Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 8021–8025

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Hydrothermal synthesis of flower-like Zn_2SnO_4 composites and their performance as anode materials for lithium-ion batteries

Ke Wang, Ying Huang*, Haijian Huang, Yang Zhao, Xiulan Qin, Xu Sun, Yanli Wang

Department of Applied Chemistry and the Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education, School of Science, Northwestern Polytechnical University, Xi'an 710072, PR China

Received 10 December 2013; received in revised form 27 December 2013; accepted 30 December 2013
Available online 10 January 2014

Abstract

Flower-like Zn_2SnO_4 composites had been prepared through a green hydrothermal synthesis. The structural, morphological and electrochemical properties were investigated by means of XRD, BET, SEM, TEM, and electrochemical measurement. The results show that the as-prepared sample is in high purity phase and of good crystallinity; meanwhile it has a particular 3-D structure and large surface area. Electrochemical measurement suggests that flower-like Zn_2SnO_4 composites exhibit better cycling properties and lower initial irreversible capacities than the solid Zn_2SnO_4 cubes. The first discharge and charge capacities of the material are 1750 mA h g^{-1} and 880 mA h g^{-1} respectively. A higher reversible capacity of 501 mA h g^{-1} was obtained after 50 cycles at a current density of 300 mA g^{-1}. The higher reversible capacity and good stability can be related to the special nanostructural features of the material. Such Zn_2SnO_4 structures synthesized by the simple and cheap method are expected to have potential application in energy storage.

Keywords: Flower-like; Hydrothermal synthesis; Lithium-ion batteries; Electrochemical properties

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are considered to be the most promising energy storage technology for next-generation portable electronic devices (e.g., laptops, cell phones, and cameras) and for powering electric vehicles (EVs) or hybrid electric vehicles (HEVs) due to their long cycle life and high specific capacity [1]. However, current LIBs predominantly use graphite as an anode material, which only has a theoretical capacity of around 372 mA h g^{-1}. Such a limited capacity significantly lags behind the rapidly growing energy demand for various electronic products, let alone EVs and HEVs. Therefore, it is highly desirable to develop alternative anode materials to meet the pressing need for energy storage requirements [2–4].

Among the candidate anode materials for LIBs, tremendous efforts have been making focus on Sn-based metal oxides and composites due to their high capacity, $Li_{4.4}Sn$, a theoretical specific capacity of 994 mA h g^{-1}, which is almost three times larger than that of conventional graphite (372 mA h g^{-1}) [5–9]. Zn_2SnO_4, an inverse spinel structured AB_2O_4 compound (space group Fd3m), has attracted considerable attention in recent years owing to its potential to be used in a wide variety of applications, such as for anodes in lithium-ion batteries [10,11]. This material, however, suffers from a rapid capacity fade due to the large volume changes during the Li-insertion/extraction processes as an anode material [12]. There have been several strategies used to mitigate the instability caused by volume changes, and among the various methods, the control of the morphology is a primary focus to alleviate volume expansion. In our previous studies, we had synthesized monodispersed solid Zn_2SnO_4 cubes. They displayed a higher capacity and better cycling stability than those previously reported due to their unique structural stability, good dispersibility and high surface area [13–15]. However, large specific volume changes during the Li insertion/extraction processes still affected their cycle performances [16–18].

Herein, we use a simple hydrothermal synthesis to obtain the flower-like Zn_2SnO_4 composites, in which the flower-like Zn_2SnO_4 structures are composed of several 1-D Zn_2SnO_4

*Corresponding author. Tel.: +86 29 88431636.
E-mail addresses: wangke815549444@gmail.com (K. Wang), yingh@nwpu.edu.cn (Y. Huang).

0272-8842/$ - see front matter © 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.12.154

nanorods. These structures generally consist of several sharp tips branching out in three dimensions with large surface area. The particular structures can provide more electrochemical active sites, and the small size can shorten the electronic diffusion length. Meanwhile, the porous nanostructures can facilitate the diffusion of electrolyte and alleviate volume change during the alloying and dealloying reactions between Sn and Li to improve the cycle performance.

2. Experimental

2.1. Sample preparation

All of the reagents were of analytical grade and were used as received without any further purification. Zinc chloride ($ZnCl_2$) and tin chloride dihydrate ($SnCl_2 \cdot 2H_2O$) were used as precursors and NaOH as the mineralizer for the hydrothermal synthesis of the flower-like Zn_2SnO_4 composites. The process began with dissolving $SnCl_2 \cdot 2H_2O$ (6 mmol) and $ZnCl_2$ (6 mmol) into 30 mL ethanol separately to form two well-distributed solutions. Then 40 mL NaOH (1 M) solution was successively added drop by drop into the tin chloride dihydrate transparent solution, while facilitated by magnetic stirring. Zinc chloride solution was added drop by drop into the above mixed solution under vigorous stirring using magnetic stirrer at room temperature until the formation of precipitate of the hybrid complex. Finally, the hybrid complex was transferred into a 200 mL teflon-lined stainless autoclave with a fill factor of approximately 70%. The autoclave was sealed and maintained in a furnace at 220 °C for 24 h. Then, the product was separated and washed for several times with ultrapure water and ethanol after the hydrothermal reaction was terminated. After these, the product was dried under vacuum at 60 °C for 12 h to obtain the precursor. Finally, the precursor was calcined at 550 °C for 2.5 h under argon atmosphere, in order to obtain the flower-like Zn_2SnO_4 composites.

