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ORIGINAL PAPER

Facile synthesis and high rate capability of $Li_4Ti_5O_{12}$/C composite materials with controllable carbon content

Guixin Wang · Kangping Yan · Zuolong Yu · Meizhen Qu

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Abstract A modified ball-milling-assisted green solid reaction method is provided to prepare $Li_4Ti_5O_{12}$/C composite materials with controllable carbon content. Thermal analysis was utilized to investigate the reaction process and the temperature for eliminating carbon. The added carbon and the time for eliminating the carbon can affect the particle size and greatly improve the cycling stability and rate performance. Besides, the particle size can reach ~60 nm, the $Li_4Ti_5O_{12}$ eliminated carbon at 600 °C has ~178% higher discharge capacity than that without added carbon after 500 cycles under the same conditions. As for the $Li_4Ti_5O_{12}$ with a carbon weight of 10.6%, the second discharge capacity can reach 177.2 and 120.8 mAh g^{-1} at 1 and 20 C rates, respectively. Its discharge capacity still remains at 118.3 mAh g^{-1} after 500 cycles under various current rates. The results are comparable to those of the reported $Li_4Ti_5O_{12}$/PAS composite.

Keywords $Li_4Ti_5O_{12}$ · Carbon · Composite · Synthesis · Electrochemical performance

1 Introduction

Along with the increasing energy emergency, novel sustainable power devices have attracted more and more attention. A growing market demand for electric vehicles and power tools makes it very necessary to develop high power batteries or hybrid capacitors. Electrode materials are crucial for high power batteries or hybrid capacitors. Among various materials, spinel $Li_4Ti_5O_{12}$ is a promising candidate due to its unique advantages. During the process of Li^+ intercalating/de-intercalating, its structure changes so little that it is also called a "zero-strain" material [1–3]. Also, $Li_4Ti_5O_{12}$ has good lithium ion mobility [4]. Its structure can be indexed to the cubic Fd3m space-group. According to the Faraday law, the theoretical capacity is 175 mAh g^{-1} when three lithium ions insert/extract during the discharge/charge process. The chemical diffusion coefficient of $Li_4Ti_5O_{12}$ is about 2×10^{-8} cm^2 s^{-1}, one order of magnitude higher than that of carbonaceous negative electrodes [5]. $Li_4Ti_5O_{12}$ has a better thermal stability performance than natural graphite [6]. Furthermore, it has excellent properties such as good power characteristic, high safety factor, long and stable voltage plateau at 1.5–1.6 V versus Li^+/Li where capacity concentrates, environmental compatibility, and so on. A high working voltage allows $Li_4Ti_5O_{12}$ to adapt to many organic electrolytes without reaction. In addition, $Li_4Ti_5O_{12}$ can combine with many electrode materials present in current batteries or capacitors to obtain new power sources, like high power batteries or hybrid capacitors.

In order to prepare $Li_4Ti_5O_{12}$, multifarious methods such as high temperature solid reaction [1–12], high energy ball milling-assisted solid reaction [13], sol–gel [14–21], hydrothermal synthesis [22], template synthesis [23, 24], rheological phase method [25], and microwave method [26, 27] are under investigation. Solid reaction is attractive and has been used in current industrial production of many commercial electrode materials because of its simple technics and relative, low cost. Special morphology or particle size is needed to improve the performance of

G. Wang (✉) · K. Yan
School of Chemical Engineering, Sichuan University,
610065 Chengdu, China
e-mail: guixin68@yahoo.com; guixin66@scu.edu.cn

G. Wang · Z. Yu · M. Qu
Chengdu Institute of Organic Chemistry,
Chinese Academy of Sciences, 610041 Chengdu, China

$Li_4Ti_5O_{12}$ [8, 13, 17, 19, 20]. Because $Li_4Ti_5O_{12}$ is insulative, metal [11, 12] or carbon [7–10, 14, 15, 28] has been added to improve its conductivity and electrochemical performance. In contrast with the added metals, carbon has a low mass density, but carbon is cheap for enhancing the conductivity and affecting the morphology and the electrochemical performance of $Li_4Ti_5O_{12}$ [7–10, 14, 15, 28]. Furthermore, carbon can improve the diffusion coefficient of lithium ions in $Li_4Ti_5O_{12}$ [9]. At present, carbon has been widely adopted to enhance the performance of electrode materials such as $LiFePO_4$ or $LiCoO_2$ in spite of the low mass density because it has a low cost and is convenient to be used. Additive carbon is mainly acquired from activated carbon, carbon black, polymer, or organic materials. Activated carbon with high surface area is interesting for the preparation of materials because of its small particle size. As for the reports, the carbon added to the precursor is burned out either in the first step or in the second step at a high temperature, leading to a high energy cost and aggregation of particles of the product. Furthermore, the carbon content will also affect the performance of $Li_4Ti_5O_{12}$.

In this study, a modified green solid reaction method with a controllable carbon content to prepare $Li_4Ti_5O_{12}$ with small particle size was provided: the precursor containing an activated carbon with high surface area was calcined first in an inert atmosphere at a high temperature to form $Li_4Ti_5O_{12}$ with a good spinel structure, and then the as-obtained product was further calcined at a relatively low temperature to move the partial carbon to obtain $Li_4Ti_5O_{12}$ with various carbon contents and particle size. It is expected to obtain a small particle size and a good morphology of $Li_4Ti_5O_{12}$ by using carbon with a high surface area as an inhibitor for the particle growth in the forming process of $Li_4Ti_5O_{12}$ and using the gases from the carbon to break up the initial aggregation formed in the high temperature process. Simultaneously, the carbon content in the $Li_4Ti_5O_{12}$ can be controlled effectively by managing the added carbon and the eliminating carbon process. As far as we know, the method has not been reported until now. Various characterization results demonstrated that the time for eliminating carbon greatly affected the particle size and the electrochemical performance of $Li_4Ti_5O_{12}$. The function of the carbon in both the synthesis process and the product was analyzed. The $Li_4Ti_5O_{12}$/C composite materials with appropriate carbon content have good electrochemical performances in respect of various current densities.

2 Experimental

2.1 Preparation

As shown in the schematic illustration, Fig. 1, a mixture of Li_2CO_3 (battery grade, 99.65%), anatase TiO_2 (~20 nm, 98.22%), a high surface area activated carbon (~2000 $m^2\ g^{-1}$), and a hexane dispersion solvent was milled with stainless steel balls at 180 rpm for 24 h. In order to study the influence of carbon on the performance of the product, the same precursor without addition of carbon was also prepared. The as-obtained black precursor slurry was moved to a quartz tube furnace to be calcined at 800 °C in N_2 atmosphere for 12 h. Then, the resulting product was further calcined at a low temperature for different durations under a controlled atmosphere to obtain $Li_4Ti_5O_{12}$ with varying carbon contents. In order to develop a green technic for production, the exhaust gases of carbon oxides as by-products could be adsorbed by a LiOH solution to prepare Li_2CO_3 material after being transformed completely to CO_2 by blowing hot air.

