

One-step synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ anode material with high performance for lithium-ion batteries

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ARTICLE INFO

Article history:

Received 25 May 2009

Received in revised form 16 December 2009

Accepted 15 January 2010

Keywords:

Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$

High-rate capability

Polyacrylate

Electric conductivity

Lithium-ion batteries

ABSTRACT

$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ anode material was simply obtained via a modified one-step solid-state reaction route using the original materials of lithium polyacrylate (PAAli) as lithium and carbon sources, and TiO_2 as titanium source. The physical characteristics of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite were investigated by X-ray diffraction, scanning electron microscopy and transmission electron microscopy techniques. The particle size of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in the composite was about 200 nm. The electrochemical properties were evaluated by electrochemical impedance spectra and constant current charge/discharge cycling. It was demonstrated that the as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite presented excellent high-rate characteristics and cycleabilities. The initial specific capacity of the composite was 130.0 mAh g^{-1} at 8.60 mA cm^{-2} , and excellent cycle performance was still maintained with the current density increase. Moreover, it was proved that the electric conductivity and cycle performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were effectively enhanced due to the uniformly dispersed pyrolytic carbon in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles.

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1. Introduction

High-rate capability lithium-ion batteries have attracted increasing attention in recent years due to their potential application in electric vehicles (EVs). Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, viewed as one promising alternative anode material to graphite in lithium-ion batteries [1–4], has received considerable interest because of its appealing advantages such as little volume change (zero-strain insertion material) during the charge/discharge processes, which enables an outstanding cycling stability; high insertion potential of ca. 1.55 V (versus Li/Li^+), which ensures high safety with electrolyte solution and also non-lithium plating. In addition, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has excellent lithium-ion mobility [5], which favors lithium-ion batteries charging/discharging fleetly.

The attractive structure and electrochemical characteristics of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material make it a candidate anode electrode for large scale applications. Recently, it was found that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ could be versatilely applied in electrochemical generators [6], all-solid-state lithium-ion batteries [7,8], asymmetric supercapacitors [9,10] and room temperature lithium metal batteries [11]. Unfortunately, pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cannot meet the need of practical application under high current

condition due to its poor electric conductivity [8,12]. Therefore, several efforts have been devoted to increase and optimize the conductivities of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, including cation doping [13–15], synthesis of nano-sized particle [16,17], and deposition of metallic grain [18] on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle surface. However, there are still great challenges to improve the high-rate capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ although cycle performance was greatly improved by these modifications.

Compared with the mentioned optimization methods to $\text{Li}_4\text{Ti}_5\text{O}_{12}$, preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles containing carbon was regarded as very effective and feasible method in the enhancement of capacity and rate capability. Wang et al. [19] obtained carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by heat-treating mixture of TiO_2 , Li_2CO_3 and sugar as starting materials. Yu et al. [20] prepared a $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite using TiO_2 -anatase, Li_2CO_3 and phenol-formaldehyde (PF) resin as raw materials. The $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composites from these methods exhibited better electrochemical properties, especially higher rate capacity, in comparison with the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$. It could be attributed to the enhanced electrical conductive network of the carbon coating on the particle surface, which improves the electric conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and hence the high-rate characteristics of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite. Guerfi et al. [21] also reported the research results of the high-rate capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ prepared by solid-state reaction with ternary precursor materials TiO_2 , Li_2CO_3 and different types of carbons. In these studies, however, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite was obtained by adding adsorbent carbon sources. The lithium sources, titanium sources and carbon sources were mixed together as the starting materials to prepare $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite.

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Thus, there were at least three reacting phases in the reaction system. It is well known that the fewer reacting phases in a reaction system, the more homogeneous specimen would be yield. It is because that it is favorable for raw materials to mix well, reacting easily and completely when there are fewer reacting phases.

In this regard, we suggest a novel and simple route to prepare the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite by sintering the precursor of polymer lithium salt and TiO_2 . Polymer lithium salt was proposed to be the source of lithium and carbon. Moreover, the polymer could effectively prevent the segregation of reacting components and the growth of crystalline grains during the synthetic process. During the heat-treatment, the lithium in polymer lithium salt reacted with titanium to form $\text{Li}_4\text{Ti}_5\text{O}_{12}$ crystal and the polymer carbon chain was pyrolyzed to form carbon, hence yielding the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite. In this paper, we presented the physical and electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ pyrolyzed from lithium polyacrylate (PAALi).

2. Experimental

2.1. Preparation of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite electrodes

The $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite was prepared as the follows. A stoichiometric amount of $\text{LiOH}\cdot\text{H}_2\text{O}$ was dissolved into an aqueous solution of polyacrylic acid (PAA) to get PAALi, followed by the addition of TiO_2 powder under continuous stirring for 6 h to obtain a homogeneous PAALi + TiO_2 slurry. Subsequently, the above mixture was dried in an oven at 100°C for 10 h and then heated at 800°C for 8 h in flowing nitrogen, followed by cooling down to room temperature naturally. The final powder was obtained by grinding. As a comparison, the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared using similar method but heated in air.

The working electrode was fabricated by mixing the active material $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite (or pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$), conductive carbon black (Super P, TIMCAL) and an aqueous binder LA132 (from Indigo, China) homogeneously in a weight ratio of 86:10:4, and then pasted uniformly onto a copper foil and dried to give the electrodes.

