

Short communication

# Preparation and characteristic of carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material

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Available online 26 June 2007

## Abstract

Carbon-coated spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anode material was prepared by heat-treating the mixture of  $\text{TiO}_2$  (anatase),  $\text{Li}_2\text{CO}_3$  and sugar. The products were characterized by X-ray diffraction, scanning electronic microscope and transmission electron microscope. A nanolayer of amorphous carbon was homogeneously coated on the surface of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particles. Electrochemical results show that the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  displays larger diffusion coefficient of lithium ions, higher rate capability and excellent reversibility. Its reversible capacity is approximately  $160 \text{ mAh g}^{-1}$  at the rate 0.1 C and good cycling behavior at different current density is achieved.

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**Keywords:** Spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ; Surface modification; Anode material; Carbon-coating

## 1. Introduction

Various kinds of methods have been applied to modify the surface of electrode materials such as coating oxides on the surfaces of cathode, depositing carbon materials, polymers and conductive agents on the surfaces of anode [1–10]. These results show that surface modification is an effective method to improve electrochemical performance of electrode materials such as irreversible capacity, reversible capacity, cycling behavior and rate capability.

In the case of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , it is regarded as an ideal anode material with long cycling stability due to zero strain or volume change when lithium intercalates into and de-intercalates from [11–17]. To improve its energy density, cycling behavior, safety and rate capability, much work has been done, for example, doping, decreasing its particle size and extending its surface area [18–22]. It has been found that high diffusion coefficient of lithium ions and electronic conductivity are essential to the good performance of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as anode material for lithium-ion batteries. However, electronic conductivity of the normal spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is not high enough. As a result, an electron conductive phase such as carbon is necessary in order to form composite electrode with adequate electronic conductivity. In this work,

we unexpectedly, for the first time, found that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particles were coated by a nanolayer of carbon. Here we reported this synthetic process and the structural and electrochemical characteristics of the prepared composite anode material.

## 2. Experimental

Virginal  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (sample A) was prepared by reacting stoichiometric amount of  $\text{Li}_2\text{CO}_3$  and  $\text{TiO}_2$  (anatase) at  $750^\circ\text{C}$  for 12 h to decompose  $\text{Li}_2\text{CO}_3$  and  $850^\circ\text{C}$  for 24 h in the air. Carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (sample B) was prepared by dispersing stoichiometric amount of  $\text{TiO}_2$  (anatase) and  $\text{Li}_2\text{CO}_3$  in the mixture solution of alcohol/deionized water/sugar (weight ratio: 3.3:1.3:1). After removing the solvent, the resulted powder was ground and heat-treated by the same process as sample A.

The crystal structures of all the samples were characterized by X-ray powder diffraction (XRD) measurement using the Bruker D8 Advanced Spectrometer with  $\text{Cu K}\alpha$  radiation source filtered by a Ni thin plate. Particle morphology was observed by scanning electronic microscopy (Philips XL 300) and transmission electronic microscope (JEOL JEM 2011).

The two-electrode coin-type half cells were assembled as follows. The working electrode was prepared by pressing a powder mixture of the sample, acetylene black and poly(vinyl difluoride) (PVDF) in a weight ratio of 80:10:10 into pellets of about 0.3 mm in thickness and about 1 cm in diameter. The electrolyte was  $1 \text{ mol l}^{-1}$   $\text{LiPF}_6/\text{EC}:\text{DMC}:\text{DEC}$  (1:1:1 in volume). Li metal was used as the counter and reference electrode and Celgard

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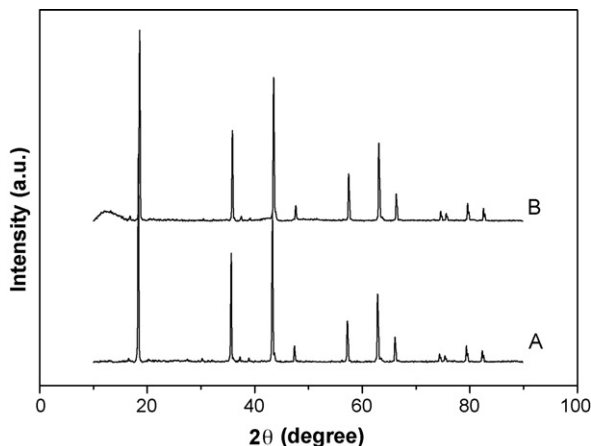


Fig. 1. XRD patterns of (A) the virginal and (B) the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

2400 as the separator. All the cells were fabricated in a glove box filled with argon gas. Discharge and charge behavior was galvanostatically performed with a cycle tester (LAND electronic Co.) controlled by a personal computer at the voltage range of 2.5–1.0 V. Cyclic voltammograms were recorded from 0.9 to 2.6 V at different scan rate using CHI660A electrochemical workstation system (Covarda).

