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High rate cycling performance of nanosized $Li_4Ti_5O_{12}$/graphene composites for lithium ion batteries

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ABSTRACT

Nanosized $Li_4Ti_5O_{12}$/graphene(LTO/graphene) materials have been successfully synthesized by a sol-gel method. The LTO/graphene composites exhibit a well-defined cubic spinel structure with an average particle size of approximately 200–500 nm. Compared with pure $Li_4Ti_5O_{12}$, LTO/graphene composites show higher specific capacity, much improved rate capability and better cycle stability when used as anode materials for lithium ion batteries. The initial capacity of the LTO/graphene composite(0.5 wt%) reaches 170.7 mAh g^{-1} at 1C, which slightly decreases to 168.5 mAh g^{-1} after 100 cycles with a capacity loss of 1.3%. More importantly, the resulting LTO/graphene (0.5 wt%) sample demonstrates remarkable rate capability in that it delivers a reversible capacity of 108.4 mAh g^{-1} in the 1000th cycle at 10C charge-discharge rate, about 2.5 times that of pristine $Li_4Ti_5O_{12}$ particles (44.1 mAh g^{-1}). The improved high-rate capability, cycling stability, fast charge-discharge performance of LTO/graphene composites can be ascribed to the improvement of lithium ion diffusion and ionic conductivity by graphene-coating.

1. Introduction

Lithium-ion secondary battery has attracted great attention as potential energy source for electric vehicles and hybrid electric vehicles due to its high energy density, higher output power and good safety performance [1]. Spinel $Li_4Ti_5O_{12}$ (LTO) has been considered as promising high safety anode materials of lithium-ion batteries because of its flat and high potential (1.55 V *vs* Li^+/Li), excellent Li-ion insertion-extraction reversibility, almost negligible volume change during charge-discharge process [2,3]. However, the poor electronic conductivity and low lithium diffusion coefficient of $Li_4Ti_5O_{12}$ degrades its electrochemical performance and prevents its practical application. Recently, some improvements on the electrochemical performance of $Li_4Ti_5O_{12}$ have been achieved by using foreign ion doping, such as Nb^{5+} [4–6], V^{5+} [7,8], Zr^{4+} [9], La^{3+} [10], Sc^{3+} [11], Al^{3+} [12], Zn^{2+} [13], Sn^{2+} [14], Mg^{2+} [15], Ta [16,17], Br^- [17], F^- [18–20], N [21] in Li sites, Ti sites or O sites in $Li_4Ti_5O_{12}$ systems.

In addition, preparation LTO/graphene composite is considered as an another effective way to solve these problems [22–30]. Moreover, the LTO/graphene composite also exhibits excellent reversibility and high-rate performance than that of the pristine $Li_4Ti_5O_{12}$ [22–24,27,28,30–32]. However, as a new anode composite material for lithium ion batteries, the performance of LTO/graphene is not satisfactory. Since the performance of the composites depends on the preparation method, the synthesis of a perfect LTO/graphene composite is still challenging. To prepare LTO/graphene composite with controlled morphology, various preparation methods, such as solid state method [32], hydrothermal route [33], solvothermal process [34], electrospinning deposition [35], microwave-hydrothermal method [36], and sol-gel method [37,38] have been proposed by many researchers. Among them, the sol-gel method is a preferred method for the synthesis of $Li_4Ti_5O_{12}$ materials with advanced properties, such as higher purity, homogeneity and small particle size due to the homogeneously mixing in atomic level [37–40].

Recently, an electrostatic assembly method was employed to synthesize graphene/metal oxide [41] or LTO/graphene hybrid [31]. In a previous paper we synthesized the $Li_4Ti_5O_{12}$/graphene composites by a solid state-assembly method, and we demonstrated that the LTO/graphene composites prepared by the solid state-assembly procedure showed better electrochemical performances [25]. In order to further improve the performance of LTO/graphene composites, in the present paper, $Li_4Ti_5O_{12}$/graphene nano-composites are first successfully synthesized by combining a sol-gel method and electrostatic assembly method.

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Thus, the pure lithium titanates were first prepared by a sol-gel method, and then a graphene oxide was coated on the prepared $Li_4Ti_5O_{12}$ by an electrostatic assembly method. Moreover, the effects of graphene oxide (GO) amount on the performances of LTO/graphene composites, such as structural properties and electrochemical properties are also carefully investigated.

2. Experimental

2.1. Material preparation

Pure lithium titanates were prepared by a sol-gel method based on citric acid using the stoichiometric amounts of lithium nitrate, tetrabutyl titanate. Citric acid was employed as a chelating reagent in this sol-gel process. First, lithium nitrate and citric acid were dissolved in deionized water to form a colorless transparent solution. Sceond, a mol ratio of tetrabutyl titanate: alcohol = 1:5 were well-mixed, and then the lithium nitrate-citric acid solution was slowly added into the tetrabutyl-alcohol solution with magnetic stirring. After that, the solution was heated gently with continuous stirring to remove the excess water at 85 °C in a thermostatic water bath to form a yellowish gel. After drying at 80 °C in air oven for 12 h, the gel was put into a vacuum drying oven and then heated at 80 °C for 6 h to allow H_2O to be evaporated. The precursors were then calcined at 800 °C for 12 h in a flowing air atmosphere to obtain the $Li_4Ti_5O_{12}$ samples. Excessive Li(5 wt%) was provided to compensate for the volatilization of Li during synthesis.

