



Layered titanate hierarchical spheres as a promising pseudocapacitive electrode material for high rate lithium ion batteries

Kunxu Zhu^a, Hanyang Gao^b, Guoxin Hu^{a,*}

^a School of Mechanical & Power Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

^b School of Mechanical Engineering, Hangzhou Dianzi University, Xiasha Higher Education Zone, Hangzhou 310018, Zhejiang Province, PR China

ARTICLE INFO

Article history:

Received 20 December 2017

Received in revised form 22 May 2018

Accepted 25 June 2018

Available online 26 June 2018

Keywords:

Lithium ion batteries

Lepidocrocite titanate

Supercritical hydrothermal reaction

Peroxotitanate complex

Electrochemical

Pseudocapacitive

ABSTRACT

Layered titanates with large interlayer spacing (ca. 0.8–0.9 nm) facilitate Li^+ movement with less resistance, and are considered suitable anode materials for high power lithium ion batteries (LIBs). Herein, lepidocrocite-type titanate hierarchical spheres (W-THSs) assembled by nanowires are synthesized by supercritical hydrothermal treatment of sodium peroxotitanate complex solution and subsequent acid washing. Nanowire components in the W-THSs interpenetrate each other to form a mesoporous network with high specific surface area ($183.6 \text{ m}^2 \text{ g}^{-1}$), which provides electrolyte penetration channels, enlarged electrode/electrolyte contact area, and short charge transport path, favoring fast Li^+ insertion/extraction. Consequently, W-THSs exhibits an excellent electrochemical performance, giving a high discharge capacity of 123.6 mAh g^{-1} even at 5.0 A g^{-1} , and still retaining 180.8 mAh g^{-1} after 500 cycles at 1.0 A g^{-1} . The rate capability of W-THSs is much superior to the compared anatase TiO_2 hierarchical spheres (AHSS) obtained by calcining W-THSs in the air. Moreover, cyclic voltammetry analyses reveal that a pseudocapacitive process occurs during the Li^+ storage in W-THSs, significantly contributing to the excellent rate capability.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Lithium ion battery (LIB), as a typical electrochemical energy storage device, has been widely used for powering the ubiquitous portable electronics and for the electrification of the transportation sector [1–3]. Recently, the rapid development and popularization of electric vehicles (EVs) and hybrid electric vehicles (HEVs) has driven LIBs into a new stage, where both high energy density and high power density are required, meanwhile good safety, long lifespan and low cost should also be taken into account [4]. However, considerable gaps still exist for the current LIBs using carbonaceous materials (mostly graphite) as anodes, especially on the fast charge/discharge capability, mainly because of the limited Li^+ diffusion coefficient and potential safety risks at high-rate operation [5]. Despite tremendous efforts have been devoted to developing alternative electrode materials with improved reaction kinetics by strategies of nanostructure design or surface modification [6], high power LIB remains a formidable challenge due to the intrinsically slow solid-state lithium diffusion. On the contrary, pseudocapacitors based on fast surface faradic redox reactions could achieve high power density, but their energy density is lower than the LIBs [7, 8]. Accordingly, it is rational and attractive to achieve battery-like energy and

pseudocapacitor-like power simultaneously by integrating diffusion-controlled Li^+ intercalation and surface-controlled pseudocapacitive redox reaction into one single electrode material.

Pseudocapacitance can be intrinsic or extrinsic to a material [9, 10]. For example, RuO_2 and its derivatives are typical intrinsic pseudocapacitive materials, which display pseudocapacitive characteristics for a wide range of particle sizes and morphologies. Impressively, Sugimoto et al. [11] reported that layered ruthenic acid ($\text{H}_x\text{RuO}_{2+0.5x}$) with expandable interlayers could exhibit high specific capacitance even at high power specifications, which is much higher than that of nanocrystalline rutile-type RuO_2 , and comparable to that of amorphous hydrated RuO_2 . This is because ions can rapidly intercalate into not only the surface or near-surface but also the interlayers of layered $\text{H}_x\text{RuO}_{2+0.5x}$. Although conventional graphite anode also possesses interlayers for Li^+ intercalation, the narrow gaps (0.34 nm) makes the charge storage limited by diffusion process. This indicates that open layered structure or expanded tunnels in crystalline structure facilitate electrode materials to realize pseudocapacitive behavior [12]. On the other hand, although pseudocapacitance can hardly exist for most materials in the bulk state, extrinsic pseudocapacitance is apparent when the materials are reduced to nanoscale with very high surface area or increased electrode/electrolyte contact area [13, 14]. Therefore, in order to realize pseudocapacitive behavior in electrodes for LIBs, materials with both open interlayers or tunnels and nanostructure should be referred and designed.