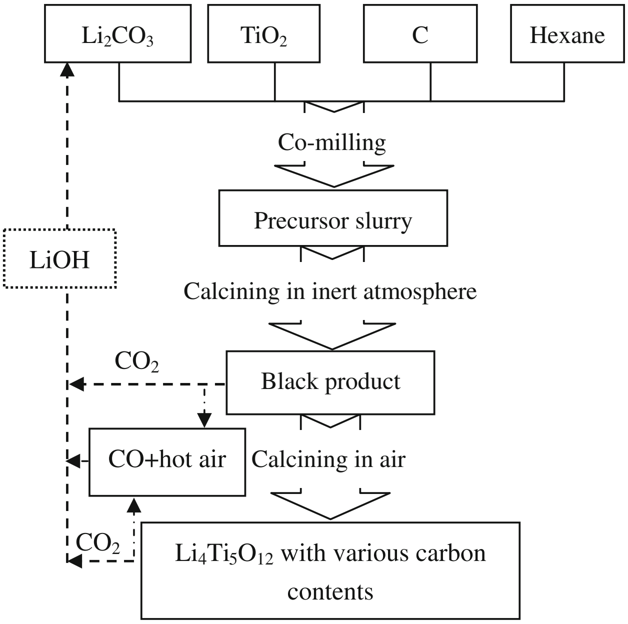


Fig. 1 Flow chart for preparing particular $Li_4Ti_5O_{12}$/C composite

2.2 Characterization

The products were characterized using transmission electron microscopy (TEM, JEOL JEM-100CX, Japan), scanning electron microscopy (SEM, JEOL JSM-5900LV, Japan), and X-ray diffraction (XRD). XRD was recorded on a Philips X'Pert MPD diffractometer using Cu Kα radiation, 40 mA current, and graphite grid. In order to analyze the reaction process and determine the carbon content in the product, thermal analysis was performed from 30 to 900 °C at 10 °C min^{-1} ramp rate under a high-purity nitrogen or air atmosphere using a NETZSCH STA 499C instrument, capable of simultaneous thermal gravimetry (TG) and differential scanning calorimetry (DSC). The room temperature conductivity was measured on a disc-shaped pellet (~30 MPa, ~3-mm thickness, and ~13-mm diameter) by a four-point probe meter (JK2812, China).

2.3 Electrochemical measurement

Prepared lithium titanium oxide was mixed with 10 wt% conductive acetylene black (Jiangxi Ganzhou Xinyang Industrial Co., China) by ultrasonic vibration in ethanol for 10 min, and then the as-obtained composite was thoroughly homogenized in an agate mortar with 5 wt% LA-132 binder (Chengdu Indigo Co., China) to make a slurry to coat a cleaned copper current collector. The sheets were rolled to get an appropriate thickness of 50 μm. After being dried at 100 °C under vacuum for 8.0 h, they were cut into 0.60 cm^2 wafers and used as working electrodes. Metal lithium was used as the counter and reference electrodes. The coin-shape lithium battery cells were assembled in an argon-filled glove box by sandwiching a microporous separator (Celgard 2400) between two electrodes [13]. A 1.0 M $\mathrm{LiPF_6}$/ethylene carbonate (EC)–diethyl carbonate (DEC) (1:1 in vol., Shenzhen Capchem Chemicals Co. Ltd, China) was used as the electrolyte. All the devices were tested between 1.0 and 3.0 V with constant current charge/discharge cycles at 298 K using a Neware battery-testing instrument (Shenzhen Neware Technology Ltd, China) under various current densities.

3 Results and discussion

3.1 Thermal synthesis

The whole chemical reaction to prepare $\mathrm{Li_4Ti_5O_{12}}$ is as follows:

$$\mathrm{2Li_2CO_3 + 5TiO_2 \rightarrow Li_4Ti_5O_{12} + 2CO_2\uparrow} \quad (1)$$

In order to investigate the reaction process, thermal analysis with simultaneous TG and DSC was conducted. Figure 2 presents the typical thermal analysis results for the ball-milled precursor slurry including $\mathrm{Li_2CO_3}$, $\mathrm{TiO_2}$, carbon, and hexane. In a high-purity nitrogen (~99.99%) atmosphere, the TG and simultaneous DSC are summarized in one panel. It is evident that there are two parts of rapid weight loss on the TG curve: one is before 300 °C, which is originated from the evaporation of solvent or absorbed water, while another is after 710 °C. From the typical peaks on the DSC curve, two endothermic reactions occur, at ~723 and ~742 °C during the programmed heating process. According to the weight loss from thermal analysis and thermodynamic calculation, the corresponding reactions are possible, namely, $\mathrm{C + TiO_2 \xrightarrow{\sim 723\,^{\circ}C} TiO + CO\uparrow}$ and $\mathrm{TiO + Li_2CO_3 \xrightarrow{\sim 742\,^{\circ}C} Li_2O + TiO_2 + CO\uparrow}$, respectively. When the temperature increases to ~755 °C, there is a small endothermic peak without any weight loss, indicating that the reaction of $\mathrm{2Li_2O + 5TiO_2 \xrightarrow{\sim 755\,^{\circ}C} Li_4Ti_5O_{12}}$ will take place. In this way, it completed the phase transitional reaction to form $\mathrm{Li_4Ti_5O_{12}}$ at ~755 °C. Therefore, the structure of $\mathrm{Li_4Ti_5O_{12}}$ could not form before 710 °C, and the weight loss after 710 °C was the result of the chemical reaction that formed spinel $\mathrm{Li_4Ti_5O_{12}}$, which was demonstrated by the XRD technique later. Considering the difference between the above mentioned thermal analysis results from the instrument and the muffle oven in the laboratory, 800 °C was chosen to synthesize $\mathrm{Li_4Ti_5O_{12}}$/C composite in this study.

In order to determine the carbon content in the product and the required temperature for the elimination of carbon, the initial black product from the first step was further investigated by thermal analysis in air atmosphere. The thermal analysis results of TG and DSC are summarized in Fig. 3. The small weight loss before 260 °C comes from the absorbed water, while there is a rapid weight loss at ~560 °C and a big endothermic peak at ~590 °C, indicating that the carbon in the product reacts with $\mathrm{O_2}$ from air from 560 °C. Furthermore, the reaction almost completes after 600 °C and a stable weight is obtained. As shown in Fig. 2, the spinel structure of $\mathrm{Li_4Ti_5O_{12}}$ could not be changed before 600 °C, which was further demonstrated by the following XRD results. Therefore, 600 °C was chosen as the temperature for eliminating carbon in the initial product.

