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Outstanding lithium-storage performance of carbon-free $Li_4Ti_5O_{12}$ anode material for rechargeable lithium-ion batteries

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ABSTRACT

In this work, carbon-free $Li_4Ti_5O_{12}$ material has been successfully prepared by using a conventional sol-gel method. X-ray diffraction (XRD) result reveals that the as-prepared pristine $Li_4Ti_5O_{12}$ sample has the spinel-type structure with a cubic lattice. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images indicate that the morphology of $Li_4Ti_5O_{12}$ material is well-crystallized with a uniform size distribution in the range of 300–700 nm. Moreover, high-resolution TEM image demonstrates that the surface of $Li_4Ti_5O_{12}$ particle is very smooth without any carbon coating. When used as anode material for lithium-ion batteries, the pristine $Li_4Ti_5O_{12}$ exhibits outstanding lithium-storage performances such as high reversible capacity, excellent rate capability and stable cycling property. Therefore, we can speculate that the as-prepared $Li_4Ti_5O_{12}$ sample without any carbon materials is a promising candidate for the application of high-performance anode for lithium-ion batteries.

1. Introduction

Nowadays, rechargeable lithium-ion batteries with high energy/power density and good safety have been regarded as one of the most promising energy devices for electric vehicles and hybrid electric vehicles [1,2]. Nevertheless, the search for advanced anode materials to meet the requirements of good rate capability and long-cycle life is still critical for high-performance lithium-ion batteries. Compared with the commercial graphite-based anodes, spinel $Li_4Ti_5O_{12}$ material has attracted great attention for lithium-ion batteries anode due to its intrinsic characteristics such as high thermal stability, good safety, excellent rate capability and long-cycle life [3–5]. Moreover, it shows a flat Li^+ insertion/extraction potential plateau at around 1.55 V (vs. Li/Li^+) and a high theoretical capacity of 175 mAh g^{-1} [6,7]. Despite of these advantages, the $Li_4Ti_5O_{12}$ material suffers from the inherent poor electronic conductivity (ca. 10^{-13} S cm^{-1}) and moderate Li^+-ion diffusion coefficient (10^{-8} cm^2 s^{-1}) [8,9], which greatly inhibit its practical application for energy storage.

Up to the present, many strategies have been devoted to solve these issues. Carbon coating [5,7,9–12] has been regarded as the most common approach to improve the lithium-storage performance of $Li_4Ti_5O_{12}$. Owing to this carbon layer, which could be able to prevent the growth of $Li_4Ti_5O_{12}$ particles during the sintering process and enhance its apparent electronic conductivity, the high-rate capability and long-cycle stability of $Li_4Ti_5O_{12}$ will be improved. For instance, Lin's group [9] reported that the carbon-coated $Li_4Ti_5O_{12}$ was prepared by using a facile one-pot sol-gel route and the obtained composite delivered high discharge capacities of 153.9 and 147.9 mAh g^{-1} at 10 and 20 C respectively. Doping with other metal ions [13–15] is another strategy to improve the intrinsic electronic conductivity of $Li_4Ti_5O_{12}$. What's more, synthesis of nanosized $Li_4Ti_5O_{12}$ particles [16,17] is a promising approach to reduce the Li^+-ion diffusion path and thus improve the Li^+-ion diffusion efficiency. However, it remains a great challenge to prepare nanostructured $Li_4Ti_5O_{12}$ materials with desirable architectures for fulfilling the requirements of excellent rate capability and stable long-cycle life.

In this current work, we designed and prepared the carbon-free $Li_4Ti_5O_{12}$ material used as anode for rechargeable lithium-ion batteries by using a simple sol-gel approach. The results showed that the well-crystallized $Li_4Ti_5O_{12}$ sample had the spinel-type structure and the surface of $Li_4Ti_5O_{12}$ particle was smooth without any carbon coating. The electrochemical measurements revealed that the pristine $Li_4Ti_5O_{12}$ anode exhibited outstanding lithium-storage performances including rate capability and long-cycle life. Thus, the as-prepared carbon-free $Li_4Ti_5O_{12}$ material can be considered as a promising anode for high-performance lithium-ion batteries.

