



A new strategy for synthesis of lithium zinc titanate as an anode material for lithium ion batteries



Baokuan Chen^a, Chaojun Du^b, Yezhen Zhang^a, Ruixue Sun^a, Li Zhou^a, Lijuan Wang^{a,*}

^a College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, China

^b School of Biochemical and Chemical Engineering, Nanyang Institute of Technology, Nanyang 473000, China

ARTICLE INFO

Article history:

Received 30 December 2014

Received in revised form 30 January 2015

Accepted 31 January 2015

Available online 2 February 2015

Keywords:

Lithium zinc titanate

Anode material

Molten-salt method

Lithium ion batteries

ABSTRACT

Lithium zinc titanate ($\text{Li}_2\text{ZnTi}_3\text{O}_8$) anode materials have been firstly synthesized via a molten-salt method using $0.38\text{LiOH}\cdot\text{H}_2\text{O}-0.62\text{LiNO}_3$ as eutectic molten salts. The effects of sintering temperature and sintering time on the structures and physicochemical properties of the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ materials are also studied in detail. It is found that $\text{Li}_2\text{ZnTi}_3\text{O}_8$ obtained by sintering at 700°C for 3 h exhibits a typical cubic spinel structure with $\text{P4}_3\text{32}$ space group. Nano-sized particles are presented and the particles are homogeneous for the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ prepared by sintering at 700°C for 3 h. Electrochemical tests demonstrate that the sample possesses large capacities. The largest capacities of 167.8 and 142.4mAh g^{-1} are delivered at 2 and 3A g^{-1} , respectively. 137.8 and 113.3mAh g^{-1} are kept for the sample at the 100th cycle at the two current densities, respectively. The large discharge specific capacities may be attributed to the good crystallinity, small particle size and low charge-transfer resistance of $\text{Li}_2\text{ZnTi}_3\text{O}_8$.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Rechargeable lithium ion batteries have been regarded as promising power sources for hybrid electric vehicles (HEVs) and electric vehicles (EVs) due to their large specific capacity, high power density, high safety and environmental friendliness. Safety is one of the paramount factors in large-format lithium ion batteries applications [1]. Generally speaking, graphite is usually used as an anode material for lithium ion batteries because of its low cost and good cyclic performance. Nevertheless, the potential safety problem limits the wide applications of carbon materials because the operating potential is so close to 0V (vs. Li/Li^+) at the end of Li^+ insertion that the dendritic lithium easily grows on the surface of carbon materials during fast-charge or over-charge [2]. In order to solve the crucial safety concern, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been proposed as a substitute anode material for lithium ion batteries due to its high safety and long cycle life. However, the small theoretical capacity of 175mAh g^{-1} , poor electronic conductivity of 10^{-13}Scm^{-1} and high intercalation potential of 1.5V (vs. Li/Li^+) prevent the practical applications of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material. Therefore, it is urgent to find out a new alternative anode material.

Cubic spinel structure lithium zinc titanate ($\text{Li}_2\text{ZnTi}_3\text{O}_8$) with a space group of $\text{P4}_3\text{32}$ was firstly researched as an anode material for lithium ion batteries by Hong etc. in 2010 [3]. According to the crystal structure [4–6], $\text{Li}_2\text{ZnTi}_3\text{O}_8$ can be described as $(\text{Li}_{0.5}\text{Zn}_{0.5})^{\text{tet}}[\text{Li}_{0.5}\text{Ti}_{1.5}]^{\text{oct}}\text{O}_4$, in which Zn exists in the tetrahedral sites and 1:3 cation ordering of $\text{Li}:\text{Ti}$ is located in the octahedral sites. Hence, a three dimensional network is formed in such a structure, where Li and Zn atoms are located in tetrahedral sites forming tunnels, benefiting to the Li^+ reversible intercalation and de-intercalation during charging and discharging. Compared with $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_2\text{ZnTi}_3\text{O}_8$ has larger theoretical capacity of 227mAh g^{-1} [3], lower preparation cost and discharge voltage plateau around 0.5V (vs. Li/Li^+), which can enhance the energy density of a full cell when $\text{Li}_2\text{ZnTi}_3\text{O}_8$ is used as an anode material [7,8].