### 3. Results and discussion

Spinel lithium titanium oxide with a nominal composition of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  can be conveniently synthesized from the conventional method. The XRD patterns of the prepared products A and B are shown in Fig. 1. It can be seen that the main phase of the reaction products are  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  with the spinel structure and there is not much evident difference in the peak intensities and positions, suggesting that the added sugar does not affect the spinel structure of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  during heat-treatment.

Scanning electronic micrographs of the prepared samples A and B are shown in Fig. 2. Both products are composed of fine particles of submicron. However, the particles of sample B appear to be finer. When transmission electronic microscope (TEM) was employed to observe the particle morphology of the sample B, a nanolayer of carbon was surprisingly found on the surface of the particles (Fig. 3) and it was homogeneously coated on  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particles. The nanolayer of carbon is amorphous since the product was sintered at temperature below  $1000^\circ\text{C}$  [11]. Evidently, it is mostly from the heat-treatment process. During the heat-treatment, the formed fine  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particles moved together to be larger particles. In the meanwhile, the added sugar was at first uniformly distributed in the matrix and turned into carbon during heat-treatment. During the agglomeration of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particles, one part of carbon was given away by producing carbon oxides to hinder the agglomeration process. The remaining carbon from sugar moved to the surface of the formed fine  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particles and appeared as a nano coating layer.

In order to measure the content of carbon-coating, we tried to measure the amount of carbon by burning the composite in air at  $1000^\circ\text{C}$  for over 2 days. However, the weight difference

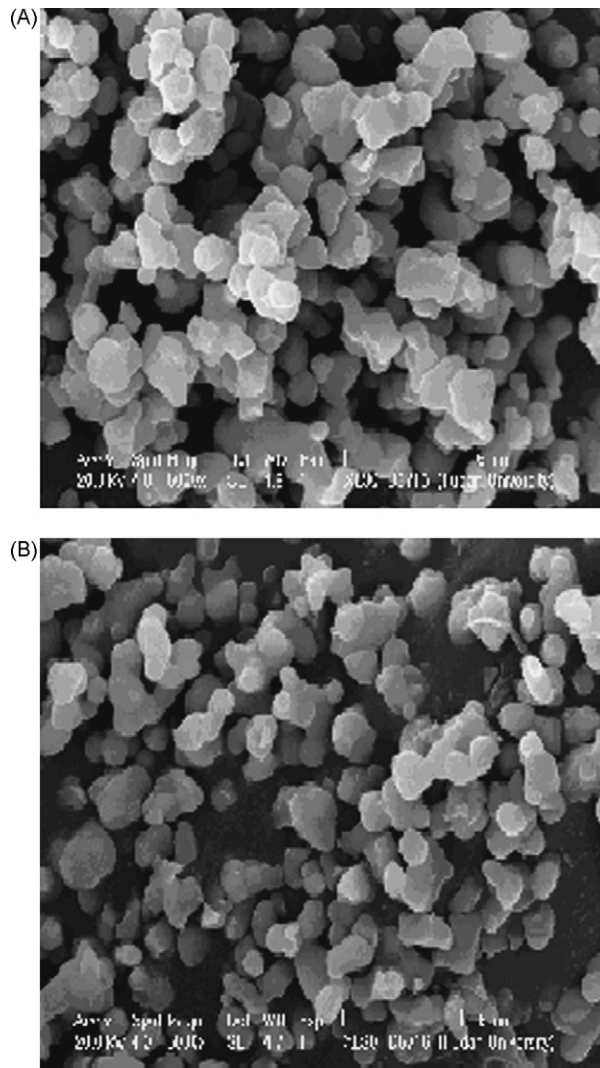


Fig. 2. SEM images of (A) the virginal and (B) the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

is within the scope of error. In addition, after the burning, the carbon-coating could not be found during the measurement of TEM. This indicates that the amount of carbon is very small. Of course, other method is necessary to find the precise content of carbon.