2. Experimental

2.1. Material preparation

The pristine $Li_4Ti_5O_{12}$ sample (P-$Li_4Ti_5O_{12}$) was prepared by using a conventional sol-gel method with lithium acetate dehydrate ($CH_3COOLi{\cdot}2H_2O$), tetrabutyl titanate ($Ti(OC_4H_9)_4$) and citric acid

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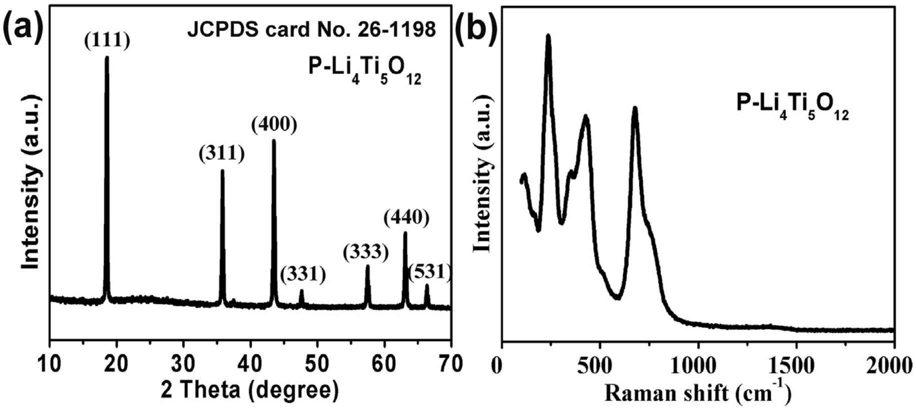

Fig. 1. (a) XRD patterns and (b) Raman spectrum of the as-prepared P-$Li_4Ti_5O_{12}$ sample.

($C_6H_8O_7{\cdot}H_2O$) as chelating agent. In a typical synthesis, the $CH_3COOLi{\cdot}2H_2O$ and $Ti(OC_4H_9)_4$ were separately dissolved in ethanol solution with Li:Ti molar ratio of 4.5:5. Afterwards, the CH_3COOLi solution was slowly added to the $Ti(OC_4H_9)_4$ solution under continuous stirring at 25 °C for 4 h. Then, the mixed solution was further added to the ethanol solution containing $C_6H_8O_7{\cdot}H_2O$. The mixture was stirred at 25 °C for 2 h and gently heated at 70 °C until a gel precursor was formed. Finally, the powder was calcinated at 350 °C for 6 h and then calcinated at 850 °C for 12 h in a flowing air atmosphere to get the P-$Li_4Ti_5O_{12}$ sample.

2.2. Material characterization

The phase and crystal structure of the as-prepared material were investigated by X-ray powder diffraction (XRD) analysis system (Xpert MPD DY1219) equipped with a Cu Kα radiation source (λ = 0.15406 nm). Raman spectroscopy was carried out on a laser Raman spectrometer (Dongwoo DM500i) with the 532 nm line of an Ar ion laser as the excitation source. The morphology and microstructure of P-$Li_4Ti_5O_{12}$ sample were recorded by scanning electron microscope (SEM, JEOL-7401) and transmission electron microscopy (TEM, JEOL, JEM-2100F). To further characterize the surface morphology of P-$Li_4Ti_5O_{12}$ particles, the high-resolution transmission electron microscopy (HRTEM) was also performed. The electronic conductivity of the as-prepared P-$Li_4Ti_5O_{12}$ material was measured with an RTS-8 linear four-point probe measurement system.