The Zn_2SnO_4 cubes are prepared via a simple co-precipitation method based on our previous research [21]. In a typical synthesis, 0.01 mol sodium citrate and 0.01 mol $ZnCl_2$ were dissolved in 100 mL ultrapure water and 0.01 mol $SnCl_4 \cdot 5H_2O$ was dissolved in 50 mL ethanol. Then the ethanol solution was added into the mixture of aqueous solution and stirred for 1 h. After that, 50 mL of aqueous solution of NaOH (2 M) was added dropwise into the mixture solution. The reaction was kept for 3 h and the products were separated by the centrifugation and then washed with ultrapure water and ethanol. Finally, the precursor $ZnSn(OH)_6$ cubes were obtained after vacuum drying at 60 °C for 12 h. The as-prepared $ZnSn(OH)_6$ cubes were calcined at 550 °C in an Ar atmosphere for 2 h with a heating rate of 3 °C min^{-1} to obtain Zn_2SnO_4 cubes.

2.2. Materials characterization

The structures of the prepared samples were characterized by X-ray diffraction analysis (XRD) (Rigaku, model D/max-2500 system at 40 kV and 100 mA of Cu Kα). The surface morphology of the composites were performed by a model Tecnai F30 G2 (FEI CO., USA) field emission transmission electron microscope (FETEM) and scanning electron microscope (SEM, SuPRA 55, German ZEISS).

Electrochemical performance was evaluated by a CR2016-type coin cell with a multi-channel current static system Land (LAND CT200IA). The anode electrodes were prepared by coating slurries consisting of the flower-like Zn_2SnO_4 composites (65 wt%) with acetylene black (15 wt%) and PVDF (20 wt%) as a binder dissolved in 1-methyl-2-pyrrolidinone (NMP) solution on a copper foil. Li foil was used as a counter electrode, and polypropylene (PP) film (Celgard 2400) as the separator. The electrolyte was a solution of 1 M LiPF6 in a mixture of ethylene (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (1:1:1, v/v/v).

3. Results and discussion

Fig. 1 shows the XRD patterns of the $ZnSn(OH)_6$ cubes, solid Zn_2SnO_4 cubes and the as-prepared flower-like Zn_2SnO_4 composites. In the XRD curve of Fig. 1, all the main diffraction peaks of the flower-like Zn_2SnO_4 composites are consistent with the JCPDS (24-1470) data of the pure reverse-spinel Zn_2SnO_4. The diffraction peaks of the solid Zn_2SnO_4 cubes are also in agreement with the standard data of flower-like Zn_2SnO_4 composites, except for an obvious peak at 26° corresponding to the (110) plane of the SnO_2,which is obtained in the sintering process of the precursor $ZnSn(OH)_6$. The reaction mechanism may be described as Eq. (1). In contrast, the flower-like Zn_2SnO_4 composites are prepared through a direct hydrothermal synthesis, so the products seem to be more pure than the solid Zn_2SnO_4 cubes.

$$ZnSn(OH)_6 = Zn_2SnO_4 + SnO_2 + 6H_2O \ (T > 550\ ^\circ C). \quad (1)$$

The N_2 adsorption–desorption measurement at a liquid N_2 temperature of −196 °C was used to study mesoporosity and

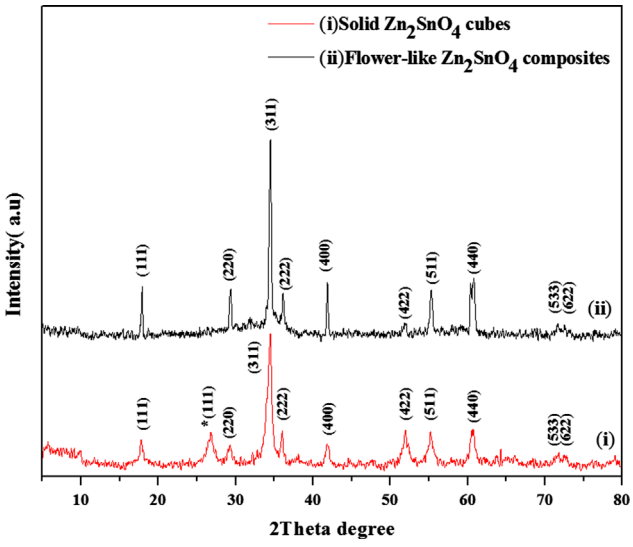

Fig. 1. XRD patterns of $ZnSn(OH)_6$ cubes, solid Zn_2SnO_4 cubes and flower-like Zn_2SnO_4 composites.