2.2. Measurements

A Q500 was used for thermogravimetric analysis (TGA) with a heating rate of $10^\circ\text{C min}^{-1}$ from 25 to 800°C at a nitrogen flow rate of 50 mL min^{-1} . X-ray diffraction (XRD) was performed on a Rigaku D/Max 2550 powder diffractometer equipped with $\text{Cu-K}\alpha$ radiation of $\lambda = 1.5418\text{ \AA}$ in the range of $10^\circ < 2\theta < 90^\circ$. Scanning electron microscopy (SEM) was conducted on a JEOL JSM-6700F scanning electron microscope at 5.0 kV. Transmission electron microscopy (TEM) was revealed by a JEOL JEM-3010 transmission electron microscope. Elemental analysis was carried out by a CARLO ERBA 1106 elemental analyzer (Italy).

The electrochemical performances of the samples were evaluated with a lithium metal foil as the counter electrode. The 2032 coin cells were assembled in an argon-filled dry box. The electrolyte was a 1.0 M LiPF_6 solution in the mixture of ethylene carbonate, dimethyl carbonate and ethylene methyl carbonate (1:1:1 by weight). The charge/discharge experiments were conducted under various current densities in the voltage range from 1.0 to 3.0 V (versus Li/Li^+). Electrochemical impedance spectra (EIS) were investigated by a Solartron 1260/1287 (UK) impedance analyzer in the frequency range of 10^{-1} – 10^6 Hz. All the tests were carried out at room temperature. The specific capacities were calculated based on the mass of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite in the electrodes.

3. Results and discussion

Fig. 1 shows the TGA curves of the mixture consisting of PAALi and TiO_2 at a heating rate of $10^\circ\text{C min}^{-1}$ from 25 to 800°C in nitrogen atmosphere. On the derivative thermogravimetry (DTG) curve, there

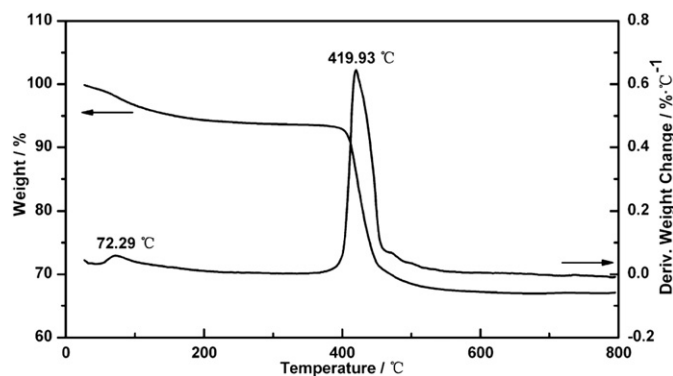


Fig. 1. TGA curve of the precursor mixture of PAALi and TiO_2 measured in nitrogen atmosphere.

is an obvious peak at 420°C , relating to the thermal decomposition of PAALi whereas the curve from 420 to 700°C mainly corresponds to the crystallization of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. When the temperature is above 700°C , the thermogravimetry (TG) curve shows nearly constant weight, indicating that the reaction is complete. Therefore, it is necessary to sinter the precursor mixture above 700°C to get the well crystallized $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In this study, the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite was obtained by sintering at 800°C for 10 h.

Fig. 2 presents the XRD patterns of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples prepared under air and nitrogen atmospheres, respectively. It is found that there is no significant difference between the XRD pattern of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ and that of pristine one, and both patterns are almost in accordance with the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cubic spinel single phase structure. The cell parameters of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ are 8.358 and 8.345 \AA , respectively. The XRD patterns correlate well with that reported [22]. This suggests that the carbon derived from the PAALi does not affect the spinel structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ during the heat-treatment. The unchanged structure characteristic of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ ensures its excellent electrochemical cycle performance as pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Presumably, there is no obvious diffraction response of the carbon because of its low content or amorphous state. Elemental analysis showed that the amount of carbon in the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite was about 4.8 wt.%.

The particle morphologies of pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite observed by SEM are shown in Fig. 3(a) and (b), respectively. It is apparent that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in both samples display regular crystalline morphology. The size of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles in the composite is much smaller than that of pristine one. This demonstrates that the polymer effectively prevented the growth of crystalline grains during heat-treatment. With SEM, it is easy to discern that the pyrolytic carbon is well dispersed among $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles, as shown in Fig. 3(b). The pyrolytic carbon connects through each $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle, which leads

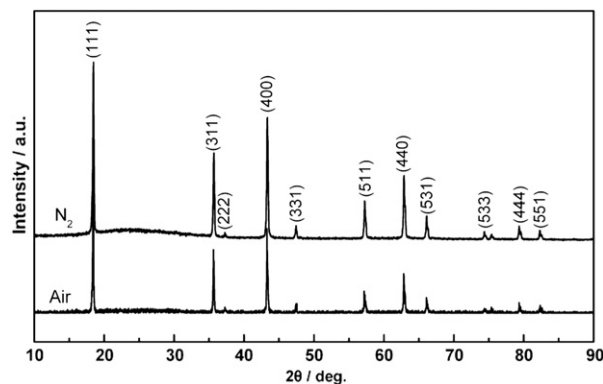


Fig. 2. XRD patterns of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared under air and nitrogen atmospheres, respectively.

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