

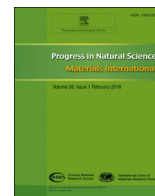
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journal homepage: www.elsevier.com/locate/pnsmi

Original Research

Double carbon decorated lithium titanate as anode material with high rate performance for lithium-ion batteries



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ARTICLE INFO

Article history:

Received 30 March 2016

Accepted 20 April 2016

Available online 30 May 2016

Keywords:

Lithium titanate

Carbon nanotubes

Lithium-ion batteries

Anode materials

ABSTRACT

Spinel lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) has the advantages of structural stability, however it suffers the disadvantages of low lithium-ion diffusion coefficient as well as low conductivity. In order to solve issues, we reported a simple method to prepare carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs ($\text{C@Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs) using stearic acid as surfactant and carbon source to prepare carbon coated nanosized particles. The obtained $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles of 100 nm in size are coated with the carbon layers pyrolyzed from stearic acid and dispersed in CNTs matrix homogeneously. These results show that the synthesized $\text{C@Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs material used as anode materials for lithium ion batteries, presenting a better high-rate performance (147 mA h g^{-1} at 20 C). The key factors affecting the high-rate properties of the $\text{C@Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs composite may be related to the synergistic effects of the CNTs matrix and the carbon-coating layers with conductivity enhancement. Additionally, the amorphous carbon coating is an effective route to ameliorate the rate capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs.

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1. Introduction

Due to its high energy density and long cycle life, rechargeable lithium ion batteries (LIBs) have attracted more attention in the past few decades and widely used in automobiles, electric vehicles and energy storage [1–3]. Taking into account the safety, cost and environmental concerns, graphite as the current commercial lithium ions anode material can not satisfy the requirements of practical applications [4]. Among the candidates, spinel lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) has received the widespread attention in recent years for high power LIBs material due to its intrinsic properties, such as structural stability, high security, environment friendly, and low cost [5–7]. In addition, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a wide charge/discharge platform of about 1.55 V (vs. Li/Li^+), which avoids the formation of solid electrolyte interface film and inhibits the deposition of lithium dendrite [8–11]. However, it suffers from some kinetic problems with poor electrical conductivity and low lithium diffusion coefficient, which results in the great decrease of charge/discharge capability. To overcome the above problems of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, many strategies have been reported to enhance the electrochemical characteristics of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials, including decreasing the particles size and designing the hierarchically structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [12–15], incorporating the second phase with

high electronic conductivity such as carbon material modification or metal particles [16–20], and doping with other metal/ nonmetal ions [21–26].

In all these efforts, pyrolytic carbon-coated along with nanotechnology is considered to be a more effective method to improve the high rate discharge performance owing to the enhancement in the conductivity as well as the shortened the diffusion of lithium ions and electrons. Generally speaking, the introduced carbon-coated in the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ materials is amorphous in structure, making it hard to ameliorate the high-rate discharge property of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material. Carbon nanotube (CNTs) possess a one-dimensional tubular structure with an aspect ratio up to 1000, has considered to be an excellent matrix to composite materials due to its inherent characteristics, such as high electrical conductivity, large surface area, chemical and mechanical stability [27–30]. In our previous work, it was found that the addition of carbon nanotubes as matrix can effectively enhance the rate property of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [28]. For $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs, due to the nanoparticles only some contact with carbon nanotubes, its high-rate discharge performance is greatly limited by the low surface electronic conductivity. Pyrolytic carbon coating technology has been approved to be an effective method to ameliorate the rate property of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material.

In this paper, the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs electrode is greatly improved by coating with a thin amorphous carbon layer on the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles/CNTs hybrid using a simple liquid phase deposition technique and subsequent calcination. Owing to the low thermal decomposition

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Peer review under responsibility of Chinese Materials Research Society.

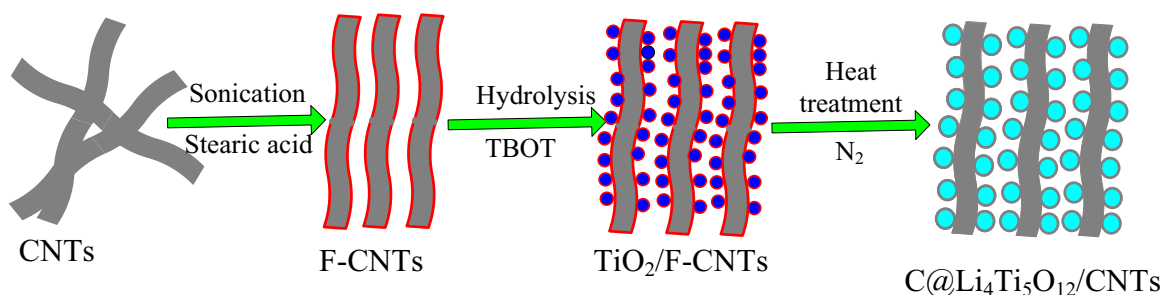


Fig. 1. Schematic illustration of the synthesis of C@Li₄Ti₅O₁₂/CNTs.

temperature and long-chain structure, stearic acid (SA) is used as an ideal organic carbon sources to form a thin amorphous carbon layer for coating Li₄Ti₅O₁₂ particle surface. In these hybrid electrodes, Li₄Ti₅O₁₂ nanoparticles are well wrapped between CNTs and the thin carbon layer. The combination of CNTs and carbon layer contributes to create a 3-dimensional (3D) conductive network to provide cross channel for electrolyte absorption and overcome the agglomeration and growth of Li₄Ti₅O₁₂ nanoparticles. In addition, the Li₄Ti₅O₁₂ nanoparticles surface coated with carbon layer can effectively separate CNTs and further set up cross conducting network to inhibit nanoparticle growth. As a result, the target product C@Li₄Ti₅O₁₂/CNTs show synergistic effect and display superior high rate performance and outstanding cycling stability as the anode materials for LIBs.

