*Journal of Computational Science & Engineering* 30 (2017) 865-867

**Available at http://www.asocse.org ISSN 1710-4068**

# Carbon modified lithium titanate using gelatin as carbon precursor and their application as anode for high performance lithium ions batteries

Tingting liang, Zhen Kong, Hongliang Li*

Institute of Materials for Energy and Environment, College of Materials Science and Engineering, Qingdao University, Qingdao 266071, China

***Abstract:*** **Spinel Li4Ti5O12 (LTO) is attractive anode material for lithium-ion batteries (LIBs) owing to their unique electrochemical properties. Therefore, Li4Ti5O12/C composite was successfully synthesized by hydrothermal method, using tetrabutyltitanate as titanium source, lithium hydroxide as lithium source and gelatin as carbon source. After the addition of gelatin, Li4Ti5O12 has better cycle performance and rate performance.**

***Keywords:*** LITHIum titanate; Gelatin; Hydrothermal; Lithium ion battery

Received 19 July 2017, Revised 23 July 2017, Accepted 25 July 2017

*Corresponding Author: Hongliang Li

## 1. Introduction

Spinel Li4Ti5O12 (LTO) has a high voltage platform at 1.55V versus Li/Li+, which can effectively avoid the formation of solid-electrolyte interphase (SEI) film and prevent the generation of lithium dendrites[1]. It also has a higher voltage specific capacity (specific capacity of 175mAh/g) and "zero strain" effect [2]. In the charge and discharge process, the volume of Li4Ti5O12 is almost constant and it has extending cycle performance. However, due to the low conductivity (10-3 S/cm) of Li4Ti5O12, the cycling stability and rate performance of pristine Li4Ti5O12 are unsatisfied[3-4]. So many researches focus on the coating of conductive material and reducing the size of particles to improve the performance of LTO have been explored. This article mainly use gelatin as a carbon source to coat Li4Ti5O12 particles in order to increase its conductivity and increasing the lithium cycle performance and rate performance.

## 2. Experimental Section

### *2.1. Sample preparation*

Firstly, 3.4 mL tetrabutyltitanate was poured into 25 mL of 2 wt% CTAB ethylene glycol solution, forming solution A. Secondly, an amount of gelatin(G) was added to 30mL of 2.25 wt% LiOH aqueous solution under stirring, resulting in solution B. Solution B was added to solution A under stirring. The resulted mixture solution was then transformed into a 100mL Teflon lined stainless steel autoclave and treated in an thermostatic oven at 180℃ for 24h. Solid was then collected by centrifugation and washed with distilled water and ethylene glycol thrice. When the solids were dried with a freezer dryer, and the white solids derived from solution containing 0 and 0.6g G were resulted. The freeze dried solids were then calcined firstly at 700℃ for 3h in $N_2$ atmosphere with a programmed tube furnace. When the samples were cooled to room temperature, white pristine LTO and black C/LTO composite were obtained. Solids derived from the original solution containing 0 and 0.6g G were designated as LTO and C/LTO-0.6, respectively.

### *2.2. Characterization*

X-ray power diffraction (XRD) patterns were recorded on a RigakuUltima IV X-ray diffractometer with Cu-Kα radiation (λ = 0.15418 nm). The morphologies and the microstructures of the samples were examined by using a JEOL JSM-7800F scanning electron microscope (SEM). The specific surface areas were estimated with the Brunauer-Emmett-Teller (BET) method with $N_2$ adsorption data in the relative pressure range of P/P0 = 0.05-0.35. The pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) model applied to the desorption branch of the N2 isotherms obtained with an Autosorb-IQ-MP/XR analyzer (Quantachrome).

### *2.3. Electrochemical Measurements*

The electrochemical performances were evaluated under the same conditions using CR2016 coin-type half cells. For preparing the working electrodes, a mixture of 80wt% active materials, 10wt% carbon black and 10 wt% polyvinylidene fluorides (PVDF) were mixed into NMP. Afterwards, the obtained slurry was cast onto a copper foil and dried in vacuum at 110℃ for 10 h. The active materials loaded on the electrode were approximately 0.6-1.0 mg per piece. The CR2016 type coin cells were assembled in a highly pure Argon-filled glove box uing pure lithium using as anode, 1mol Ł-1 LiPF6 (Shenzhen Capchem Technology Co., Ltd, China) as the electrolyte and Celgard 2400 membrane as separator. The cells cycled at the potential range of 0.8-3 V on a Land testing system. Cyclic voltammetry (CV) measurements were performed at a scan rate of 2 mV s-1, 5 mV s-1, 10 mV s-1 between 0.8 and 3V.