* Corresponding author.

E-mail addresses: hanyang.gao@163.com (H. Gao), hugx@sjtu.edu.cn (G. Hu).

Among a variety of potential alternative anode materials for LIBs (e.g., TiO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Co_3O_4 , CuO , SnO_2 , Si/C) [15–26], layered titanate materials can be promising candidates for high power LIBs, because the interlayer space between the titanate layers is large enough (ca. 0.8 nm) to facilitate Li^+ diffusion with less resistance. This high Li^+ mobility in layered titanates is actually resulted from their pseudocapacitive behavior, especially in nanosized titanates [12, 27–31].

In this work, protonic layered titanate hierarchical spheres (W-THSs) consisting of interpenetrating nanowires were synthesized by supercritical hydrothermal treatment of sodium peroxotitanate complex solution and subsequent acid washing. The sodium peroxotitanate complex solution was obtained by dissolving Low-cost H_2TiO_3 powder in NaOH solution with the help of H_2O_2 . The W-THSs have a mesoporous hierarchical architecture with high specific surface area, beneficial to electrolyte penetration, electrode/electrode contact, and short charge transport path. As a result, W-THSs exhibited an excellent electrochemical performance when used as LIB electrode. The rate capability of W-THSs was much superior to the anatase TiO_2 hierarchical spheres (AHSs) obtained by calcining W-THSs at 450°C for 2 h. Furthermore, the reaction kinetics in W-THSs was investigated by cyclic voltammetry measurements, demonstrating a pseudocapacitive process significantly contributed to the Li^+ storage in W-THSs.

2. Experimental

2.1. Reagents and materials

Commercial titanic acid powder (H_2TiO_3 , 98%, ca. 1 μm in diameter) was purchased from XuanCheng JingRui New Material Co., Ltd. Other reagents including sodium hydroxide (NaOH , AR, $\geq 96\%$), hydrogen peroxide solution (H_2O_2 , AR, 30% in water), and hydrochloric acid solution (HCl , AR, 36–38% in water) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Materials synthesis

First, sodium peroxotitanate complex solution was prepared by referring to our previous reports [17, 18]. Typically, 0.3 g of NaOH was dissolved in 7.5 ml of deionized water, and then 0.2 g of H_2TiO_3 powder and 2.5 ml of H_2O_2 solution were added into this NaOH solution. After magnetic stirring for 30 min at 30°C , H_2TiO_3 powder was completely dissolved and a pale yellow solution was formed. Then, the obtained solution was transferred into a stainless-steel reactor made of pressure-resistant tube and adaptor [32, 33]. The reactor was subsequently heated to 390°C for 20 min in a tube furnace. The heating power of the furnace was regulated by an intelligent program so that the reactor reached 390°C within 8 min. So the reaction time mentioned above included the ramp up time. The reaction was terminated by submerging the reactor in ice-cold water. The resultant white precipitates were neutralized with 0.1 M HCl solution for several hours and washed with deionized water until pH ~ 7 reached. Finally, layered titanate hierarchical spheres (W-THSs) powder was obtained after dried at 80°C for 6 h. To make a comparison, anatase TiO_2 hierarchical spheres (AHSs) were obtained by further calcining the W-THSs at 450°C for 2 h in the air.

2.3. Materials characterization

The phase compositions were identified by X-ray diffraction (XRD, D8 Advance, Bruker) with $\text{Cu K}\alpha$ ($\lambda = 0.15418\text{ nm}$) radiation. Raman spectrum was measured on a Raman microscope (Senterra R200-L, Bruker Optics) with an excitation wavelength of 532 nm. The thermo gravimetric analysis was performed on a TA discovery TGA at a heating rate of $10^\circ\text{C}/\text{min}$ in air. The morphologies were characterized using scanning electron microscope (SEM, FEI sirion200) and transmission

electron microscope (TEM, JEOL JEM-2100F, 200 kV). The N_2 adsorption-desorption isotherms were obtained by a Micromeritics TriStar II 3020 apparatus (Micromeritics, USA). Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas, and Barrett-Joyner-Halenda (BJH) method was used to calculate the pore size distribution.

