

Enhanced rate performance of nanosized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composites as anode material by a solid state-assembly method



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ARTICLE INFO

Article history:

Received 18 April 2015

Received in revised form 2 May 2015

Accepted 4 May 2015

Available online 5 May 2015

Keywords:

Lithium-ion batteries

Lithium titanate

Graphene

High rate performance

ABSTRACT

Nanosized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene materials have been successfully synthesized by a solid state-assembly method. As the anode materials for lithium ion batteries, nanosized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene exhibits higher specific capacity, much improved rate capability, and better cycle stability than the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In the potential range of 1.0–2.0 V at room temperature, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene with weight ratio of LTO:GO to 1000:5 shows discharge capacities of more than 144 and 96.2 mAh g^{-1} after 100 cycles at 1C and 3C charge-discharge rates, while the correspond discharge capacities of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are only 108 and 75.4 mAh g^{-1} , respectively. The resulting $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene (1000:5) sample demonstrates remarkable rate capability in that it delivers a reversible capacity of 53.4 mAh g^{-1} in the 1000th cycle at 10C charge-discharge rate, about 240% that of pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles (22.2 mAh g^{-1}). The low charge-transfer resistance and large lithium ion diffusion coefficients confirmed that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene materials possessed better electronic conductivity and lithium ion mobility. The present work demonstrates that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /graphene composite is a promising anode material for high-rate and long life lithium ion batteries and this simple preparation method makes its production on a large scale.

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1. Introduction

Lithium-ion secondary battery, with its larger energy density, higher output power and better safety performance, has been already proposed as potential energy source for electric vehicles and hybrid electric vehicles. Developing anode materials with high safety is one of the key challenges for lithium-ion batteries. Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) provides excellent performances such as small dimensional change during charge-discharge process and high insertion potential of 1.55 V vs Li^+/Li [1–5]. These features indicate that LTO is a most promising anode material for lithium-ion batteries used in the fields of hybrid electric vehicles and large-scale energy storage, in which long cycle life, high safety, the high structure stability, thermodynamics stability and high rate capability are highly desired. Despite that, the poor electronic conductivity (ca. $10^{-13} \text{ S cm}^{-1}$) and lithium diffusion coefficient (ca. 10^{-9} to $10^{-13} \text{ cm}^2 \text{ s}^{-1}$) of LTO degrades its electrochemical performance and hinders practical application for high current applications before any materials modifications. So far, the

conductivity and rate performance of LTO have been achieved by using foreign atoms doping [4,6–14], nanostructures [15–17] and electronically conductive coatings [18–25]. Among these methods, preparation of LTO/carbon composites by a facile route is practicable and economical for large-scale industrialization [21,26].

Graphene, a form of carbon experimentally demonstrated in 2004, has attracted much attention in the field of material science due to its strictly 2-dimensional(2D) structure, which results in its superior electronic conductivity, excellent thermal properties and mechanical properties [27,28]. These remarkable characteristics of graphene make it a promising candidate for lithium-ion batteries and other electrochemical energy devices [28–32]. Recently, it has been noted that the combination of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and graphene to fabricate LTO/graphene composite is a reasonable approach to improve high-rate capability and electrical conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [33–37]. The synthesis technologies of LTO/graphene composite such as hydrothermal route [21], sol-gel method [26], electrospinning deposition [33], solvothermal process [35], microwave-hydrothermal method [38], and solid state method [39], have been reported by many researchers. However, the soft chemistry methods mentioned above have some disadvantages, such as complicated synthetic routes and high synthetic cost, and it is difficult to commercial application. From a commercial viewpoint, the solid state synthesis is a facile and economical

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preparation route to achieve high performance LTO/graphene composites due to simple synthesis method and low synthesis cost. Moreover, it is also believed that there is a strong electronic coupling between graphene and titanate nanoplates, and the interaction between graphene and Ti-based compound surface is more complicated [35,40]. Therefore, a simple and general preparation method for LTO/graphene composites with high electrochemistry performance is still lacking.

Recently, an electrostatic assembly method was employed to synthesize graphene/metal oxide [30] or LTO/graphene hybrid [34]. Nevertheless, to our knowledge, there was no report that prepared homogeneous LTO/graphene composites by coupling the solid state method with electrostatic assembly method. In this paper we have demonstrated a simplified strategy to prepare homogeneous LTO/graphene composite in a facile solid state-assembly method. The fabrication process consists of four steps: (1) preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by solid state, (2) pre-modification of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with amine groups, (3) coating of a graphene oxide on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by electrostatic assembly, and (4) finally conversion LTO/graphene composite. Furthermore, a careful investigation has been carried out to give new insights into the weight ratio of LTO: graphene oxide (GO), structural properties, rate performance, and the modifying effect on the conductivity of the material.

2. Experimental

2.1. Material preparation

Pure lithium titanates were synthesized by solid-state reaction. TiO_2 and Li_2CO_3 used as raw materials were mixed by ball milling for 4 h in ethanol slurry, followed by drying at 80°C for 6 h. Finally, the powders were calcined at 850°C for 12 h in a flowing air atmosphere to obtain the samples. Excessive Li(5 wt%) was provided to compensate for the volatilization of Li during synthesis.

