Sol–gel synthesis and electrochemical performance of Li$_4$Ti$_5$O$_{12}$/graphene composite anode for lithium-ion batteries

Hongfa Xiang, Bingbing Tian, Peichao Lian, Zhong Li, Haihui Wang*

School of Chemistry & Chemical Engineering, South China University of Technology, Guangdong, Guangzhou 510640, PR China

**A R T I C L E   I N F O**

Article history:
Received 12 November 2010
Received in revised form 9 April 2011
Accepted 11 April 2011
Available online 20 April 2011

Keywords:
Li$_4$Ti$_5$O$_{12}$
Graphene
Lithium-ion battery
Sol–gel
Safety

**A B S T R A C T**

Li$_4$Ti$_5$O$_{12}$/graphene composite was prepared by a facile sol–gel method. The lattice structure and morphology of the composite were investigated by X-ray diffraction (XRD) and scanning electronic microscopy (SEM). The electrochemical performances of the electrodes have been investigated compared with the pristine Li$_4$Ti$_5$O$_{12}$ synthesized by a similar route. The Li$_4$Ti$_5$O$_{12}$/graphene composite presents a higher capacity and better cycling performance than Li$_4$Ti$_5$O$_{12}$ at the cutoff of 2.5–1.0 V, especially at high current rate. The excellent electrochemical performance of Li$_4$Ti$_5$O$_{12}$/graphene electrode could be attributed to the improvement of electronic conductivity from the graphene sheets. When discharged to 0 V, the Li$_4$Ti$_5$O$_{12}$/graphene composite exhibited a quite high capacity over 274 mAh g$^{-1}$ below 1.0 V, which was quite beneficial for not only the high energy density but also the safety characteristic of lithium-ion batteries.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Lithium-ion batteries are now not only widely used as energy storage devices for portable electronic devices, but also have been come into use for electric vehicles (EV), hybrid electric vehicles (HEV) and plug-in hybrid electric vehicles (PHEV) due to their high energy density and long lifetime. For the development of large-scale lithium-ion batteries for the vehicle applications, it is very important to improve power density and cycling performance of the state-of-the-art batteries. Comparing to widely-used graphite anode, spinel Li$_4$Ti$_5$O$_{12}$ has a very flat plateau at around 1.5 V versus Li$^+$/Li and displays excellent reversibility and structural stability as a zero-strain insertion material in the charge–discharge process [1]. The high voltage plateau can avoid furious reductive decomposition of carbonate solvents so that solid electrolyte interface (SEI) layer is negligible. Moreover, the operation potential at 1.5 V versus Li$^+$/Li is quite gentle for some solvents or additives to be applied in the electrolyte [2,3]. So the lithium-ion batteries with Li$_4$Ti$_5$O$_{12}$ anodes are applicable in more circumstances, with important advantages in terms of cycling performance and thermal stability, although the output voltage of lithium-ion batteries with Li$_4$Ti$_5$O$_{12}$ anodes is lower than that of lithium-ion batteries with carbonaceous anodes.

The major obstacle to the practical applications of Li$_4$Ti$_5$O$_{12}$ is its intrinsically poor conductivity at room temperature ($<10^{-13}$ S cm$^{-1}$) [4,5]. Several methods have been utilized to improve the electronic conductivity of Li$_4$Ti$_5$O$_{12}$, such as doping with foreign metal ions [6–10], surface modification or coating with conductive carbon or metal material [11–16] and preparation of composites containing some excellent conductive components [17,18]. Among these methods, preparation of Li$_4$Ti$_5$O$_{12}$-based composites using high conductive and low-cost carbon materials by a facile route is practicable and economical for large-scale industrialization.