Thus, deducting the weight of absorbed water before 260 °C and the $\mathrm{Li_4Ti_5O_{12}}$ after 600 °C, the carbon weight content C^1 (wt%) in the initial product could be calculated using the following formula (the superscript “1” means the first step for forming spinel structure):

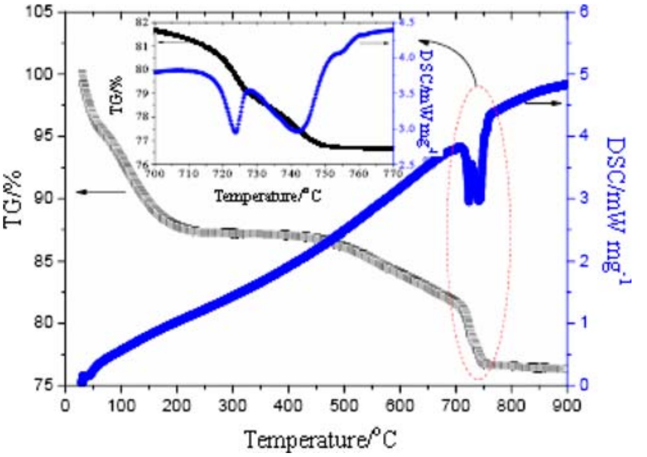


Fig. 2 Thermal analysis curves of the precursor containing carbon in a high-purity $\mathrm{N_2}$ atmosphere

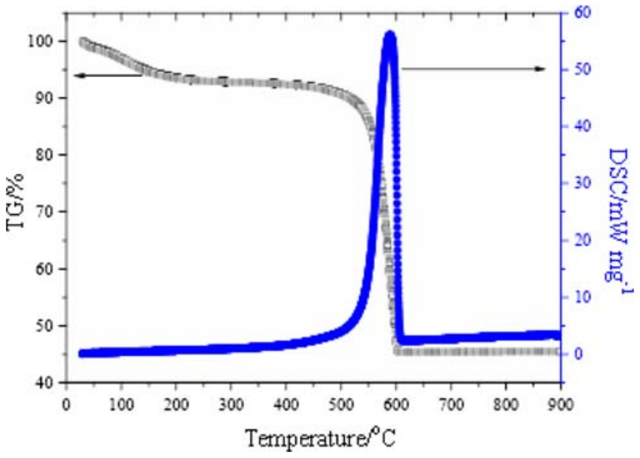


Fig. 3 Thermal analysis curves of the initial $Li_4Ti_5O_{12}$ obtained from the first step in an air atmosphere

$$C^1\ (wt\%) = W^1_{loss} - W^1_{water} - W^1_{Li_4Ti_5O_{12}} \tag{2}$$

According to the calculation, the carbon weight content in the initial product from the first step was 47.7 wt%. By further subtracting the weight loss after eliminating the carbon from 47.7 wt% at 600 °C, the carbon content C^2 (wt%) in the other products was determined by the formula (the superscript "2" means the second step for eliminating carbon).

$$C^2\ (wt\%) = C^1 - W^2_{loss} = 47.7\ wt\% - W^2_{loss} \tag{3}$$

Based on the above method, about 1 g $Li_4Ti_5O_{12}$/C composite material was further calcined at 600 °C in air, and the relationship between the carbon content in the $Li_4Ti_5O_{12}$/C composite and the calcining time for eliminating the carbon is provided in Fig. 4. The carbon content decreases almost linearly with the increase of calcining time firstly, which might be originated from the quick reaction of surface carbon on the product with oxygen. With the prolonging of the calcining time, the carbon within/among/under the product would be burnt to bring nonlinear relationship between the carbon content and the calcining time because the diffusion of the oxygen through the $Li_4Ti_5O_{12}$ eliminated carbon became the control step for the further oxidation of carbon.

3.2 XRD analysis

Figure 5 shows the XRD patterns of three kinds of products: $Li_4Ti_5O_{12}$ with no addition of carbon, initial $Li_4Ti_5O_{12}$ obtained from the first step without eliminating carbon, and $Li_4Ti_5O_{12}$ eliminated carbon at 600 °C. Obviously, they all have a good spinel structure, and each peak is well indexed with the standard peak in the JPCDS card No. 49-0207. They have a cubic crystalline and an Fd-3m space group. The strongest peak is corresponding to the (111) plane. Furthermore, there is no diffraction peak of carbon in the initial product, suggesting that the crystal structure of the carbon in the product is not very good, and the carbon may be amorphous because the carbon content is 47.7 wt%. According to the physicochemical characters and the thermal analysis, the $Li_4Ti_5O_{12}$ with no addition of carbon or eliminated carbon at 600 °C is white, and the carbon content is zero, whereas the $Li_4Ti_5O_{12}$ obtained from the first step without eliminated carbon is black and the carbon content is ~47.7 wt%. Under the same conditions, the $Li_4Ti_5O_{12}$ with no addition of carbon has the strongest peak intensity, indicating that the grain size is the largest. In order to avoid the possible influence of amorphous carbon on the background signal of the diffraction peaks, grain size evaluation was only conducted on the $Li_4Ti_5O_{12}$ without carbon. Calculating from the main peaks

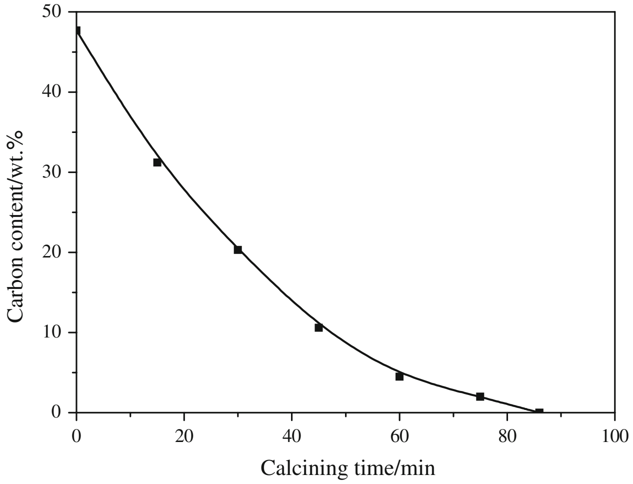


Fig. 4 Effect of calcining time on the carbon content in the $Li_4Ti_5O_{12}$/C composite at 600 °C