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## 3. Results and discussion

### *3.1. Structure and Morphology*

Figure 1 shows the XRD patterns of LTO and LTO/C-0.6 calcined at 600 ℃ for 3h. From the Figure 1, we can see that there are obviously peaks at 2θ = 18, 36, 43, 47, 57, 63 and 66, corresponding the crystal faces of (111), (311), (400), (331), (511), (440) and (531). Such a pattern is consistent with JCPDS Card No. 490207, indicating that LTO and LTO/C-0.6 have been synthesized successfully. From LTO/C-0.6, it can be seen that there is no obvious carbon peak, indicating that the carbon incorporated is amorphous one.

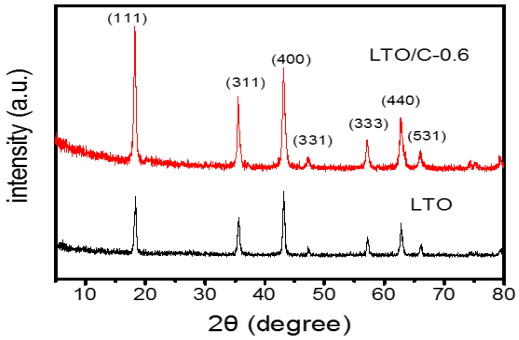


**Figure 1. XRD patterns of LTO and LTO/C-0.6.**

Figure 2 is the SEM images of LTO (a, c) and LTO/C-0.6 (b, d) at different magnifications. From Figure2 it can be seen that both LTO and LTO/C composites show spherical morphology. From (c) and (d), it can be seen that hydrothermally synthesized LTO and LTO/C-0.6 both consist of numerous smaller Li4Ti5O12 particles. What's more, with the gelatin addition, the spherical LTO/C-0.6 become more porous, which will be beneficial to the transfer and diffusion of lithium ions and is helpful for the improvement of battery performance.

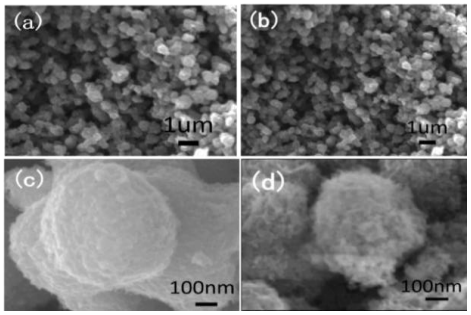


**Figure2.SEM images of (a, c) LTO and (b, d) LTO / C-0.6 at different magnifications.**

In order to further investigate the pore structure of LTO and LTO/C-0.6, we carried out nitrogen adsorption and desorption tests. Figure3 shows the nitrogen adsorption-desorption curves and the BJH pore size distribution curves (inset) of LTO (a) and LTO/C-0.6 (b). Both the isotherms show type IV physisorption according to the IUPAC classification and exhibit a representative H1-type hysteresis loop, [5-6]indicating the existence of abundant mesoporous structures in the carbon modified Li4Ti5O12 architectures derived from the hydrothermal process. However, the LTO/C-0.6 curve shifted to a relatively high pressure, indicating an increase in pore size. The pore size distributions of LTO and LTO/C-0.6 are 3.9nm and 15.5nm, respectively. The pore size of LTO/C-0.6 is larger than that of LTO, which is helpful for the transfer and diffusion of lithium ions and for the improvement of the rate performance. The specific surface area, pore volume and pore size of LTO and LTO/C-0.6 are shown in Table 1. As can be seen from the table, the specific surface area of the sample increases with the addition of gelatin, indicating that the gelatin as a carbon source increases the specific surface area of the LTO, which is helpful the performance of the battery.