2. Experimental

The CNTs was purchased from Shenzhen Nanotech Port Co. Ltd. All other reactants were analytically pure and used without further purification.

The C@Li₄Ti₅O₁₂/CNTs were synthesized by an in situ liquid phase deposition route. The amount of CNT in C@ Li₄Ti₅O₁₂/CNTs was predetermined by 10 wt%. The predetermined amounts of stearic acid in C@Li₄Ti₅O₁₂/CNTs were 6, 12 and 24 wt%, respectively. Take 6 wt% stearic acid for example, 0.06 g stearic acid and 0.1 g CNTs were ultrasonically dispersed in 50 mL ethanol for 1 h, followed by the addition of tetrabutyl titanate solution (3.4 g) to form a suspension. Then, 0.562 g lithium acetate was dissolved into 1 mL water and 29 mL ethanol, and then dropped into the above suspension slowly. Continue to stir after 24 h, the mixed solution was treated at 60 °C in drying oven. The precursor was calcined at 400 °C for 4 h, and heated up to 750 °C for another 10 h under N₂ to obtain C@Li₄Ti₅O₁₂/CNTs. In contrast, Li₄Ti₅O₁₂/CNTs were also prepared under the same condition without the presence of stearic acid.

The morphologies and microstructures analyses of the as-synthesized powders were conducted by Rigaku/mac250 X-ray diffraction (XRD), ZEISS supra 55 field emission scanning electron microscopy (FE-SEM) and JEOL JEM-200CX transmission electron microscopy (TEM). The carbon contents in C@Li₄Ti₅O₁₂/CNTs were determined by an EMIA-820V carbon-sulfur analyzer. Electrochemical performances of Li₄Ti₅O₁₂/CNTs and C@Li₄Ti₅O₁₂/CNTs were investigated in CR2032 coin-type cells. The working electrodes were composed of active material, carbon black and polyvinylidene fluoride (8:1:1 in weight) on Cu foil. Battery assembled were conducted in an argon-filled glove box using a metallic lithium foil as the counter electrode, a Celgard 2400 polypropylene film as the separator and 1 M LiPF₆ in ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate (1:1:1 in volume) as the electrolyte. The charge/discharge properties were tested on LAND CT2001A battery test system (Wuhan Jinnuo Electronics, Ltd.) at room temperature. Tested voltage window and current

densities were 1.0–2.5 V and 0.2–20 C, respectively. The electrochemical impedance spectra (EIS) were measured at room temperature on a CHI660C electrochemical workstation (Shanghai Chenhua Co.). The amplitude of the AC signal was 5 mV over a frequency range of 100 kHz–0.01 Hz.

3. Results and discussion

Based on the above, our synthetic route was different from the previous reported synthesis of carbon-coated Li₄Ti₅O₁₂/CNTs materials, in which the Li₄Ti₅O₁₂ nanoparticles and CNTs were mixed mechanically for each other [31–33]. The overall fabrication procedure of the C@ Li₄Ti₅O₁₂/CNTs is schematically illustrated in Fig. 1. Firstly, CNT surface was functionalized using stearic acid, which facilitates the dispersion of CNTs in the ultrasound treatment. Then, TiO₂ nanoparticles were uniformly coated on the CNTs surface by controlled hydrolysis of tetrabutyl titanate. Finally, the TiO₂/CNTs were in situ transformed into Li₄Ti₅O₁₂/CNTs and the carbon layers coated on Li₄Ti₅O₁₂ nanoparticles surface were achieved by annealing for pyrolysis of stearic acid.

Fig. 2 shows the XRD patterns of the C@Li₄Ti₅O₁₂/CNTs with different stearic acid contents. It is observed that the majority of the diffraction peaks of all the samples can be identified as the spinel structure Li₄Ti₅O₁₂ (JCPDS Card No.49-0207). It is obvious that no diffraction peaks appear for CNTs matrix and carbon from pyrolysis of stearic acid due to its amorphous structure. In other word, the presence of the carbon does not influence the structure of Li₄Ti₅O₁₂. In addition, with the increase of the amount of stearic acid, the intensity of the diffraction peak of the C@Li₄Ti₅O₁₂/CNTs is significantly increased. It is very obvious that minor impurity

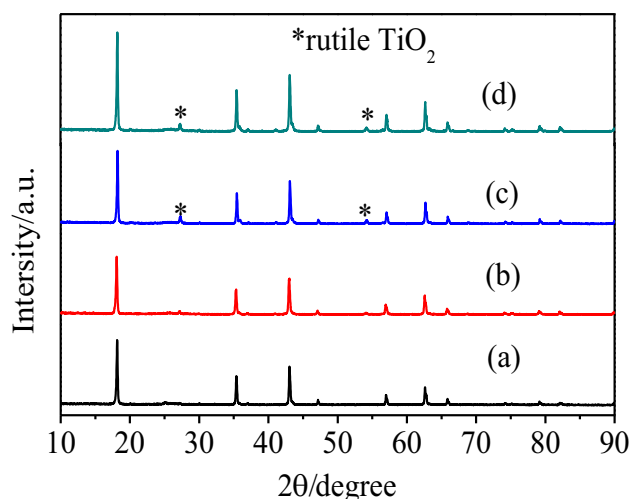


Fig. 2. XRD patterns of (a) Li₄Ti₅O₁₂/CNTs, (b) C@Li₄Ti₅O₁₂/CNTs with 6 wt% stearic acid, (c) C@Li₄Ti₅O₁₂/CNTs with 12 wt% stearic acid and (d) C@Li₄Ti₅O₁₂/CNTs with 24 wt% stearic acid.

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