], Dong Luo [a], Xiaowei Li [a], Zhengxi Zhang [a, c, **], Li Yang [a, b, c, *], Shin-ichi Hirano [b]

[a] School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China
[b] Hirano Institute for Materials Innovation, Shanghai Jiao Tong University, Shanghai 200240, PR China
[c] Shanghai Electrochemical Energy Devices Research Center, Shanghai 200240, PR China

HIGHLIGHTS

- Four hierarchical structures of TiO_2 were prepared by facile routes.
- The unique architecture endowed the TiO_2 superior physical and chemical properties.
- The as-prepared TiO_2 exhibited impressive cycling performance and rate capability.

ARTICLE INFO

Article history:
Received 12 December 2015
Received in revised form
23 February 2016
Accepted 26 February 2016
Available online 19 March 2016

Keywords:
Hierarchical structure
Curved nanosheets
Titanium dioxide
Anode materials
Lithium-ion batteries

ABSTRACT

Titanium dioxide (TiO_2) has been considered to be a promisingly alternative anode material for lithium-ion batteries and thus attracted wide research interest. But, its practical application in lithium-ion batteries is seriously impeded by low capacity and poor rate capability. In the present work, the electrochemical performance of TiO_2 is significantly improved by elaborately fabricating hierarchical structures. These as-prepared four hierarchical structure TiO_2 assembled by different building blocks (TO_2-2 h, TO_2-6 h, TO_2-18 h and TO_2-24 h) all exhibit impressed performance. More importantly, the TO_2-6 h constructed by curved nanosheets exhibits the best performance, delivering a capacity of 231.6 mAh g^{-1} at 0.2C after 200 cycles, and capacities of 187.1 and 129.3 mAh g^{-1} at 1 and 10C after even 1200 cycles, respectively. The results indicated that design and fabrication of hierarchical structure is an effective strategy for significantly improving the electrochemical performance of TiO_2 electrodes, and the electrochemical performance of hierarchical structure TiO_2 is heavily dependent on its building blocks. It is suggested that thus excellent electrochemical performance may make TiO_2-6 h a promising anode material for advanced lithium-ion batteries with high capacity, good rate capability and long life.

1. Introduction

Rechargeable lithium-ion batteries (LIB) with both high energy density and long cycling life are the most widely used energy sources for various portable electronic devices and electric vehicles in particular [1–3]. Currently, to meet the exploded global demand for electric vehicles powered by LIBs, it is necessary to further promote the research and development of LIBs from the aspects of energy density, power density, cycling life, and particularly safety issues [4]. As is well known, great efforts have been devoted to find and develop new alternative anode materials to replace the current graphite anode materials, which is mainly ascribed to the prominent disadvantages of graphite anode materials, such as formation of lithium (Li) dendrite at a low Li-intercalation potential (0.1 V vs. Li/Li^+) and decomposition of the SEI film at higher temperatures, can cause short circuiting as well as ignition safety accidents of the batteries [5]. Recently, transition metal oxides and transition metals, such as GeO_2, Fe_2O_3, SnO_2, Sn, Ge, Si and so on, with high capacities from 700 to 4200 mAh g^{-1} and better overcharge protection than graphite anodes, have been widely researched as alternative anode materials to replace the graphite anodes, which is in increasing focus as the solution for preparing the high

* Corresponding author. School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China
** Corresponding author. School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China
E-mail addresses: zhengxizhang@sjtu.edu.cn (Z. Zhang), liyangce@sjtu.edu.cn (L. Yang).

http://dx.doi.org/10.1016/j.jpowsour.2016.02.082
0378-7753/

energy density and safety LIBs [2,6–9]. However, the practical use of these promising transition metal oxides and transition metals anode materials is severely impeded by major difficulties which are attributed to insufficient ions and electrons transport properties and particularly their large even huge volume expansion (more than 300%) during lithiation process, causing the capacity fading quickly, power density poor and cycling life shortened.