So far, $\text{Li}_2\text{ZnTi}_3\text{O}_8$ has been synthesized via conventional solid-state reaction method [9–11], modified solid-state reaction route [3,12], combining the sol-gel chemistry and electrospinning technique [13]. High temperature solid-state reaction is the primary industrial method. However, long ball-milling or grinding time, high sintering temperature and long sintering time are needed and result in a large particle size and the aggregation of the final product. In addition, it is difficult to mix the raw materials homogeneously by the solid-state process and impurity phases can also be found in the final product. In a word, the electrochemical performance of the product obtained via a high temperature solid-state route will be adversely influenced by the factors mentioned

* Corresponding author. Tel.: +86-377-63513540; fax: +86-377-63168316.
E-mail address: lijuanw123@163.com (L. Wang).

above. For a solution route, although high reaction temperatures are not required and large capacities can be delivered, long reaction time and some additional processes, such as stirring and heating, are also needed. Therefore, a simple and convenient route to synthesize $\text{Li}_2\text{ZnTi}_3\text{O}_8$ with good electrochemical performance is highly desired.

Molten-salt synthesis has been proven to be a simple one-pot method to obtain single-phase cathode or anode for lithium ion batteries [14,15]. In comparison with the conventional solid-state reaction, the molten-salt method shows an accelerated reaction rate and controllable particle morphology because the molten salt has a high ion diffusion rate and strong dissolving capability. Using eutectic molten mixed lithium salts allows the salts to be uniformly mixed with solid oxide particles at a relative low temperature. As a liquid ion diffuses much more quickly than a solid ion, molten lithium salts can easily adhere to the surface of the solid particles and infiltrate the inside of the solid particles, accelerating the exchanges and reactions between the ions [14].

In the work, we firstly synthesize the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ anode materials via a molten-salt method using $0.38\text{LiOH}\cdot\text{H}_2\text{O}-0.62\text{LiNO}_3$ (with a melting point of 175.6°C) as eutectic molten salts. The effects of sintering temperature and sintering time on the

structures and physicochemical properties of the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ materials are also studied in detail.

2. Experimental

2.1. Synthesis of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ materials

The $\text{Li}_2\text{ZnTi}_3\text{O}_8$ anode materials were synthesized by a molten-salt method using $0.38\text{LiOH}\cdot\text{H}_2\text{O}-0.62\text{LiNO}_3$ (with a melting point of 175.6°C) as eutectic molten salts. In a typical process, TiO_2 (anatase, A.R.), $\text{LiOH}\cdot\text{H}_2\text{O}$ (A.R.), LiNO_3 (A.R.) and $\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$ (A.R.) were ground in an agate mortar for 0.5 h at a $\text{Li}/\text{Zn}/\text{Ti}=2.2:1:3$. The molar ratio of $\text{LiOH}\cdot\text{H}_2\text{O}$ to LiNO_3 was 0.38:0.62. The mixture was dried at 120°C for 12 h in vacuum, pre-heated at 250°C for 3 h and subsequently heated at 600°C for 4 h in air. Finally, the pre-heated powder was divided into four parts and sintered at 650, 700, 750 and 800°C for 1 h, respectively. The obtained materials were denoted as LZTO-650-1, LZTO-700-1, LZTO-750-1, LZTO-800-1, respectively. In addition, the samples of LZTO-700-3 and LZTO-700-5 with the third-stage sintering time for 3 and 5 h were also fabricated, respectively.

2.2. Physical characterization and electrochemical measurements

The thermal behavior of the precursor was characterized by thermogravimetry (TG) and differential thermogravimetric (DTG) analyses in air from room temperature to 900°C using a RD496 thermal analyzer at a heating rate of $10^\circ\text{C}\text{min}^{-1}$.

Structural and crystallographic analyses of the products synthesized were taken from the powder X-ray diffraction data obtained using a Bruker D8 Advance X-ray Diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The diffraction patterns were recorded in the 2θ range from 5 to 85° with a scanning speed 6°min^{-1} . The morphologies and particle sizes of the samples were observed by a SU8020 (Japan) scanning electron microscope (SEM). The specific surface areas and pore size distributions were measured by a specific surface area and pore size distribution analyzer (3H-2000PS2) via nitrogen adsorption. The specific surface areas were measured by the Brunauer–Emmett–Teller (BET) technique. The pore size distributions were analyzed by Barrett–Joyner–Halenda (BJH) method. The nanoscale microstructure was examined by a high-resolution transmission electron microscope (HR-TEM) (Tecnai G2 F20).