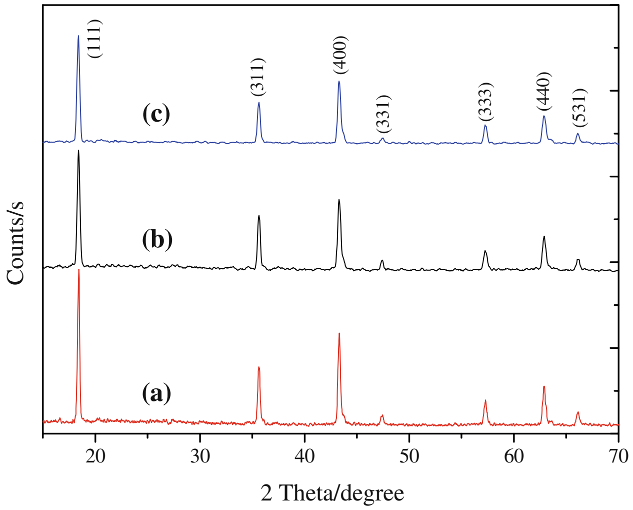


Fig. 5 XRD patterns of different $Li_4Ti_5O_{12}$ samples, **a** no added carbon, **b** 47.7 wt% carbon, and **c** eliminated carbon at 600 °C

of (111), (311), (400), (333), and (440) planes with the Scherrer's formula, the average crystallite size of the $Li_4Ti_5O_{12}$ with no added carbon or eliminated carbon at 600 °C are ~71 and ~41 nm, respectively. The decreased crystallite size is originated from the added carbon to the precursor because of the same reaction technics. Beside the changes of the crystal size, the changes of particle size were also demonstrated by the following SEM and TEM images.

3.3 SEM analysis

Figure 6 provides the SEM images of three kinds of $Li_4Ti_5O_{12}$ samples: $Li_4Ti_5O_{12}$ with no added carbon, initial $Li_4Ti_5O_{12}$ obtained from the first step without eliminating carbon, and $Li_4Ti_5O_{12}$ eliminated carbon at 600 °C. Obviously, the $Li_4Ti_5O_{12}$ with no added carbon has a bigger particle size (>1 μm mostly) than the others, while the agglomeration is serious and the shape is not regular (Fig. 6a). After adding carbon to the precursor, the particle size and the morphology were meliorated. The particles of the initial $Li_4Ti_5O_{12}$ obtained from the first step in an inert atmosphere have a wide particle size distribution from ~100 nm to ~1.5 μm, and small fragments increase obviously in spite of some big agglomerations or sheet-like shapes. However, those of the $Li_4Ti_5O_{12}$ eliminated carbon at 600 °C has many tiny fragments and quasi-spheres, and the particle size of the $Li_4Ti_5O_{12}$ apparently becomes smaller and more homogeneous, ranging from ~60 to ~200 nm. The good morphology with quasi-sphere shape might be attributed to the effects of the gases from the oxidization of the carbon within/among the product. The above results were further demonstrated by the TEM images shown in Fig. 7.

3.4 TEM analysis

Figure 7 offers the TEM images of $Li_4Ti_5O_{12}$ with various carbon contents: 47.7 wt% carbon, 10.6 wt% carbon, and 0.0 wt% carbon. In this section, except for the initial $Li_4Ti_5O_{12}$ with 47.7 wt% carbon, the other $Li_4Ti_5O_{12}$ samples were obtained by calcining the same initial $Li_4Ti_5O_{12}$ with 47.7 wt% carbon under an air atmosphere at 600 °C for different times. According to the TEM analysis, the fuscous particles might be $Li_4Ti_5O_{12}$ fragments and the tinty particles might be carbon because of their different lattice parameters. With the prolonging of calcining time, the carbon content and particle size of $Li_4Ti_5O_{12}$ decrease, while small fragments increase in size. The initial $Li_4Ti_5O_{12}$ with 47.7 wt% carbon has a wide distribution of particle size from ~65 to ~300 nm, consistent with the above SEM results. When the partial carbon is eliminated, the particle size of the $Li_4Ti_5O_{12}$ with 10.6 wt% carbon ranges from ~60 to ~130 nm, and some carbon particles cover the as-synthesized $Li_4Ti_5O_{12}$. When the carbon is burnt off, the fragments are maximized and most particle sizes can reach ~60 nm. Thus, a good spinel structure $Li_4Ti_5O_{12}$ with controllable carbon content could be gained facilely by managing the temperature and the time for eliminating carbon in an air atmosphere. At the same time,

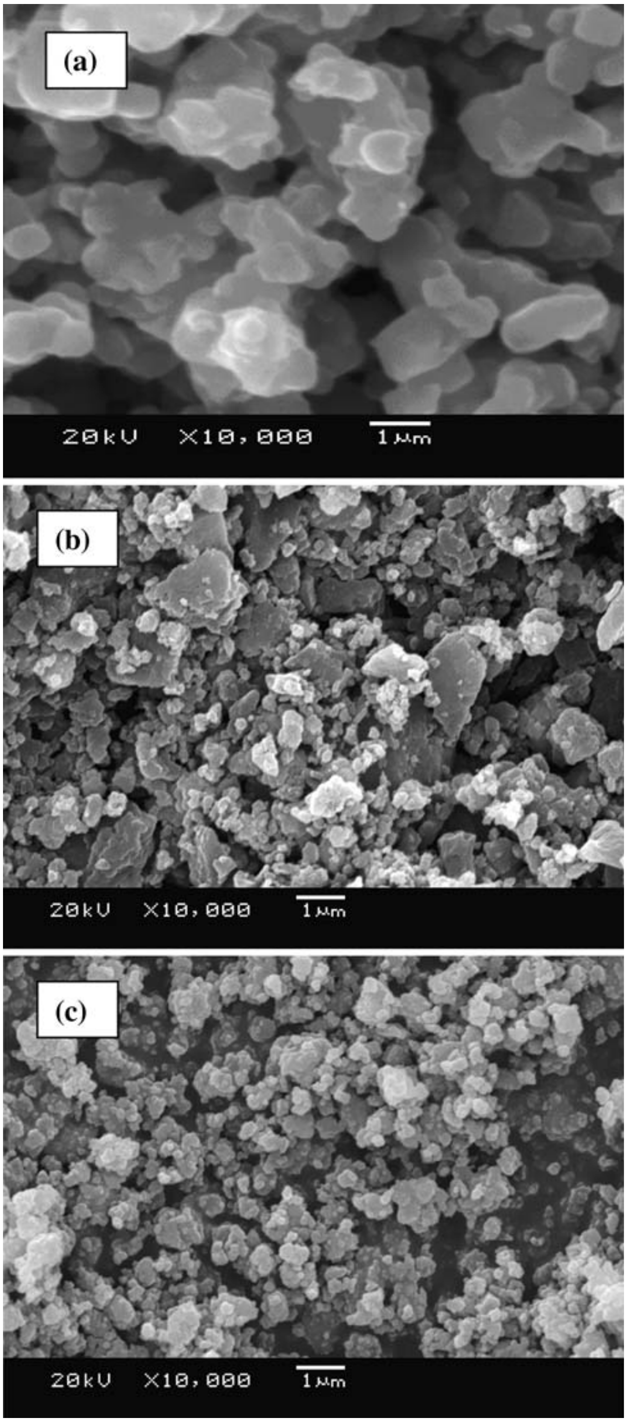


Fig. 6 SEM images of various $Li_4Ti_5O_{12}$ samples, **a** no added carbon, **b** 47.7 wt% carbon, and **c** eliminated carbon at 600 °C