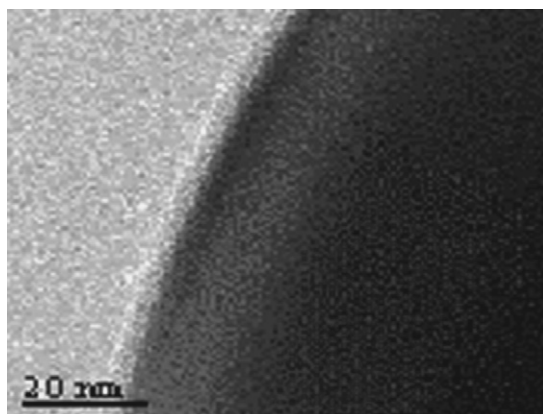


Fig. 3. TEM image of the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

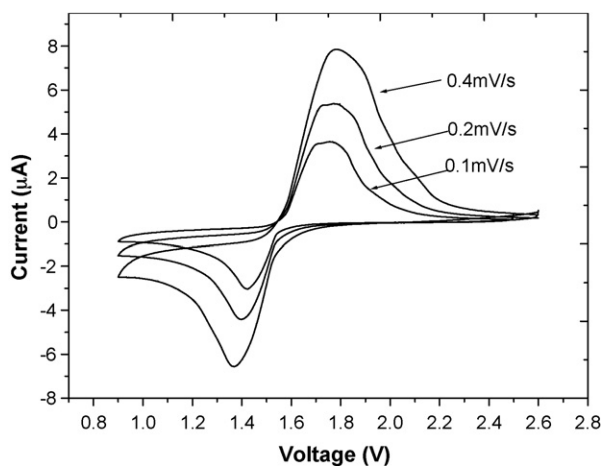


Fig. 4. Cyclic voltammograms of the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  at different scan rate.

Cyclic voltammograms of the sample B at the scan rates of 0.1, 0.2 and  $0.4 \text{ mV s}^{-1}$  between 2.6 and 0.9 V are shown in Fig. 4. The ratios of  $I_{\text{pa}}/I_{\text{pc}}$  are very close to 1, which suggests that the kinetics of lithium intercalation into and de-intercalation from the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  displays good reversibility. There is a linear relationship between  $I_{\text{pa}}$  and square root of scan rate. Consequently, diffusion coefficient of lithium ions was roughly estimated by cyclic voltammetry since the intercalation and de-intercalation is also a redox process. Here we utilized the reduction process for the estimation. It is known that there is a following equation [23]:

$$I_p = 2.69 \times 10^5 A n^{2/3} C_0 D^{1/2} v^{1/2} \quad (\text{at } 25^\circ \text{C}) \quad (1)$$

where  $I_p$  is the peak current of reduction peak,  $n$  the number of electrons per molecule during the intercalation,  $A$  the surface area of the anode (geometric surface area of the electrode is used instead),  $C_0$  the concentration of lithium ions,  $D$  is the diffusion coefficient of lithium ion and  $v$  is the scan rate. According to the Eq. (1), the diffusion coefficient of lithium ions in the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  was roughly calculated to be  $5.43 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ , about one order of magnitude higher than that of the virginal sample A. The latter is about  $7.97 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ , which is close to the reported value [20]. As observed from SEM, the particles of the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  are smaller, and in the meanwhile there is a conductive carbon layer on the surface of the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . It is well known that the carbon-coating on electrode materials such as  $\text{LiFePO}_4$  and  $\text{TiO}_2$  is a good way to improve its cycling performance [2,24]. The main reason is perhaps due to the increase of the electronic conductivity and the consequent increase of diffusion coefficient of lithium ions. Of course, further direct evidence is necessary. Since both smaller particle and carbon favor the mobility of lithium ions during the redox process, a higher diffusion coefficient of lithium ions in the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is achieved.

The discharge/charge profiles in the first cycle of the virginal (sample A) and the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (sample B) at 0.1 C ( $0.16 \text{ mA cm}^{-2}$ ) are shown in Fig. 5. The discharge capacity in the first cycle of sample B is  $155.7 \text{ mAh g}^{-1}$ , much higher than

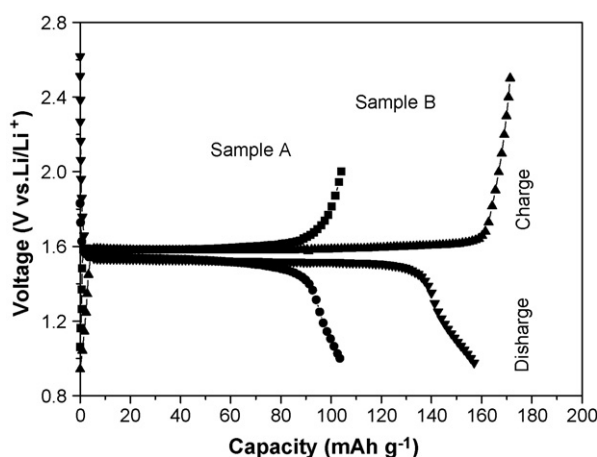


Fig. 5. The discharge/charge profiles in the first cycle of the virginal (sample A) and the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (sample B) at 0.1 C.