2.3. Electrochemical measurements

CR2032 coin-type cells were used to evaluate the lithium-storage performance of the as-prepared P-$Li_4Ti_5O_{12}$ anode material. The working electrodes were prepared by spreading the slurry of the active material (85 wt%), super P (10 wt%) and poly(vinylidene fluoride) binder (5 wt%) dissolved in *N*-methylpyrrolidone solvent, which was uniformly spread on a Cu foil and dried at 110 °C overnight to remove the residual solvent. The coin cells were assembled in an Ar-filled glove box using pure lithium foil as the counter electrode, the microporous polypropylene membrane (Celgard 2400) as the separator. The electrolyte was 1 M $LiPF_6$ solution in ethylene carbonate (EC): diethyl carbonate (DEC): ethyl methyl carbonate (EMC) with a volume ratio of 1:1:1. The mass loading of the working electrode was about 2.8 mg cm^{-2}. The charge/discharge tests were carried out over potential ranging from 1.0 V to 2.5 V (vs. Li^+/Li) at different current rates based on the theoretical capacity of 175 mAh g^{-1}. The electrochemical impedance spectroscopy (EIS) measurement was carried out on an electrochemical workstation (PARSTAT) in the frequency range of 0.01 Hz to 100 kHz by applying an AC signal of 5 mV. All the electrochemical measurements were performed at room temperature (25 °C).

3. Results and discussion

The XRD patterns of the as-prepared P-$Li_4Ti_5O_{12}$ sample are shown in Fig. 1a. All of the diffraction peaks of P-$Li_4Ti_5O_{12}$ can be indexed to a cubic spinel structure with Fd-3m space group, which are in good

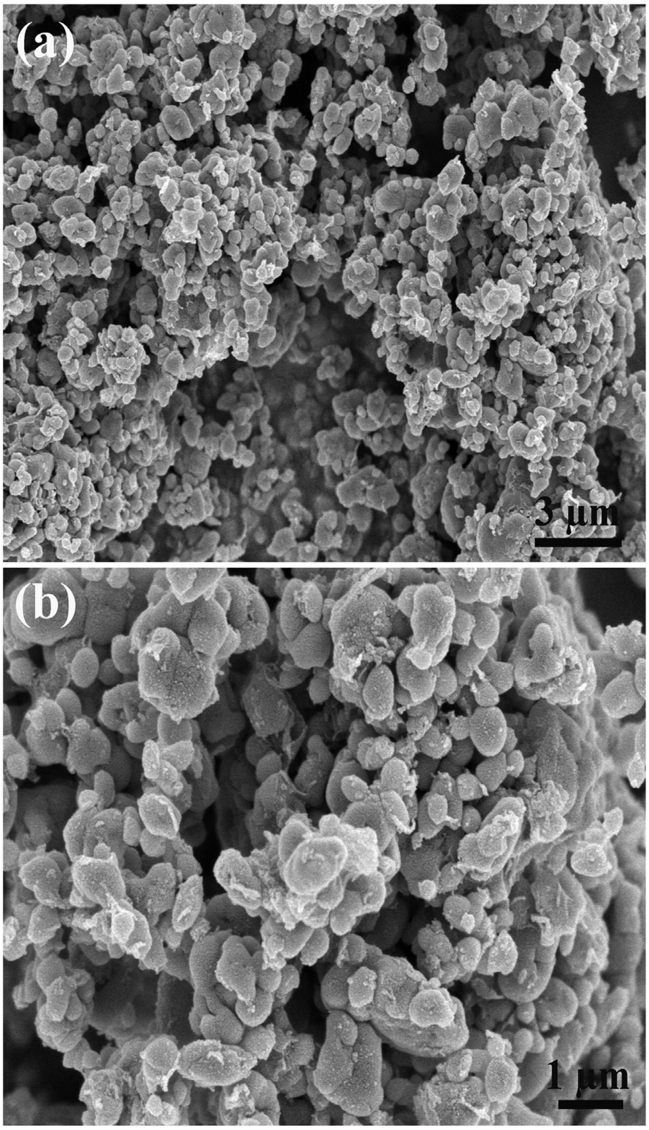

Fig. 2. SEM images of the obtained P-$Li_4Ti_5O_{12}$ particles.