In recent years, graphene with superior electronic conductivity, high surface area of over 2600 m$^2$/g, excellent thermal properties and mechanical properties, has attracted much attention in the field of material science [19,20]. Graphene and graphene-based composites have been widely investigated in the lithium-ion batteries and other electrochemical devices [21–26]. In the composites consisting of graphene and metal oxides, graphene usually plays a vital role as a conductive component [21,22,25]. Besides its excellent conductivity, the advantage of high surface area can improve the interfacial contact with the poor-conductive particles. Recently, Zhu and his coworkers have prepared graphene-embedded Li$_4$Ti$_5$O$_{12}$ nanofibers by electrospinning deposition and got improved electrochemical performance [27]. But the preparation is very intricate and difficult to scale up. In this paper, we propose to prepare Li$_4$Ti$_5$O$_{12}$/graphene composite in a facile sol–gel method. Furthermore, the electrochemical performance of this composite is investigated by
2. Experimental

2.1. Materials synthesis

Li₄Ti₅O₁₂/graphene composite was synthesized by a facile sol–gel method. Lithium acetate (CH₃COOLi), tetraethyl titanate (Ti(OC₄H₉)₄) and graphene sheets (8 wt.% of the theoretical Li₄Ti₅O₁₂) were mixed in ethanol under vigorously stirring to form a sol. The molar ratio of Li and Ti was set at 4:5. The graphene sheets were prepared from graphene oxide by rapid thermal expansion at 1050 °C in nitrogen atmosphere [28]. Graphene oxide was obtained from graphite powder following the method described by Hummers [29]. After the sol was dried at 120 °C for 10 h, a gel was formed and then calcined in nitrogen atmosphere at 800 °C for 12 h to obtain the final powder. For comparison, pristine Li₄Ti₅O₁₂ powder was prepared in a similar way without graphene added, and the details also can be found in our previous work [6]. The final products of Li₄Ti₅O₁₂/graphene and Li₄Ti₅O₁₂ are black and light blue, respectively.

2.2. Cell assembly

The electrochemical performance of Li₄Ti₅O₁₂ and the Li₄Ti₅O₁₂/graphene composite was investigated using coin cells (CR2032). In order to make an electrode laminate, a slurry containing 82 wt.% Li₄Ti₅O₁₂ or Li₄Ti₅O₁₂/graphene and 10 wt.% Super P carbon black and 8 wt.% polyvinylidene fluoride (PVDF) dispersed in N-methyl-2-pyrrolidinone (NMP) was cast onto a copper current collector. After vacuum drying at 70 °C, the laminate was punched into discs (Ø14 mm) for assembling the cells. The mass loading in the electrode was controlled at about 1.5 mg cm⁻². Celgard 2400 microporous polypropylene membrane was used as separator. The electrolyte consisted of a solution of 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, w/w). Highly pure lithium foil was used as the counter electrode. Finally, the coin cells were assembled in an argon-filled glove box (Mikrouna, super 1220) where the oxygen and moisture contents were less than 1 ppm.

2.3. Characterization

The crystal structure of the powder was characterized on a Bruker D8 Advance X-ray diffraction using a Cu Kα radiation source (λ = 1.5406 Å). The diffraction data were collected for 2s at each 0.02° step width over a 2θ range from 10° to 80°. The particle size and morphology were observed by scanning electron microscopy (SEM, LEO 1530 VP). The carbon content in the Li₄Ti₅O₁₂/graphene composite was determined by an element analyzer (Vario EL III).

The assembled cells were galvanostatically cycled at different current rates on a multi-channel battery cycler (Neware BTS2300, Shenzhen). Here all the current rates, either for the pristine Li₄Ti₅O₁₂ or the Li₄Ti₅O₁₂/graphene composite, were determined from the theoretical capacity (175 mAh g⁻¹) of Li₄Ti₅O₁₂. The voltage cutoffs for the discharge–charge tests were set at 2.5–1.0 V or 2.5–0 V. All the tests were performed at room temperature.

3. Results and discussion

3.1. Preparation of the Li₄Ti₅O₁₂/graphene composite

For all the graphene-based composites, one of the key issues is the graphene chosen for the preparation of the composites. The properties of the used graphene materials significantly depend on their synthesis methods. As we all know, graphene materials can be prepared in many ways. The most popular way is to prepare graphene oxide first and then get graphene sheets by chemical reduction or thermal reduction [30–32]. In our previous work, we prepared high quality graphene sheets with fewer layers (about 4 layers) and large specific surface area (492.5 m² g⁻¹) through thermal exfoliation of graphene oxide [28]. The initial reversible
specific capacity was as high as 1264 mAh g\(^{-1}\) at a current density of 100 mA g\(^{-1}\). The capacity still kept 848 mAh g\(^{-1}\) after 40 cycles. Recently, these graphene sheets have been used to successfully prepare the Fe\(_3\)O\(_4\)/graphene composite. Owing to fewer layers and higher surface area of as-prepared graphene sheets, it is more facile to disperse them in the ethanol solution and form a homogeneous sol. Herein, we use this kind of graphene to prepare the Li\(_4\)Ti\(_5\)O\(_12\)/graphene composite.