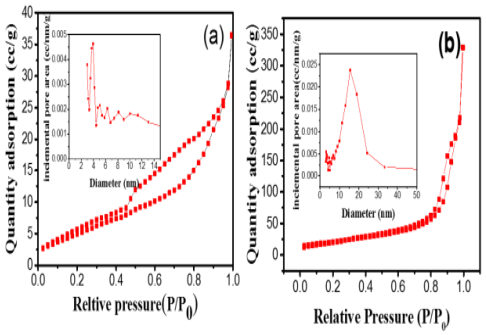


**Figure3The nitrogen adsorption-desorption isotherms and corresponding pore size distribution curves (inset) of (a) LTO and (b) LTO/C-0.6**

### *3.2 Electrochemical Performance*

Figure 4(a) shows the cycle performance of LTO and LTO/C-0.6 at current density of 200 mA g-1 and (b) shows the rate performance of them at different current density. From the Figure 4(a), we could see that the specific capacity of LTO/C-0.6 was 175mAh g-1 after 300 cycles at a current density of 200 mA g-1, whereas the specific capacity of LTO first cycle was only 162mAh g-1 and dropped to 101.2 mAh g-1 after cycling 300, indicating that the addition of G helps to improve the cycle performance. It can be seen from Figure 4(b) that the rate performance of LTO/C-0.6 is better than that of LTO, and the specific capacity of LTO/C-0.6 reaches 149mA g-1 even at the current density of 5000 mA g-1. Figure 4(c) displays the charge and discharge performance of LTO/C-0.6 at different rates. Relatively high specific discharge capacities of 226.2，221.3，190.2, 176.3, 159.7 and 149.3 mAh • g-1 were observed when the rates of LTO/C-0.6 is set at 200, 500 ,1000, 2000, 4000 and 5000 mA • g-1, respectively. With the increasing of charged and discharged rates, a significant decrease in specific capacity value and a decrease in the discharge voltage plateau were observed, which are related to the slow Li-ion diffusion kinetics at high discharge rates.



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**Table 1. Specific surface Area, Pore Volume and Average pore size of LTO and LTO/C-0.6**

| Samples | Surface area ($m^2$/g) | Pore volume (cc/g) | Pore size (nm) |
|---|---|---|---|
| LTO | 20.578 | 0.057 | 3.857 |
| LTO/C-0.6 | 76.494 | 0.513 | 15.487 |

Even at a high current rate of 5000 mA • g-1, a reversible capacity of 149.3mAh g-1 could still be remained, confirming that the gelatin as carbon source is beneficial to increase the ionic and electronic conductive in the electrode made of the LTO/C-0.6. Figure 4(d) displays the CV of LTO/C-0.6, and the CV curve show a set of redox peaks at different scan rates. At the scan rate of 2mv s-1, the position of the cathode peak is 1.37 V, corresponding to the discharge platform and insert Li+ into LTO. The position of the anode peak at about 1.82 V corresponds to the charging platform and de-insert of Li+ from LTO. When the scan rate increased to 5mv s-1, the anodic peak position increases to 1.98 V, which is higher than anodic peak obtained under 2mv s-1, which may be due to irreversible capacity and structural changes. The cathode peak position dropped to 1.23V when the scan rate increased to 10 mv s-1, the position of the cathode peak and that of the anode peak do not change at scan rate higher than 5 mv s-1, which can be ascribed to the excellent charge and discharge performance of the material at high magnifications.

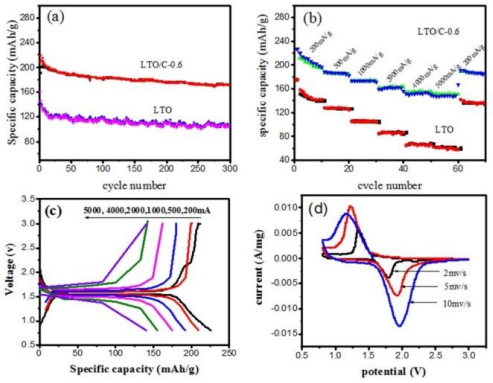


**Figure 4(a). cycle performance of LTO and LTO/C-0.6 at current density 200mA/g, (b,c) LTO and LTO/C-0.6 at different current density rate performance (d) CV curves of LTO/C-0.6 at different scan rate.**

## 4. Conclusions

In summary, pristine LTO and carbon modified LTO namely LTO/C-0.6 composite with spherical morphology have been prepared by hydrothermal method. The gelatin has been used as carbon precursor for the modification of LTO. With the addition of G, the LTO/C-0.6 shows porous structure and delivers excellent electrochemical performance. The specific capacity of LTO/C-0.6 can reach 175mAh g-1 after 300 cycles. What's more, the specific capacity of LTO/C-0.6 can be kept at 149.3mAh g-1 even under a current density of 5000mA g-1. This study demonstrated also that G can be a promising carbon precursor for the modification of other kinds of metal oxides to improve their electrochemical properties.

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