Journal of Power Sources 273 (2015) 128–135

Contents lists available at ScienceDirect

Journal of Power Sources

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

One-step solution-combustion synthesis of complex spinel titanate flake particles with enhanced lithium-storage properties

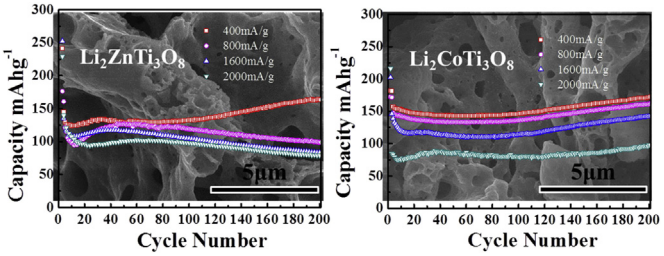
Xue Li, Qian Xiao, Bo Liu, Huangchang Lin, Jinbao Zhao*

State Key Lab of Physical Chemistry of Solid Surfaces, Department of Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

HIGHLIGHTS

- Fast solution-combustion in few minutes is developed to prepare complex spinel titanate electrodes for the first time.
- Combustion synthesis in liquid phase ensures excellent homogeneity of the product with a porous surface area.
- The synthesized electrodes exhibited great cycling stability and high rate performance even at 2000 mA g^{-1} for 200 cycles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 July 2014
Received in revised form
20 August 2014
Accepted 30 August 2014
Available online 10 September 2014

Keywords:
Anode electrode
Complex spinel titanate
Porous flake-like structure
Lithium ion battery
Solution-combustion synthesis

ABSTRACT

In this work, we report the formation of porous $Li_2MTi_3O_8$ (M = Zn, Co) flakes (hereafter referred to as f-$Li_2MTi_3O_8$) via a facile one-step solution-combustion in less than 10 min. As anodes for rechargeable lithium-ion batteries, the synthesized f-$Li_2MTi_3O_8$ exhibits high reversible charge–discharge capacity, great cycling stability and high rate performance. These results can be attributed to the intrinsic characteristics of spinel $Li_2MTi_3O_8$ flakes, in which a porous framework could provide a diffusion space for lithium ion insertion into and extraction from the anode material, resulting in excellent cycle performance, even cycling at high rate of 2000 mA g^{-1}.

1. Introduction

Compared with the conventional graphitic carbon anode materials, spinel $Li_4Ti_5O_{12}$ (LTO) exhibits a relatively flat and high lithium insertion/extraction voltage at approximately 1.55 V (*vs* Li^+/Li), much higher than the operating voltage of graphitic anodes (about 0.1 V); thus, the formation of solid-electrolyte interphase (SEI) layers and the electroplating of lithium can be avoided [1–4]. However, the LTO electrodes suffered from low theoretic capacity of 175 mA h g^{-1}, which may prevent it from large-scale applications.

More recently, the spinel structure $Li_2MTi_3O_8$ (M = Zn, Co) has attracted increasing attention for lithium ion batteries because of its high specific lithium storage capacity and cycling stability. $Li_2CoTi_3O_8$ [5,6] and $Li_2ZnTi_3O_8$ [7] are both cubic structures with similar lattice constants. H. Kawai et al. reported that bulk $Li_2CoTi_3O_8$ exhibits higher reactivity than $Li_2MgTi_3O_8$ and $Li_2ZnTi_3O_8$ towards lithium insertion [6]. Hong et al. [8] reported the fabrication and application of multi-component compounds of $Li_2MTi_3O_8$ (M = Co, Zn) using titanate nanowires as a precursor. Wang et al. [7] synthesized $Li_2CoTi_3O_8$ fibers by an electrospinning method. And in

* Corresponding author. Tel./fax: +86 5922186935.
E-mail address: jbzhao@xmu.edu.cn (J. Zhao).

http://dx.doi.org/10.1016/j.jpowsour.2014.08.129
0378-7753/

order to improve the electrical conductivity, Xu et al. [9] presented a sol–gel route to prepare $Li_2ZnTi_3O_8$/C nanocomposite. Most of the existing techniques, however, require multi-step and laborious procedures as well as are only applicable to certain predecessor.