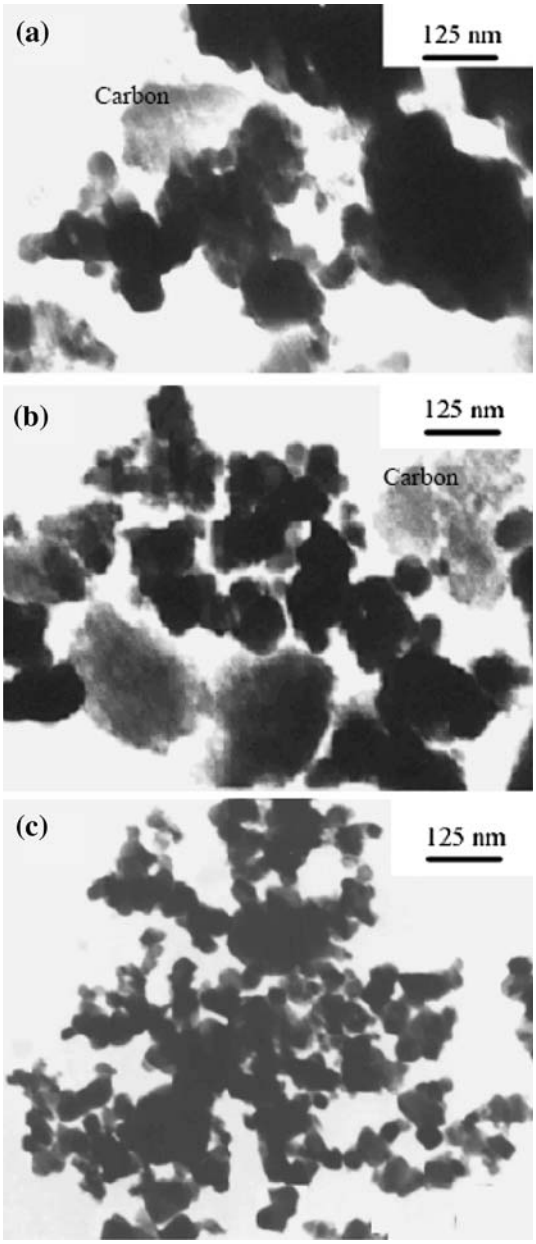
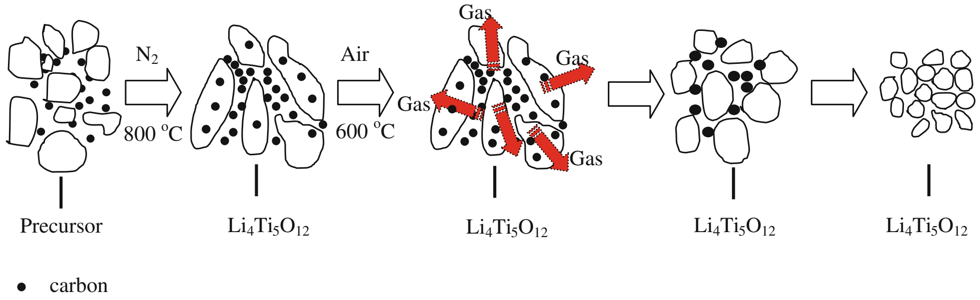


Fig. 7 TEM images of the $Li_4Ti_5O_{12}$ with different carbon contents when carbon was eliminated at 600 °C, **a** 47.7 wt%, **b** 10.6 wt%, and **c** 0.0 wt%

the product eliminated carbon, unlike that prepared with no addition of carbon, was very loose and easy to be dispersed.

Combining the above micrographic characteristics and the changes in particle size of $Li_4Ti_5O_{12}$, carbon is the key to break up the agglomerations of initial $Li_4Ti_5O_{12}$ formed at a high temperature to produce more fragments. Thus, carbon in the product will affect the particle size and morphology of the $Li_4Ti_5O_{12}$ because the gases from the carbon in the second step are relevant to the carbon content. Besides taking part in the reaction to prepare $Li_4Ti_5O_{12}$, the carbon in the precursor could confine the particle size growth [7]. Therefore, the function of carbon in the synthesis process could be described as follows, and the possible schematic diagram is provided in Fig. 8. When the precursor is calcined in a N_2 atmosphere, the carbon is always present among/within the particles of these samples: the initial precursor including Li_2CO_3 and TiO_2; then the mixture of Li_2CO_3, TiO_2, and $Li_4Ti_5O_{12}$; and eventually the pure-phase $Li_4Ti_5O_{12}$. With many partition walls, carbon confines the grain growth of $Li_4Ti_5O_{12}$ during its spinel structure formation process, which was confirmed by the above XRD results. Simultaneously, carbon might be included in the aggregations of $Li_4Ti_5O_{12}$, and so the carbon positioning among/within many $Li_4Ti_5O_{12}$ particles would react with O_2 from air to produce gases when the initial product was further calcined in an air atmosphere at a low temperature. Results of mass spectrography analysis also showed that the exhaust gases produced during the process of eliminating carbon under air atmosphere was a mixture of nitrogen from air, carbon monoxide, and carbon dioxide. According to the gas equation of $pV = nRT$, a higher temperature will lead to a higher pressure if the volumes were not changed. With an increase of temperature, the gases produced from carbon will break up the aggregations of $Li_4Ti_5O_{12}$ so that the particle size becomes small to obtain loose particles. Also, the morphology is affected by the scouring of the carbon oxides produced. Therefore, carbon oxides play an important role in thinning the particle size and changing the morphology of $Li_4Ti_5O_{12}$. It is possible to use carbon to control the

Fig. 8 Possible scheme for the synthesis process of the $Li_4Ti_5O_{12}$ with added carbon