X-ray diffraction (XRD) patterns of the Li\(_4\)Ti\(_5\)O\(_12\) and the Li\(_4\)Ti\(_5\)O\(_12\)/graphene composite are shown in Fig. 1. The diffraction peaks of the two samples are similar and conform to JCPDS card No.49-0207 in accordance with the spinel Li\(_4\)Ti\(_5\)O\(_12\) standard, indicating that both represent a single-phase cubic structure with Fd3m space group. There is no any other impurity phase detected. Usually graphene is apt to stack into multilayers and form a graphic structure. Here Li\(_4\)Ti\(_5\)O\(_12\) particles prohibit the stack by jamming the graphene sheets, and thus no any diffraction according to graphic structure was detected. Moreover, graphene in the composite is in amorphous form. In addition, the result obtained from the element analyzer indicates that the amount of carbon in the Li\(_4\)Ti\(_5\)O\(_12\)/graphene is about 7.8 wt.%, which is basically in agreement with the content of the graphene sheets added into the synthetic system.

Fig. 2 shows the SEM images of Li\(_4\)Ti\(_5\)O\(_12\) and the Li\(_4\)Ti\(_5\)O\(_12\)/graphene composite powders. From Fig. 2a and b, it is clear that the size of the obtained Li\(_4\)Ti\(_5\)O\(_12\) powder is about 5–10 μm, and the primary particles is in the size of 200–800 nm. However, the Li\(_4\)Ti\(_5\)O\(_12\)/graphene composite with the size of 1–5 μm is composed of the graphene sheets and Li\(_4\)Ti\(_5\)O\(_12\) particles less than 100 nm (Fig. 2c and d). It seems that the introduction of graphene sheets in the sol–gel process is helpful to suppress the aggregation of Li\(_4\)Ti\(_5\)O\(_12\) particles under high temperature, possibly because of the partition effect of the graphene sheets. The smaller size of the Li\(_4\)Ti\(_5\)O\(_12\) particles means the shorter diffusion distance for lithium ions. So the Li\(_4\)Ti\(_5\)O\(_12\)/graphene composite should be a promising anode material with excellent cell performances. Additionally, almost all the Li\(_4\)Ti\(_5\)O\(_12\) particles are anchored on the surface of the highly conductive graphene sheets. Even though the oxygen-containing groups on the graphene sheets has been remarkably reduced after the heat treatment at the high temperature (1050 °C), there are still plenty of the polar groups left, which interact strongly with the metal ions in the sol. The interaction is helpful to anchor the Li\(_4\)Ti\(_5\)O\(_12\) particles on the graphene sheets. Additionally, lots of cavities in the graphene sheets can accommodate the Li\(_4\)Ti\(_5\)O\(_12\) particles. As a result, the homogeneous and stable Li\(_4\)Ti\(_5\)O\(_12\)/graphene composite has been prepared successfully, as shown in Fig. 2c and d.

### 3.2. Electrochemical performance

The electrochemical performance of the Li\(_4\)Ti\(_5\)O\(_12\)/graphene composite was investigated by comparing with the pristine Li\(_4\)Ti\(_5\)O\(_12\). Fig. 3 shows the initial discharge–charge curves of the cells with the electrodes using Li\(_4\)Ti\(_5\)O\(_12\) and the Li\(_4\)Ti\(_5\)O\(_12\)/graphene composite at 0.2 C (a) and 10 C (b) between 1.0 and 2.5 V.

![Fig. 3.](image)

**Fig. 3.** The initial discharge–charge curves of the cells with the electrodes using Li\(_4\)Ti\(_5\)O\(_12\) and the Li\(_4\)Ti\(_5\)O\(_12\)/graphene composite at 0.2 C (a) and 10 C (b) between 1.0 and 2.5 V.

The discharge plateau of the former is about 1.5 V, but the latter has only a discharge plateau of 1.4 V. The significant difference between Li\(_4\)Ti\(_5\)O\(_12\) and its composite demonstrates that graphene in the Li\(_4\)Ti\(_5\)O\(_12\)/graphene composite remarkably improves the reversible capacity of Li\(_4\)Ti\(_5\)O\(_12\), especially at the higher current rate.