Different from these studies, we succeeded in synthesizing $Li_2MTi_3O_8$ (M = Zn, Co) flake particles (f-$Li_2MTi_3O_8$) by a one-step solution-combustion. To the best knowledge, there has been no report on the preparation of flake $Li_2MTi_3O_8$ using combustion method. And compared with conventional synthesis methods, this route is easy to control, and has two special advantages at least: (1) one-step heating treatment shortens the reaction time and resultantly reduces the energy cost; (2) combustion synthesis in liquid phase ensures excellent homogeneity of the product with a high surface area [10–12]. The morphology, crystal structure, and electrochemical properties of the as-prepared $Li_2MTi_3O_8$ (M = Co, Zn) electrodes were investigated in detail. The results of electrochemical measurements indicate that such $Li_2MTi_3O_8$ (M = Co, Zn) anode material with porous flake-like structure exhibits an excellent cycling stability and high rate capability.

2. Experimental section

2.1. Synthesis

The f-$Li_2ZnTi_3O_8$ powders were prepared by solution-combustion synthesis using titanyl nitrate [$TiO(NO_3)_2$] aqueous solution, $Zn(NO_3)_2$ and $LiNO_3$ as the oxidant precursors and glycine as the fuel with the stoichiometric amounts of titanyl nitrate (0.0362 mol), 1.67 g of $LiNO_3$ (0.0241 mol), 3.57 g of $Zn(NO_3)_2{\cdot}6H_2O$ and 3.00 g of glycine (0.400 mol). The amount of fuel needed (stoichiometry) can be derived from the valency of the ions. In our work, the oxidizer/fuel ratio is determined by the previous reports [13]. The synthesis of [$TiO(NO_3)_2$] aqueous solution is described as followed. The transparent titanyl nitrate solution was prepared by adding nitric acid into $TiO(OH)_2$ under continuous stirring. Here $TiO(OH)_2$ was synthetized in advance by slowly dropping tetrabutyltitanate [$Ti(C_4H_9O)_4$] into dilute ammonia solution under ice-water bathing with vigorous stirring to precipitate. Stoichiometric amount of $LiNO_3$ was then added to the achieved solution, followed by the introduction of glycine as the fuel. Afterward the mixed solution was taken in an alumina crucible, placed into a muffle furnace preheated to 800 °C to sinter for 10 min. Then the reaction crucible was removed from the furnace and cooled naturally in the atmosphere.

The f-$Li_2CoTi_3O_8$ particles were prepared via the similar route but with 3.49 g of $Co(NO_3)_2$ (0.0120 mol) instead of $Zn(NO)_3{\cdot}6H_2O$.

The b-$Li_2ZnTi_3O_8$ particles were prepared via the similar route with the f-$Li_2ZnTi_3O_8$ but without the glycine as the burning agent. And the b-$Li_2CoTi_3O_8$ were prepared via the similar route with the f-$Li_2CoTi_3O_8$ but without the glycine as the burning agent.

2.2. Characterization

The X-ray diffraction (XRD) patterns were recorded with Philips X'pert Pro Super X-ray diffractometer and CuKα radiation. The X-ray photoelectron spectroscopy (XPS) analysis was performed with QUANTUM 2000 SCANNING ESCA MICROPROBE spectrometer using a focused monochromatized AlKα radiation (1486.6 eV). The pass energy was 60 eV for the survey spectra and 20 eV for particular elements. The morphologies of the as-prepared materials were characterized by field emission scanning electron microscope (LEO 1530, HITACHI S-4800). The specific surface area of porous $Li_2MTi_3O_8$ (M = Zn,Co) was measured by the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption and desorption isotherms on a Tristar 3000 system.