Another promising candidate of nanostructural TiO_2 is advantageous due to its small volumetric expansion (below 4%), excellent structure stability, high voltage plateau of above 1.7 V and greater overcharge protection than graphite, hence has attracted great research interest as promising anodes for electric vehicles in consideration of safety [10]. However, there are still some shortcomings of nanostructural TiO_2 should not be ignored, such as low theoretical specific capacity, poor electronic conductivity, and inclined to agglomeration after long-term lithiation/delithiation cycle, which hinder the practical application of nanostructural TiO_2 anode material in LIBs. It can be accepted that the solution for effectively circumventing this limitation is through purposely designed and fabricated satisfying nano/micro hierarchical structures assembled by variously nanosized building blocks with high specific surface area [11]. The nanostructural units can offer enhanced kinetics attribute to shorten Li-ion and electron diffusion distances and large interfacial contact areas, favoring high power density. Micron-sized secondary structures can provide good material stability and high energy density. So, the nano/micro hierarchical electrodes not only retain the advantages of nanometer-sized building blocks, but also possess the merits of nano/micro-sized assemblies [12]. In this regard, besides superior lithium storage, they also ensure less agglomeration and better strain relaxation upon long-term cycling. And then, there are rich pores in nano/micro hierarchical structures derived from the interspaces and interface among building blocks due to the assembly of building blocks is not dense. Absolutely, these porous structures can ensure dramatically high contact interface between the Li-ion hosting materials and the electrolyte, shortened diffusion path for Li-ion and easy accommodation of strain during cycling, ultimately improving the capacity, rate capabilities, high structural stability and longer cycling life. So far, various hierarchically structured TiO_2 anodes have been fabricated and used to improve the electrochemical performance of LIBs, such as hierarchical nanotube-constructed porous TiO_2-B spheres [13], TiO_2 hollow microspheres assembled by nanotubes [14], hierarchical TiO_2 hollow microspheres assembled by nanocrystals [15], porous TiO_2-B constructed by nanosheets [16], self-assembled ultrathin anatase TiO_2 nanosheets [17]. The current research focus of TiO_2 anode materials is to improve the specific capacity, rate capabilities, and long-term cycle life by nanoscale structure design [18]. Therefore, development of facile and reliable strategies for synthesizing TiO_2 with hierarchical architectures constructed by nanometer-sized building blocks and desired performance is indispensable, and it will play a positive role in promoting development of LIBs with high safety, long life and high energy density.

Herein, an interesting hierarchical structure of nano/micro particles constructed by curved nanosheets (denoted as TiO_2-6 h) has been prepared by a facile one-pot hydrothermal assisted with calcination. The roll nanosheets and rich pores or interspaces among the roll nanosheets and particularly in the roll inner surface of curved nanosheets provide this hierarchical nanostructure with larger specific surface area and free space, which can dramatically increase the contact interface between the active material and the electrolyte, shorten the diffusion distance for Li-ion and facilitate the accommodation of strain during cycling, finally resulting in enhanced kinetics. In addition, the secondary structures can prevent the nanosheet units from agglomerating and provide good material stability. Expectedly, the TiO_2-6 h exhibits impressive performance, delivering a capacity of 231.6 mAh g^{-1} at 0.2C after 200 cycles, and capacities of 187.1 and 129.3 mAh g^{-1} at 1 and 10C after 1200 cycles, respectively. To insight into the influence of structures on the electrochemical performance, other three control samples with different nanometer-sized building blocks (denoted as TiO_2-2 h, TiO_2-18 h and TiO_2-24 h, respectively) are prepared, and evaluated under the same conditions with TiO_2-6 h. Finally, it is found that the electrochemical performance of TiO_2 prepared in this work is heavily dependent on its structure. It is suggested that thus excellent electrochemical performance coupled with facile preparation method may make TiO_2-6 h Ns an attractive candidate anode material for lithium-ion battery applications. More importantly, lots of work about hierarchical structure TiO_2 anode materials with improved performance have been reported, but the internal relation between electrochemical properties and building blocks of hierarchical structures was rarely reported. Thus, our study provides valuable insights into the role of optimizing building blocks in improving the electrochemical performance of hierarchical structure TiO_2 anode materials. The results of this work show that the electrochemical performance of hierarchical structure TiO_2 anode materials could be further improved by ration design from building block level. This work may be also used for providing guidance for preparing other hierarchical structure anode materials with improved performance, such as iron oxide and lithium titanate, by optimizing building blocks.

2. Experimental section

2.1. Preparation of TiO_2 sample

In a typical synthesis, 1 mL of tetrabutyl titanate (TBT) was slowly dropped into 60 mL of 0.2 M NaOH aqueous solution containing 0.05 wt% of H_2O_2. After stirring for 0.5 h, the obtained solution was transferred into a Teflon-lined stainless steel autoclave, and then placed in an oven at 180 °C for 2–24 h. After cooled down to room temperature, the white precipitation was collected through centrifugation, washed with deionized water and ethanol thoroughly, followed by re-dispersed in 50 mL of 0.1 M HCl and stirred for 24 h to exchange Na^+ by H^+ completely. After that, the white precipitation was re-collected through centrifugation, washed with deionized water and ethanol thoroughly, and dried in an oven at 70 °C under vacuum for 12 h. Finally, the TO_2-2 h, TO_2-6 h, TO_2-18 h, and TO_2-24 h were prepared through their precursors (obtained from hydrothermal reaction for 2, 6, 18, and 24 h, respectively) calcination at a temperature of 400 °C for 1 h with a ramping rate of 3 °C min^{-1} in air.

2.2. Materials characterizations

The field emission scanning electron microscopy (FE-SEM, JEOL JSM-7401F) and transmission electron microscopy (TEM, JEOL JEM-2010) coupled with an energy dispersive X-ray spectrometer (EDX) and a selected area electron diffraction pattern (SAED) were used to investigate the morphologies and microstructures of the as-prepared samples. The X-ray diffraction measurement (XRD, Rigaku, D/max-Rbusing Cu K radiation), laser Raman spectroscopy measurement (Renishaw in Via), and X-ray photoelectron spectroscopy (XPS) measurement (experiments carried out on an AXIS ULTRA DLD instrument with using aluminum K X-ray radiation) were used to study the crystal structures and compositions of samples. The surface area was