The cycling stability of the cells with the electrodes using Li\(_4\)Ti\(_5\)O\(_12\) and the Li\(_4\)Ti\(_5\)O\(_12\)/graphene composite at 0.2 C and 10 C are investigated, as shown in Fig. 4. At 0.2 C, the discharge capacity of the Li\(_4\)Ti\(_5\)O\(_12\)/graphene is slightly higher than the capacity of the Li\(_4\)Ti\(_5\)O\(_12\) and the specific capacity retention during 100 cycles is 94%. At 10 C, the discharge capacity of the Li\(_4\)Ti\(_5\)O\(_12\)/graphene is 110 mAh g\(^{-1}\), which is much higher than that of Li\(_4\)Ti\(_5\)O\(_12\) (84 mAh g\(^{-1}\)). The improvement in capacity retention especially in high rate capacity can be attributed to the introduction of superior conductive graphene. On the one hand, the graphene sheets induce the formation of fine Li\(_4\)Ti\(_5\)O\(_12\) nanoparticles in the sol–gel synthesis. The reduced size means the shortened diffusion distance for lithium ions and thus the kinetics of lithium insertion/extraction is accelerated. On the other hand, the electronic conductivity of the Li\(_4\)Ti\(_5\)O\(_12\) nanoparticles anchored to the graphene sheets is significantly improved.

Recently, Amine and his co-workers reported that a new phase generated after the spinel/rock-salt phase transition of Li\(_4\)Ti\(_5\)O\(_12\)
with extra lithium insertion [33]. Our recent work also indicated that the extra capacity of the Li$_4$Ti$_5$O$_{12}$ anode below 1.0 V function to postpone overcharge and withstand high voltage in a full cell, e.g. LiNi$_{0.5}$Mn$_{1.5}$O$_4$/Li$_4$Ti$_5$O$_{12}$ [34]. Now we propose that the Li$_4$Ti$_5$O$_{12}$/graphene composite could provide higher capacity than the pristine Li$_4$Ti$_5$O$_{12}$ in the low voltage range (<1.0 V) from the graphene sheets. Fig. 5 shows the initial voltage profiles of the cells with the electrodes using Li$_4$Ti$_5$O$_{12}$ and the Li$_4$Ti$_5$O$_{12}$/graphene composite when discharging and charging between 2.5 and 0 V. For the pristine Li$_4$Ti$_5$O$_{12}$ definitely the discharge curve can be separated into two sections, 2.5–1.0 V region and 1.0–0 V region, with the total specific capacity of 270 mAh g$^{-1}$, which is close to the results of Ge’s and Borghols’s works [35,36]. In the first section, the capacity of about 160 mAh g$^{-1}$ is corresponding to the transition from the spinel (Li$_4$Ti$_5$O$_{12}$) to the rock-salt structure (Li$_7$Ti$_5$O$_{12}$). However, in the following section (1.0–0 V), the discharge capacity is over 110 mAh g$^{-1}$, which is higher than the theoretic capacity for the single phase transition from Li$_7$Ti$_5$O$_{12}$ to Li$_8.5$Ti$_5$O$_{12}$ (about 87.5 mAh g$^{-1}$) based on the mass of the original Li$_4$Ti$_5$O$_{12}$. The extra capacity is mainly attributed to the lithium storage in the conductive carbon black and to the side reaction between the electrolyte and the electrode [2]. In our previous investigation, we proposed that the capacity of this section (below 1.0 V) was helpful to postpone the overcharge distort and thus improve the safety characteristic of the full cells [34]. So the higher capacity below 1.0 V is more advantageous for the safety of the relative lithium-ion batteries. For the Li$_4$Ti$_5$O$_{12}$/graphene composite, the discharge curve is similar as that for Li$_4$Ti$_5$O$_{12}$. In the region above 1.0 V, the discharge capacity is nearly equal to that of the pristine Li$_4$Ti$_5$O$_{12}$. However, in the region below 1.0 V, the discharge capacity of 270 mAh g$^{-1}$ is much higher than that of Li$_4$Ti$_5$O$_{12}$ (110 mAh g$^{-1}$). Comparing with the voltage profiles of pure graphene anode in our previous work [28], we conclude that the difference of the discharge capacity between Li$_4$Ti$_5$O$_{12}$/graphene composite and Li$_4$Ti$_5$O$_{12}$ below 1.0 V is mainly due to the lithium storage in the graphene sheets. During the charging process, the sloping lines in the regions of 0.5–1.5 V and 1.6–2.5 V correspond to total charge capacity of 125 mAh g$^{-1}$, which is obviously different from nearly vertical lines in the same regions for the pristine Li$_4$Ti$_5$O$_{12}$. The sloping charging curve is also the main character of graphene during charging, based on the previous literatures [28,30,31]. In addition, it is also obvious that the smaller voltage drop from the voltage gap between the charging plateau and the discharging plateau is also attributed to the introduction of highly conductive graphene. Compared with the cells cycled between 2.5 and 1.0 V, both the cells have the reduced coulombic efficiencies in the region of 2.5–0 V. 76.9% for Li$_4$Ti$_5$O$_{12}$ and 65.8% for the Li$_4$Ti$_5$O$_{12}$/graphene composite. The main reason for the reduced coulombic efficiency is possibly the irreversibly reductive decomposition of the solvents at the low potential (<1 V vs. Li$^+$/Li) [2,34]. Especially, for the Li$_4$Ti$_5$O$_{12}$/graphene composite, more side reactions on the active graphene sheets with high specific surface area lead to low coulombic efficiency (65.8%), which is also common in the pure graphene anode [28,30].