After that, the LTO/graphene composites were obtained using an electrostatic assembly method. Firstly, the pre-formed LTOs were immersed in the 1 g L^{-1} poly (allylamine hydrochlorine) (PAH) solution for 1 h. Secondly, the LTOs were dried at 80 °C for 6 h. Thirdly, GO prepared by modified Hummers method and the LTO were mixed to form aqueous suspensions. These suspensions were vigorously stirred together to form a slurry with various weight ratio of GO:LTO (=0.1 wt%, 0.2 wt%, 0.5 wt% and 1 wt%). Finally, 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

Structural analyses of the as-prepared $Li_4Ti_5O_{12}$ and LTO/graphene samples were performed by the X-ray diffraction (XRD, Cu-Kα radiation, DX2700, Dandong Haoyuan,China) and Raman spectroscopy (Renishaw inVia, Britain) using 532 nm excited laser. The particle morphologies of the samples were observed under a scanning electron microscopy (SEM, EVO HD 15, Zeiss, German). A Quanta-450 SEM instrument was used to image the materials and to collect EDX maps of as-prepared powders. The detailed nanostructure of the LTO/graphene sample was studied on a transmission electron microscope(TEM, JEOL2100).

2.3. Electrochemical measurements

The electrochemical performances of $Li_4Ti_5O_{12}$ and LTO/graphene composites were carried out in 2025 coin-type cells. The working electrodes were prepared by mixing 80 wt% active material, 10 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) dispersed in N-methyl-2-pyrrolidinone (NMP), and then following by coating the slurry onto copper current collector and drying at 80 °C. The fabricated electrodes were dried again at 120 °C for 4 h in vacuum and cut into circles with diameter 15 mm in size. The high-purity lithium metal was used as the cathode while the electrolyte solution was 1 M LiPF6 in EC:DMC (1:1 by volume) mixture solution. The coin-cells were assembled in a glove box(Universal 2440/750, Mikrouna) filled with high-purity argon, using a polypropylene membrane (Celgard 2400) as the separator.

Charge-discharge performance was characterized galvanostatically on Land 2000T(China) tester at different current densities over a voltage range of 1.0-2.0 V versus Li/Li^+ electrode at room temperature. Cyclic voltammogram was recorded from 1 V to 2.5 V with a scan rate of 0.1 mV s^{-1} by CHI 660a electrochemical workstation. The electrochemical impedance spectroscopy (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

The X-ray diffraction patterns (XRD) of the sol-gel prepared LTO/graphene composites with various amounts of GO:LTO (=0.1 wt%, 0.2 wt%, 0.5 wt% and 1 wt%) are shown in Fig. 1. For comparison, the XRD pattern of the $Li_4Ti_5O_{12}$ sample prepared by sol-gel method is shown in the bottom of the figure. The diffraction peaks of all samples are similar and can be indexed to spinel $Li_4Ti_5O_{12}$ (JCPDS card No.49-00207). In addition, for all the LTO/graphene composites, no any diffraction peaks of graphitic structure were detected, which is similar to the results of LTO/graphene composites reported by literatures [17,25,32,36,37].

Fig. 2 shows the Raman spectra of $Li_4Ti_5O_{12}$ and LTO/graphene samples. Similarly as the results of literatures [10,13,25,36], five main Raman bands peaked at about 234, 348, 423, 674 and 744 cm^{-1} can be contributed to the features of the spinel $Li_4Ti_5O_{12}$. For all the LTO/graphene samples, two new bands in the range of 1200–1460 cm^{-1} and 1470–1730 cm^{-1} were detected, which are attributed to D-band and G-band of the graphene. Moreover, the intensities of D-band and G-band in Fig. 2 increase with an increase in the amounts of graphene in the composite. This result clearly indicates that the LTO/graphene composite materials were successfully obtained by this sol-gel-assembly method.

Fig. 3a and b show the SEM images of the as-prepared $Li_4Ti_5O_{12}$ and LTO/graphene composite(0.5 wt%). As seen in Fig. 3, the two samples have uniform particle size distribution with little agglomeration. In the magnified SEM image of $Li_4Ti_5O_{12}$/graphene shown in Fig. 3c, it is difficult to distinguish $Li_4Ti_5O_{12}$ and graphene. The composite is well crystallized with uniform and narrow size distribution in the range of 200–500 nm. Different from those of $Li_4Ti_5O_{12}$, some particles in LTO/graphene (Fig. 3b and c) are covered by a thin film.

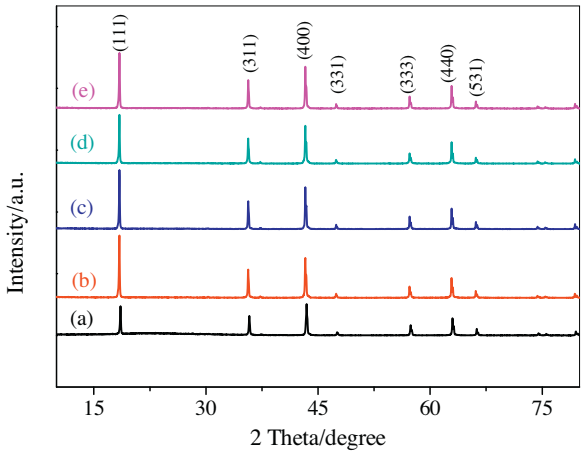

Fig. 1. XRD pattern of sol-gel prepared LTO/graphene composites with various amounts of GO:LTO: (a)$Li_4Ti_5O_{12}$; (b) 0.1 wt%, (c) 0.2 wt%, (d) 0.5 wt%, and (e) 1 wt%.