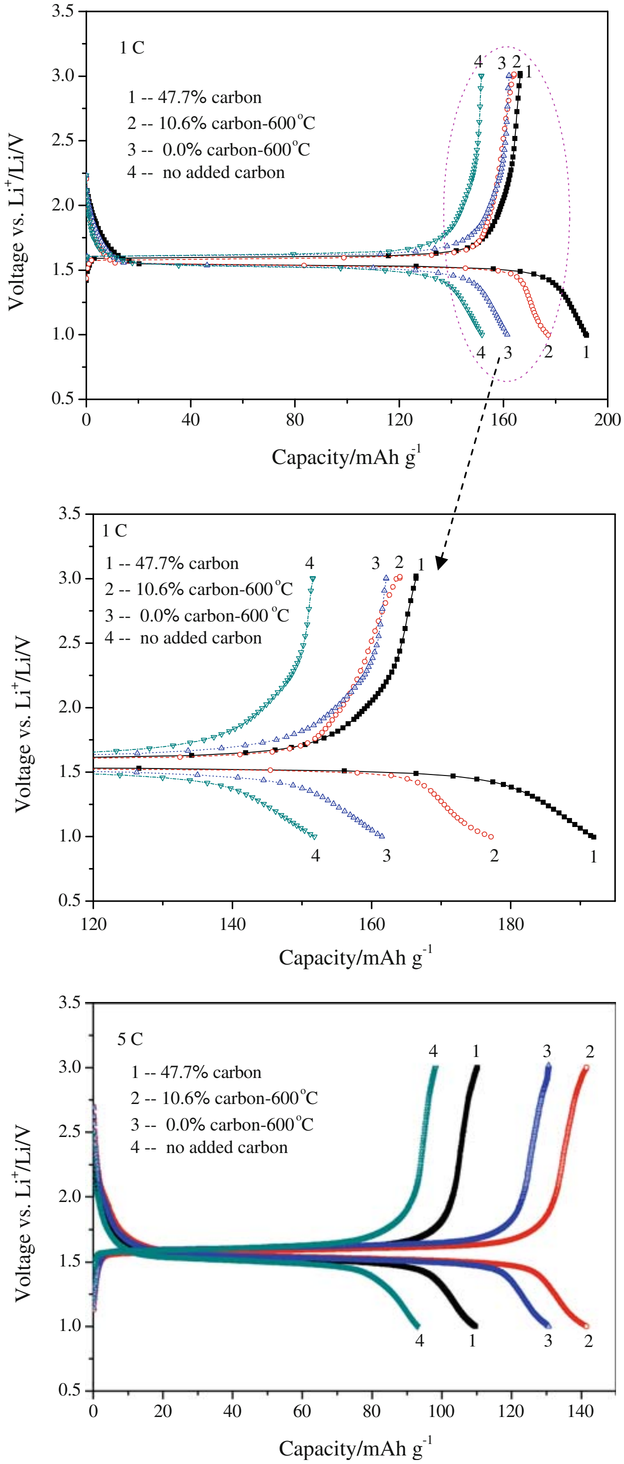


Fig. 9 The second galvanostatic charge/discharge curves of different $Li_4Ti_5O_{12}$ samples under various current densities

particle size of the product via managing the synthesis technics and added carbon. At the first step, a good spinel structure of $Li_4Ti_5O_{12}$ is formed, while using carbon to confine its grain growth in an inert atmosphere, followed by breaking up the initial $Li_4Ti_5O_{12}$ aggregations produced at a high temperature via utilizing the gases produced from carbon at a relatively low temperature in an atmosphere containing oxygen, and as a result of which spinel $Li_4Ti_5O_{12}$ with a special morphology and particle size will be obtained successfully.

3.5 Electrochemical characterization

Figure 9 illustrates the typical second galvanostatic charge/discharge curves of various $Li_4Ti_5O_{12}$ samples at different current rates of 1 and 5 C. 10.6 wt% carbon at 600 °C or 0.0 wt% carbon at 600 °C, respectively, means the carbon content in the product or the temperature for eliminating carbon was 600 °C. These curves all have a flat charge plateau corresponding to Li^+ ions extraction, and a flat discharge plateau corresponding to Li^+ ions insertion, indicating that there is a two-phase reaction based on the Ti^{4+}/Ti^{3+} redox couple [1, 20]. When the coin lithium cells were tested, the open current voltage (OCV) reached $\sim$3.1 V and discharged first between the voltage range of 1.0 and 3.0 V, and then the second charge/discharge capacities were chosen to compare the performance. $Li_4Ti_5O_{12}$ is inserted with Li^+ ions at first step and then the extracted Li^+ ions in cycle [13]. The corresponding electrochemical reaction is

$$Li_4Ti_5O_{12} + xLi^+ + xe^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Li_{4+x}Ti_5O_{12}(0 \le x \le 3) \tag{4}$$

The maximum number of inserted Li^+ ions is 3, and the obtained compound is $Li_7Ti_5O_{12}$ with a theoretical capacity of 175 mAh g^{-1}. When Li^+ ions are inserted in $Li_4Ti_5O_{12}$, the chemical valence of Ti changes from +4 to +3 gradually, corresponding to the reduction reaction of $Ti^{4+} + e^- \rightarrow Ti^{3+}$ that occurs at $\sim$1.5 V versus Li^+/Li. Vice versa, when Li^+ ions are extracted from the $Li_7Ti_5O_{12}$, it leads to an oxidation reaction of $Ti^{3+} - e^- \rightarrow Ti^{4+}$ that occurs at $\sim$1.6 V versus Li^+/Li. In fact, the charge/discharge capacity and the voltage plateau are affected by current density because of the polarization from the velocity inconsistency between the electron transfer and the reaction of Li^+ ions insertion/extraction. In order to investigate the reversibility of Li^+ ions insertion/extraction, the coulombic efficiency η of the cell can be calculated by the following formula:

$$\eta = \frac{C_d}{C_c} \tag{5}$$

where, C_d and C_c are the discharge capacity and the charge capacity, respectively.