The 3rd, 50th and 100th voltage profiles of the cells with the electrodes using Li$_4$Ti$_5$O$_{12}$ and the Li$_4$Ti$_5$O$_{12}$/graphene composite between 2.5 and 0.5 V are shown in Fig. 6. It is clear that the coulombic efficiencies keep at a high level above 95%, not like the initial cycle. The 3rd, 50th and 100th reversible capacities of Li$_4$Ti$_5$O$_{12}$ are 206, 189 and 185 mAh g$^{-1}$, respectively. The Li$_4$Ti$_5$O$_{12}$/graphene composite exhibits higher reversible capacities of 269 (3rd), 236 (50th) and 228 mAh g$^{-1}$ (100th). Both Li$_4$Ti$_5$O$_{12}$ and the Li$_4$Ti$_5$O$_{12}$/graphene composite have visible capacity fading in the first 50 cycles and good cyclability in the next 50 cycles. Overall, it can be concluded that both Li$_4$Ti$_5$O$_{12}$ and the Li$_4$Ti$_5$O$_{12}$/graphene composite cycled in the region of 2.5–0 V have good cycling performance. It is worth noting that the capacity of the discharge plateau at ∼1.5 V is decreasing even though the total discharge capacity keeps stable with the cycle number increasing. The reason for this interesting phenomenon should be a subject of further study. In brief, the Li$_4$Ti$_5$O$_{12}$/graphene composite can release...
much higher capacity than Li_4Ti_5O_12, especially in the region of 1.0–0 V, which is quite beneficial for not only the high energy density but also the safety characteristic of relative lithium-ion batteries.

4. Conclusions

The Li_4Ti_5O_12/graphene composite has been prepared by a facile sol–gel process. There is no impurity phase detected but pure Li_4Ti_5O_12 cubic phase with Fd3m space group in the composite. SEM results indicate that homogeneous composite powders are composed of graphene sheets and fine Li_4Ti_5O_12 nanoparticles. We have demonstrated that the Li_4Ti_5O_12/graphene composite has higher capacity, especially at high current rate, and better cycling performance than the pristine Li_4Ti_5O_12. Above all, when discharged to 0 V, the Li_4Ti_5O_12/graphene composite exhibits a quite high capacity of 430 mAh g^{-1}. The higher capacity than Li_4Ti_5O_12, especially in the region of 1.0–0 V, is quite beneficial for not only the high energy density but also the safety characteristic of relative lithium-ion batteries. All the results suggest that the Li_4Ti_5O_12/graphene composite is a promising anode material for the high-energy and highly safe lithium-ion batteries.

Acknowledgements

This work was supported by National Science Foundation of China (grant no. 21006033), Program for New Century Excellent Talents in Chinese Ministry of Education (No. NECT-07-0307) and the Fundamental Research Funds for the Central Universities, SCUT (2009220038).

References