The electrochemical measurements were performed using CR2025 coin-type cells. For the fabrication of the anode electrodes, 85 wt.% $\text{Li}_2\text{ZnTi}_3\text{O}_8$ was mixed with 10 wt.% acetylene black and

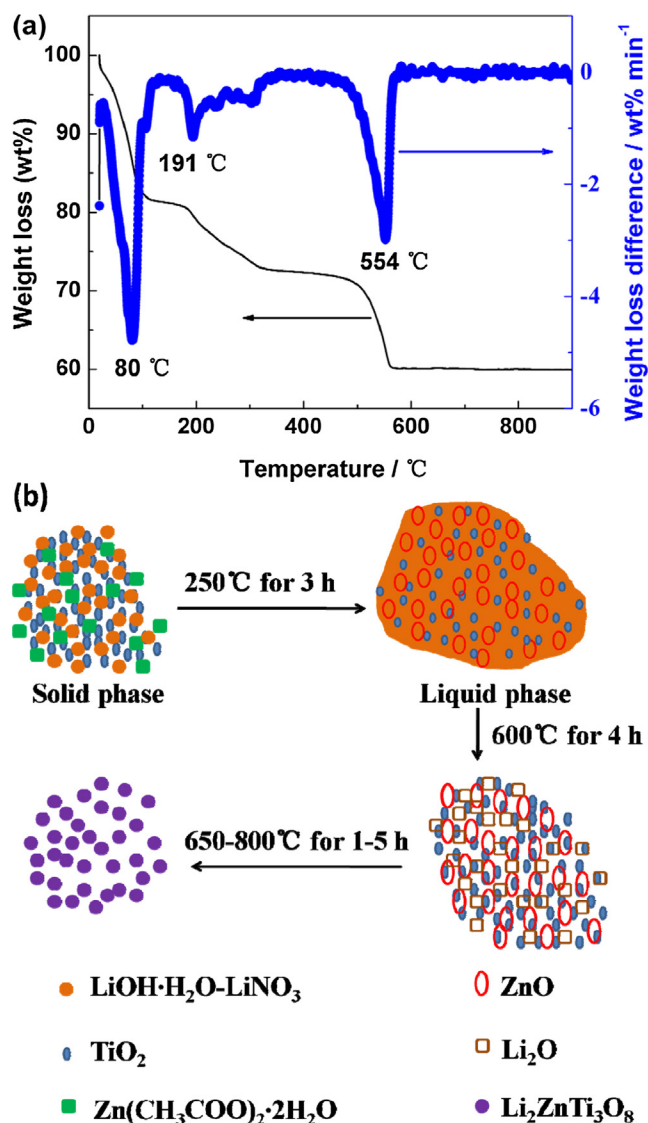


Fig. 1. TG–DTG curves of the precursor of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (a) and schematic model of the synthetic procedure for $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (b).

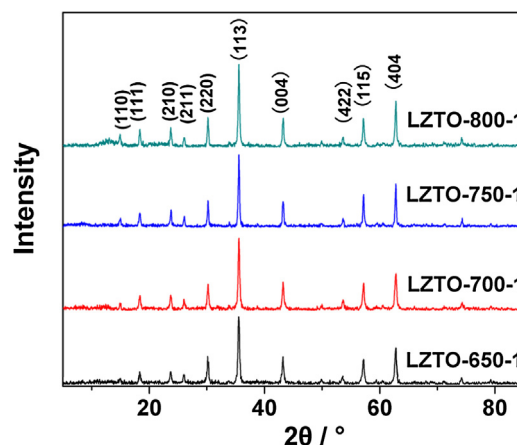


Fig. 2. X-ray diffraction patterns of the as-prepared $\text{Li}_2\text{ZnTi}_3\text{O}_8$ anode materials synthesized at different sintering temperatures of $650\text{--}800^\circ\text{C}$.

Download English Version:

<https://daneshyari.com/en/article/6612079>

Download Persian Version:

<https://daneshyari.com/article/6612079>

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