2.4. Electrochemical measurement

Before fabricating electrodes, both W-THSs and AHSs were heated at 150°C for 20 min to remove the adsorbates. During the electrode fabrication, a slurry was first prepared by mixing 80 wt% active materials, 10 wt% carbon black (Super P, TIMICAL), and 10 wt% polyvinylidene difluoride (PVDF, ARKEMA) in *N*-methylpyrrolidone (NMP). The slurry was then uniformly cast onto a Cu foil, vacuum dried at 80°C for 12 h, and cut into disks. The mass loading of active materials in the electrode is $1.8\text{--}1.9\text{ mg cm}^{-2}$. CR2032 coin cells were finally assembled in an Ar-filled glove box (H_2O , $\text{O}_2 < 1\text{ ppm}$), with lithium foil as the counter electrode, Celgard 2400 as the separator, and 1 M LiPF_6 in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1 in volume) as the electrolyte. Galvanostatic charge/discharge curves were recorded on a Land CT2001A battery tester in a voltage range of 1.0 and 3.0 V vs. Li/Li^+ . Cyclic voltammetry (CV) curves were measured by a CHI 660D electrochemical workstation at scan rates of 0.1, 0.2, 0.5, 1.0 mV s^{-1} .

3. Results and discussion

3.1. Material synthesis and characterization

Peroxotitanate complex in form of $[\text{TiO}(\text{O}_2)(\text{OH})_2]^{2-}$ is stabilized by hydroxyl and peroxy groups, so it will precipitate when hydroxyl and peroxy groups are released [33, 34]. Herein, the very high temperature in supercritical hydrothermal reaction significantly accelerated the decomposition of peroxotitanate complex, and the excellent mass transfer characteristic of supercritical water resulted from its low viscosity, high diffusivity and low surface tension facilitated a rapid nucleation and growth of materials [33]. As a result, W-THSs were successfully synthesized after supercritical hydrothermal reaction for 20 min and subsequent acid washing.

Based on the XRD pattern in Fig. 1a, the crystal structure of W-THSs is indexed to a body-centered orthorhombic structure with unit cell parameters $a = 0.3780\text{ nm}$, $b = 1.8687\text{ nm}$, and $c = 0.2978\text{ nm}$, i.e., a layered lepidocrocite titanate ($\text{H}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_{4.0}\cdot\text{H}_2\text{O}$, $x \sim 0.7$, \square : vacancy), which is in good coincidence with previous reports [35–37]. The broad peak at $2\theta = 9.6^\circ$ corresponding to a d -spacing of 0.92 nm is ascribed to the interlayer (020) diffraction of lepidocrocite titanate, while other peaks at $2\theta = 24.6^\circ$, 48.3° , and 62.5° are ascribed to (110), (200), and (002) reflections. As shown in Fig. 1d, $\text{H}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_{4.0}\cdot\text{H}_2\text{O}$ has lepidocrocite-type host layers in which TiO_6 octahedra are connected with each other via edge-sharing. This layered structure with an interlayer spacing of 0.92 nm is very open and could facilitate the Li^+ diffusion during charge/discharge processes. However, W-THSs are thermodynamically metastable and were transferred into anatase TiO_2 product after calcination at 450°C for 2 h, as identified by the XRD pattern of AHSs [38, 39]. During the calcination, layered structure of lepidocrocite titanate shrank locally through a dehydration reaction (Fig. 1b) and then TiO_6 octahedra underwent a rearrangement, finally leading to the formation of anatase phase (Fig. 1d right).

This conclusion is further confirmed by the Raman scattering data. As shown in Fig. 1c, several broad bands near 183, 280, 386, 445, 680, and 920 cm^{-1} were observed in the Raman spectrum of W-THSs, which are very similar to the published values of lepidocrocite-type titanate $\text{H}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_{4.0}\cdot\text{H}_2\text{O}$ [36, 40, 41]. These bands are mainly ascribed to the Ti—O lattice vibrations within the 2D TiO_6 octahedral host layers of lepidocrocite titanate. The distinct bands near 280, 445, and 680 cm^{-1} are three A_g modes, which indicate that the W-THSs have a

Download English Version:

<https://daneshyari.com/en/article/6673900>

Download Persian Version:

<https://daneshyari.com/article/6673900>

[Daneshyari.com](https://daneshyari.com)