that of sample A. Sample A displays only  $103.6 \text{ mAh g}^{-1}$ . As to why the virginal  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  displays smaller reversible capacity than the normal reported value such as about  $150 \text{ mAh g}^{-1}$  at 0.1 C [17], it can be ascribed to the different thickness of the electrode pellets. In our case, it is about 0.3 mm on one side, much higher than the normal way in practical lithium ion battery, about 0.1 mm for the double sides. It is well known that the thickness of the electrodes affects much the capacity. When it is small, rate capability will be better. In addition, it can be seen that the coulomb efficiency of both samples are very close to 100%, which suggest the products have good reversibility.

The relationship of the reversible capacity of the virginal and the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  at 0.1 C with cycle number is shown in Fig. 6. Both samples do not present evident capacity fading. It is attributed to the good stability of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  framework and to the very small change of the cubic unit cell occurring during lithium intercalation and de-intercalation [11–22].

Discharge capacity of the virginal and the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  in the range of 0.16 ( $0.1 \text{ C}$ )– $3.2 \text{ mA cm}^{-2}$  ( $2 \text{ C}$ ) between 1 and 2.5 V is shown in Fig. 7. Compared to the virginal  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  powder, the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  presents higher

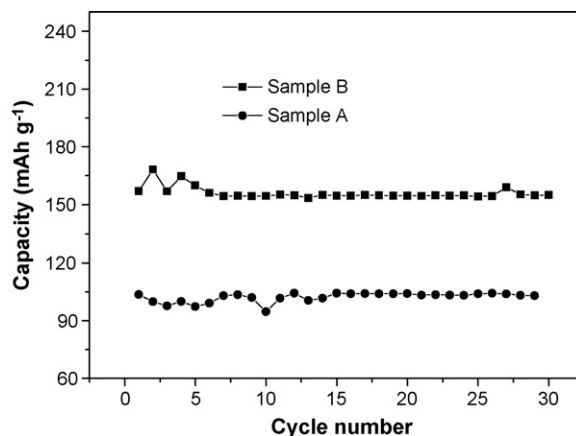


Fig. 6. The relationship of the reversible capacity of the virginal (sample A) and carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (sample B) at 0.1 C with cycle number.

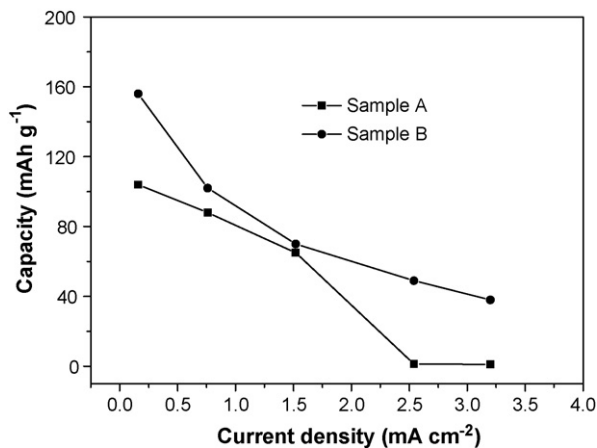


Fig. 7. Discharge capacity of the virginal (sample A) and carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (sample B) in the range of 0.16 (0.1 C)–3.2  $\text{mA cm}^{-2}$  (2 C), between 1 and 2.5 V.

reversible capacity at the same current density, indicating more satisfactory rate capability. It is known that a redox process in this kind of electrode material can be finished only when lithium ions and electrons take part in. As above mentioned, the diffusion coefficients of lithium ions and the electronic conductivity are increased for the nano carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . In addition, smaller particle size or larger surface area is achieved. Consequently, the rate capability of the carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is ameliorated.

#### 4. Conclusion

Carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  was obtained by adding sugar to the precursors,  $\text{TiO}_2$  and  $\text{Li}_2\text{CO}_3$ . The added sugar does not affect the spinel structure, and decreases the particle size by inhibiting the agglomeration of particles during the heat-treatment. Partial sugar remains on the surface of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as a nano carbon layer. This layer favors the diffusion of lithium ions and redox process. As a result, compared to the conventional synthesized  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , the nano carbon-coated  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  has higher capacity and better rate capability.

#### Acknowledgements

Financial supports from Shanghai Science & Technology Committee (0552nm05025 and 04QMX1406), National Basic

Research Program of China (973 Program No: 2007CB209700) and China Natural Science Foundation (50573012) are greatly appreciated.

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