GO was prepared by a modified Hummers method [30]. Wrapping GO onto the surface of as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples was achieved by the following steps. The Pre-formed LTOs were firstly immersed in the 1 g L^{-1} poly (allylamine hydrochlorine) (PAH) solution for 1 h. Subsequently, the LTOs were dried at 80°C for 6 h. Aqueous suspensions of LTO and GO then were vigorously stirred together to form a slurry with various weight ratio of LTO: GO (1000:1, 1000:2, 1000:5, and 1000:10 wt). Subsequently, the slurry was stirred for 3 h, which was then dried at 80°C , and annealed at 400°C for 2 h under N_2 atmosphere to obtain the homogeneous LTO/graphene composites.

2.2. Material characterization

Phase identification of the as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LTO/graphene samples was characterized by X-ray diffraction (XRD, Cu-K α radiation, DX2700, Dandong Haoyuan, China) and Raman spectroscopy (Renishaw inVia Britain) using 532 nm excited laser. The morphology of the samples was observed by scanning electron microscopy (SEM, EVO HD 15, Zeiss, German). The detailed nanostructure of the LTO/graphene samples was studied on a transmission electron microscope (TEM, JEOL2100).

2.3. Electrochemical measurements

Electrochemical performance was measured using two-electrode 2025 coin-type cells. In order to make an electrode laminate, a uniform slurry containing 80 wt.% active material, 10 wt.% acetylene black and 10 wt.% polyvinylidene fluoride (PVDF) dispersed in N-methyl-2-pyrrolidinone (NMP) was cast onto an copper current collector. The obtained slurry was dried at 80°C for

2 h and pressed at a pressure of 5 MPa. The fabricated electrodes were dried again at 120°C for 4 h in vacuum and cut into circles with diameter 15 mm in size. Following evaporation of the solvent and drying, electrodes were assembled in a glove box (Universal 2440/750, Mikrouna) filled with high-purity argon, using a polypropylene membrane (Celgard 2400) as the separator. In the half-cells, various LTO composite materials were used as working electrode and high-purity lithium metal as counter electrode. The electrolyte solution was 1 M LiPF₆ in EC:DMC (1:1 by volume).

Charge-discharge performance was characterized galvanostatically on Land 2000T (China) tester at 1C, 3C, 5C and 10C charge-discharge rate over a voltage range of 1.0–2.0 V versus Li/Li⁺ electrode at room temperature ($1\text{C} = 175\text{ mA g}^{-1}$). The electrochemical impedance spectroscopies (EIS) measurement was performed by a CHI 660a electrochemical workstation, and the frequency ranged from 0.01 Hz to 100 kHz with ac signal amplitude of 5 mV.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LTO/graphene composites with various weight ratio of LTO:GO (1000:1, 1000:2, 1000:5, and 1000:10 wt). The diffraction patterns of all samples are similar and conform to JCPDS card No.49-0207 in accordance with the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase with Fd-3m space group with a cubic lattice. Similar as the XRD patterns of most LTO/graphene composites [26,38,39], no any diffraction peaks according to graphitic structure was detected, most likely because they are below the limits of detection by XRD or graphene in the LTO/graphene composite is in amorphous form.

Raman spectra of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LTO/graphene samples are shown in Fig. 2. Each spectrum shows five main Raman bands peaked at about 234, 348, 423, 674 and 744 in the range of 200–1000 cm^{-1} , representing the features of the spinel structure ($\text{A1g} + \text{Eg} + 3\text{F2u}$), which are similar to those of the previously reported $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [2,38,41]. Note that these peaks intensity of LTO/graphene composites is weakening in Fig. 2. Moreover, in the LTO/graphene composites (from curve b to curve e in Fig. 2), two new bands in the range of 1200–1460 cm^{-1} and 1470–1730 cm^{-1} were detected. According to Shi et. al [38], these two bands are attributed to the D-band (K-point phonons of A1g symmetry) and

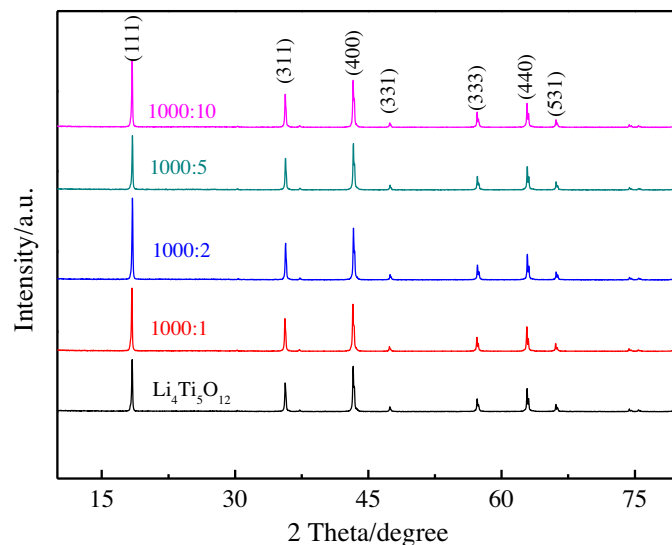


Fig. 1. XRD pattern of as-prepared pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LTO/graphene composites various weight ratio of $\text{Li}_4\text{Ti}_5\text{O}_{12}$:GO ($\text{Li}_4\text{Ti}_5\text{O}_{12}$: GO=1000:1, 1000:2, 1000:5, and 1000:10).

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