2.3. Electrochemical characterizations

Electrochemical evaluations were carried out by galvanostatic cycling the electrodes which were constructed with the as-prepared LTO samples in a CR2016-type coin cell. The working electrodes were formed by casting the slurry, which is composed of 80 wt% active materials, 10 wt% carbon black, and 10 wt% polyvinylidene fluorides (PVDF) dissolved in N-methylpyrrolidinone (NMP) onto aluminum current collector foil. Afterward, the electrodes were dried under vacuum at 110 °C for 12 h. The cells were assembled with the cathodes as above prepared, and lithium metal as anodes. The electrolytes contained 1 mol L^{-1} $LiPF_6$ solution in a 1:1 (v:v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). All assembly processes of the test cells were carried out in an argon-filled glove box. Galvanostatic charge/discharge experiments were performed at different current densities between 0.02 V and 3.00 V (*vs* Li/Li^+) using a CT2001A cell test instrument (LAND Electronic Co.). The electrochemical impedance spectra (EIS) of the $Li_2MTi_3O_8$ (Zn, Co) electrodes discharged at different voltages were measured in the frequency range of 10 mHz–100 kHz by using two-electrode coil cells with Li metal as the counter electrode via an Autolab PGSTAT 101 cell test instrument.

3. Results and discussion

Fig. 1 shows XRD patterns of the as-prepared f-$Li_2MTi_3O_8$ (M = Zn, Co). All the diffraction peaks in Fig. 1a can be indexed to a cubic spinel structure of $Li_2ZnTi_3O_8$ (JCPDS No. 86-1512). Nine main characteristic peaks for $Li_2MTi_3O_8$, 2Θ = 14.9, 18.3, 27.2, 26.1, 30.2, 35.5, 43.2, 57.1, 62.5 marked by their indices 110, 111, 210, 211, 220, 311, 400, 511, 440. Since both of the samples have the spinel structures with very close lattice parameters, the similar diffraction peaks with higher crystalline can be found in Fig. 1b, which can be indexed to $Li_2CoTi_3O_8$ of space group $P4_332$ (JCPDS No. 89-1309).

SEM images of f-$Li_2ZnTi_3O_8$ and f-$Li_2CoTi_3O_8$ are shown in Fig. 2. Both of the samples prepared via the combustion method exhibit micron-size secondary particles composed of nanometer-size primary particles in flaky morphology with embedded pores, which is obtained because of concomitant formation of material with vigorous evolution of large volume of gases during the combustion reaction. And the formation reason of flake structure can be explained from the following aspects: 1) In our experiment, we have observed a vigorous reaction similar to the explosion at around 250 °C (the decomposition temperature of the glycine is 248 °C). It indicates the crystal growth in this route is fast and the volume expansion is momentary. As a consequence, the irregular flakes tend to be formed rather than the specific morphology. 2) In theory, there is not only redox reaction but also complexation between glycine and metal salts during the solution combustion [14]. Therefore, we hypothesize that the flake morphology maybe associated with the way of complexation. For the two samples, the high magnification images shown in Fig. 2e end f indicate a unique architecture containing agglomeration of uniform particles. And compared with the f-$Li_2ZnTi_3O_8$, the f-$Li_2CoTi_3O_8$ was formed by the smaller grains (about 100 nm).

Nitrogen adsorption experiment was carried out to evaluate the specific surface areas of the as-prepared f-$Li_2MTi_3O_8$ (M = Zn, Co) flake particles. As shown in Fig. 3, BET surface areas were 6.2 and 7.8 m^2 g^{-1} for f-$Li_2ZnTi_3O_8$ and f-$Li_2CoTi_3O_8$ flake particles, respectively, through calculation from N_2 isotherms at 77 K. And there is limited meso-pore (pores 2 and 8 nm) for both samples. The as-obtained samples have appreciable BET surfaces than micron-materials though in micrometer scale, which will be helpful to enhance the electrochemical performance because of their high