From the charge/discharge curves under various current densities, we note that the $Li_4Ti_5O_{12}$ samples have different voltage plateaus, suggesting that the ohmic polarization is dissimilar [10]. At a current rate of 1 C (175 mA g^{-1} current density), the $Li_4Ti_5O_{12}$ containing carbon has a high charge/discharge capacity (even more than its theoretical capacity of 175 mAh g^{-1}) and the coulombic efficiency is more than 100%, which is also found in another research study [28]. The $Li_4Ti_5O_{12}$ with 47.7 wt% carbon has the highest discharge capacity of 191.9 mAh g^{-1} with a corresponding coulombic efficiency of 115.3%, while the $Li_4Ti_5O_{12}$ with 10.6 wt% carbon has a discharge capacity of 177.2 mAh g^{-1} with a corresponding coulombic efficiency of 108.0%. Relatively, the $Li_4Ti_5O_{12}$ with no added carbon or eliminated carbon has a low discharge capacity, and the coulombic efficiency is close to 1. Furthermore, the $Li_4Ti_5O_{12}$ eliminated carbon at 600 °C has a higher discharge capacity than that with no added carbon because of the smaller crystallite size and particle size for Li^+ ions transfer. During the discharge process, Li^+ intercalates into the $Li_4Ti_5O_{12}$, while the carbon in the $Li_4Ti_5O_{12}$ will also react with Li^+ ions [29, 30]. The latter reaction would lead to an irreversible capacity included in the discharge capacity. As for the $Li_4Ti_5O_{12}$ with no added carbon or eliminated carbon, the coulombic efficiency is close to 100%, indicating that the reversibility of Li^+ ions insertion/extraction is good. However, the potential plateaus change greatly with an increase in current. When current rate increases to 5 C, the charge/discharge plateau becomes short and departs level slowly because a high current will lead to a large polarization, similar to that found in the previous article [10]. Different from that at 1 C rate, proper carbon content is beneficial in improving the rate capability, and the ohmic drop becomes serious with respect to the $Li_4Ti_5O_{12}$ without added carbon. Because particle with large size has a long process for Li^+ ions diffusion, the $Li_4Ti_5O_{12}$ with 47.7 wt% carbon declines quickly when current rate increases from 1 to 5 C rate. The second discharge capacity of the $Li_4Ti_5O_{12}$ with 47.7 wt% carbon declines to 109.9 mAh g^{-1} with a corresponding coulombic efficiency of 98.7%, while that of the $Li_4Ti_5O_{12}$ with 10.6 wt% carbon declines to 141.6 mAh g^{-1} with a corresponding coulombic efficiency of 99.5%. In addition, the $Li_4Ti_5O_{12}$ eliminated carbon at 600 °C also has high capacity retainability and reaches 130.8 mAh g^{-1} with a corresponding coulombic efficiency of 99.0%, which is due to the size effect of small particle. The $Li_4Ti_5O_{12}$ with no added carbon has a big capacity fade, and the discharge capacity declines to 93.5 mAh g^{-1} with a corresponding coulombic efficiency of 96.1%, indicating that the carbon plays an important role in enhancing the electrochemical performance of $Li_4Ti_5O_{12}$.

Figure 10 shows the rate capability characteristics of various $Li_4Ti_5O_{12}$ samples under different current densities. Obviously, the $Li_4Ti_5O_{12}$ with 10.6 wt% carbon has a better rate performance than that of other samples, and its second discharge capacity at 20 C rate still keeps 120.8 mAh g^{-1}, 68.2% of that at 1 C rate. Furthermore, the $Li_4Ti_5O_{12}$ with 47.7 wt% carbon or eliminated carbon at 600 °C has a better performance than that of the $Li_4Ti_5O_{12}$ with no added carbon. The respective second discharge capacity at 20 C rate of the $Li_4Ti_5O_{12}$ with no added carbon, $Li_4Ti_5O_{12}$ with 47.7 wt% carbon, $Li_4Ti_5O_{12}$ with 10.6 wt% carbon, and $Li_4Ti_5O_{12}$ eliminated carbon at 600 °C is 41.0, 60.9, 120.8, and 96.2 mAh g^{-1}, corresponding to the capacity retainability ratio to 1 C rate of 27.0, 31.7, 68.2, and 59.6%. Furthermore, the capacity fade trend changes slowly for the $Li_4Ti_5O_{12}$ with 10.6 wt% carbon when current increases. The improved rate capability originates from the combination of the carbon and the small particle size.

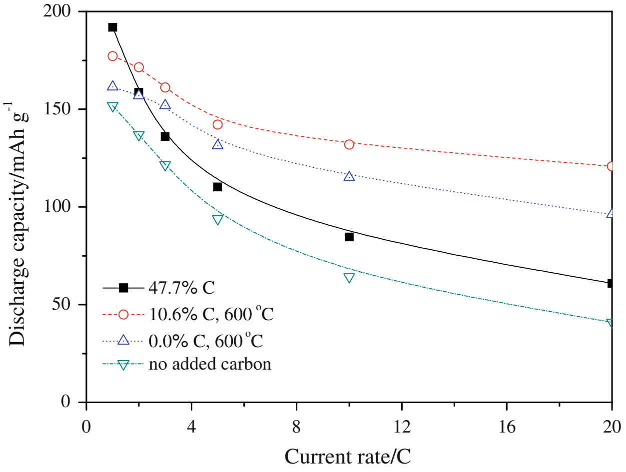


Fig. 10 Effect of current density on the second discharge capacities of various $Li_4Ti_5O_{12}$ samples

Figure 11 presents the cycle performance of various $Li_4Ti_5O_{12}$ samples under different current densities, and the key data are summarized in Table 1. The $Li_4Ti_5O_{12}$ without added carbon has a relatively low discharge capacity and a poor cycling performance, and the discharge capacity declines from 160.0 to 36.1 mAh g^{-1} after 500 cycles when the current rate increases from 1 to 10 C. However, the electrochemical performances of the $Li_4Ti_5O_{12}$ with added carbon have been improved differently, especially for the sample eliminated partial carbon at 600 °C. Under the same conditions, the $Li_4Ti_5O_{12}$/carbon composite (47.7 wt% carbon) without further elimination of carbon has a high initial discharge capacity of 260.2 mAh g^{-1}, and declines to 65.1 mAh g^{-1}. When the $Li_4Ti_5O_{12}$/carbon composite (47.7 wt% carbon) undergoes further elimination of partial carbon at 600 °C, the cycling performance has been enhanced greatly. The $Li_4Ti_5O_{12}$ with 10.6 wt% carbon has good power characteristic and cycling performance, and the discharge capacity declines from 198.3 to 118.3 mAh g^{-1} after 500 cycles. The

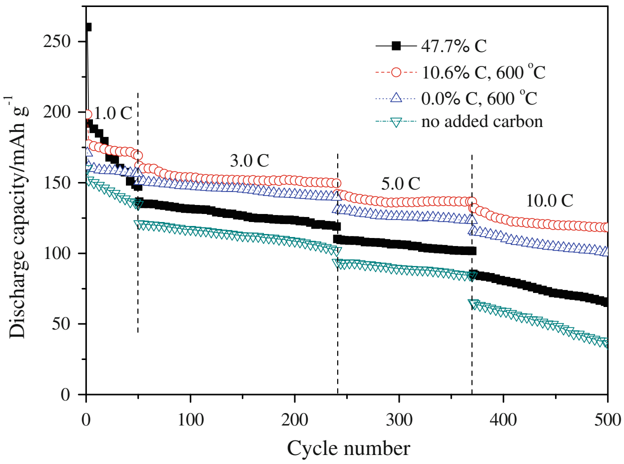


Fig. 11 Cycle performance of various $Li_4Ti_5O_{12}$ samples

retained discharge capacity is as ~3.3 times and ~1.8 times as that with no added carbon and that with 47.7 wt% carbon, respectively. The rate performance and cycling performance of the prepared $Li_4Ti_5O_{12}$/C composite are comparable with those of the $Li_4Ti_5O_{12}$/polyacene composite reported previously [10]. Furthermore, the $Li_4Ti_5O_{12}$ eliminated carbon at 600 °C also has a better cycling performance than that either without added carbon or the initial product without eliminating carbon, and the discharge capacity declines from 171.0 to 100.2 mAh g^{-1}, which is attributed to the small particle size.

It is noted from the above analysis that the carbon content in the product affects the cycling stability and the rate capability of $Li_4Ti_5O_{12}$, suggesting the carbon content should be optimized to match the electrochemical performance. More or less carbon will not benefit the electrochemical performance of $Li_4Ti_5O_{12}$ because the carbon in the $Li_4Ti_5O_{12}$/carbon composite affects the particle size, improves the conductivity, stores, and penetrates liquid electrolyte containing Li^+ ions [28]. When the carbon in the composite is eliminated at a low temperature, the produced carbon oxide gases will break up the initial aggregations formed at high temperature to produce small fragments, which is demonstrated by the above SEM and TEM images. Small particle size, relating closely to the temperature and time for eliminating the carbon, ensures a short diffusion path and large surface reaction sites during the charge/discharge processes [8, 17]. Also, carbon can store electrolyte for the reaction of Li^+ ions' insertion/extraction, similar to the function of carbon nanotubes [31, 32]. Activated carbon with a high surface area may be beneficial in storing electrolyte to enable Li^+ ions to insert/extract easily because of the high adsorption capability. At the same time, electrolyte can penetrate easily to minimize the ionic resistance. Similar to the carbon in $LiFePO_4$, carbon particles can form good conductive dot paths to enhance the conductivity of electrode materials [28, 32–36], and the conductivity is affected by the carbon content. Adopting 4-probe method, the specific conductivities of the $Li_4Ti_5O_{12}$ with 47.7 wt% carbon, $Li_4Ti_5O_{12}$ with 10.6 wt% carbon, and $Li_4Ti_5O_{12}$ with no added carbon or eliminated carbon were ~0.6, ~0.08, and ~10^{-9} S cm^{-1}, respectively. The conductivity of the $Li_4Ti_5O_{12}$ without carbon agreed well with the report [10]. Consequently, carbon in the $Li_4Ti_5O_{12}$ will affect the ohmic polarization because of the combination of storing electrolyte and specific conductivity. More carbon will result in less permeability for Li^+ ions [28] and less $Li_4Ti_5O_{12}$ as an active component in the electrode, while less carbon could not form effective

Table 1 Summarization of the cycling performance of various $Li_4Ti_5O_{12}$ samples

Sample rate versus capacity (mAh g^{-1})	Sample			
	No added carbon	47.7 wt% carbon	10.6 wt% carbon at 600 °C	0.0 wt% carbon at 600 °C
1 C				
1st capacity	160.0	260.2	198.3	171.0
2nd capacity	151.8	191.9	177.2	161.5
50th capacity	134.6	147.3	169.2	156.5
3 C				
51st capacity	121.0	136.6	162.0	151.0
240th capacity	102.0	119.0	149.6	139.6
5 C				
241st capacity	93.6	110.1	142.0	131.0
370th capacity	84.1	101.7	136.5	123.3
10 C				
371st capacity	65.0	85.5	132.0	116.0
500th capacity	36.1	65.1	118.3	100.2

electronic paths to decrease resistance. Therefore, the carbon content in the $Li_4Ti_5O_{12}$ plays an important role for synthesizing $Li_4Ti_5O_{12}$/C composite material with good electrochemical performance, and the carbon content needs further optimizing, like the minimum amount of carbon for effectively electronic wiring active materials [28].

4 Conclusions

A modified green solid reaction method that contains two steps has been proven to be useful in synthesizing $Li_4Ti_5O_{12}$/C composite material with controllable carbon content. The results of thermal analysis indicate that the spinel structure of $Li_4Ti_5O_{12}$ cannot form until 710 °C, and the proper temperature for eliminating carbon should be 600 °C. A decrease of the $Li_4Ti_5O_{12}$ particle size was clearly demonstrated after the elimination of partial or all of the carbon from the initial product, and the particle size could reach ~60 nm when the carbon was eliminated. The carbon in the precursor may confine the growth of particles, and the gases from carbon in the process of eliminating carbon will break up the initial $Li_4Ti_5O_{12}$ aggregations to form small fragments and change the morphology by the scouring function. XRD results show that the $Li_4Ti_5O_{12}$, whether with no added carbon or added carbon, has a good spinel structure except the peak intensity. Galvanostatic charge/discharge testing results confirm that proper carbon content and small particle size can enhance the electrochemical performance of $Li_4Ti_5O_{12}$ at various current densities. The discharge capacity of the $Li_4Ti_5O_{12}$ eliminated carbon at 600 °C reaches 100.2 mAh g^{-1}, ~178% higher than that of the $Li_4Ti_5O_{12}$ with no added carbon after 500 cycles under the same conditions. The second discharge capacity of the $Li_4Ti_5O_{12}$ with 47.7 wt% carbon declines from 260.2 to 60.9 mAh g^{-1} when current rate increases from 1 to 20 C, indicating that big particle size and more carbon will not benefit the power characteristic in spite of good conductivity. The $Li_4Ti_5O_{12}$ eliminated partial carbon at 600 °C has a good rate capability and cycling stability. As for the $Li_4Ti_5O_{12}$ with 10.6 wt% carbon, the second discharge capacity at 20 C rate still retains the values of 120.8 mAh g^{-1}, 68.2% of those at 1 C rate, and the discharge capacity can still reach 118.3 mAh g^{-1} after 500 cycles at various rates of 1, 3, 5, and 10 C, which are comparale with those of the reported $Li_4Ti_5O_{12}$/PAS composite [10]. The balance of carbon content and particle size are therefore a key factor for the enhancement of the electrochemical performance.

It is interesting to form a good spinel structure of $Li_4Ti_5O_{12}$ in an inert atmosphere first, and then to use the gases produced in the process of eliminating carbon at a low temperature in an atmosphere containing oxygen to break up the initial aggregations to obtain a particular $Li_4Ti_5O_{12}$. Managing the temperature and time for eliminating carbon can control the carbon content and the particle size of the $Li_4Ti_5O_{12}$. This technique is compatible with current industrial equipment for the preparation of materials and can easily be performed. The exhaust gases can also be reused to prepare raw materials. Therefore, the modified solid reaction is of great interest to the development of particular $Li_4Ti_5O_{12}$/C composite materials with good electrochemical performance.

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