Enhanced electrochemical performance of a LTO/carbon nanotubes/graphene composite as an anode material for Li-ion batteries

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Abstract. A $Li_4Ti_5O_{12}$/carbon nanotubes/graphene composite has been successfully prepared by a solid-state method. For comparison, pure LTO and $Li_4Ti_5O_{12}$/graphene composite were also synthesized using the same method. The materials were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) to confirm the structure and morphology. The results reveal that LTO particles are well dispersed and wrapped in the graphene sheets with cross-linked carbon nanotubes. The electrochemical results show that the $Li_4Ti_5O_{12}$/carbon nanotubes/graphene composite exhibits the best rate capacity, which lead to a charge capacity of 169.0, 168.5, 167.1, 153.2, 144.5, 131.5 mAh g^{-1} at 0.2, 0.5, 1, 3, 5 and 10 C, respectively between 1 and 3 V (1 C = 160 mAh g^{-1}). The synergistic effect of graphene and carbon nanotubes constructing 3D networks could enhance the electronic conductivity of $Li_4Ti_5O_{12}$/carbon nanotubes/graphene composite.

1. Introduction

In recent years, rechargeable lithium-ion batteries (LIBs) have been considered as a promising power system for energy storage. Lithium ion batteries are rapidly replacing conventional lead-acid batteries in our daily life from personal portable equipment to large-scale electric energy storage applications such as electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1, 2]. Spinel $Li_4Ti_5O_{12}$ (LTO) has been regarded as an ideal anode material for LIBs because it possesses some unique advantages, such as the negligible volume variation during insertion/extraction of the lithium ion and the high redox plateaus at around 1.55 V (vs Li/Li^+) [3, 4]. However, the LTO also has some inherent disadvantages. The poor electronic conductivity ($< 10^{-13}$ S cm^{-1}) an sluggish Li^+ diffusion coefficient ($10^{-13} - 10^{-9}$ cm^2 s^{-1}) of LTO, which results in low capacities at high current rates [5]. In order to overcome the drawbacks, many effective strategies have been executed, such as designing LTO nanostructures, doping with ions and surface coating with some conductive components (carbon, graphene, carbon nanotubes) [6-8]. Notably, the surface coating with some conductive components has been proved to be an effective and facile way to improve the electronic conductivity and Li^+ diffusion ability of LTO.

To our best knowledge, graphene and carbon nanotubes are two new type nano-carbon materials. which have been widely used in LIBs [9, 10]. However, most studies are limited to graphene or carbon nanotubes modifying electrode materials alone. It is meaningful to combine graphene with carbon nanotubes together to modify electrode materials, which could construct a three dimensional (3D) conducting networks and improve the electrochemical performances. For example, Lei et al.

synthesized a three-dimensional LiFePO$_4$/carbon nanotubes/graphene composite by wet ball milling followed by a two-step heat treatment process [11]. In our paper, we have prepared a LTO/carbon nanotubes/graphene composite by a two step solid-state method follow by sintering in a box furnace under air atmosphere. By contrast, the LTO/graphene composite and pure LTO are also synthesized by the same method, and the electrochemical performances of these three materials are discussed.

2. Experiments and Methods

2.1 Synthesis and characterization

Pure LTO powders were synthesized by solid-state reaction. In brief, a stoichiometric amount of anatase-TiO$_2$ (Chongqing Xinhua Chemical Co., Ltd.), Li$_2$CO$_3$ (Sichuan Tianqi Lithium Industries Inc., China) and anhydrous ethanol were mixed by ball milling at 300 rpm for 15 h using zirconia as the milling media, the mass ratio of the materials to zirconia balls was selected to be 1:20. The mixture was subsequently dried at 85°C for 5 h. Finally, the mixed solid powders were calcined at 800°C for 10 h in an air atmosphere to obtain pure LTO. The molar ratio of Li:Ti was 4:5 and excessive Li (5%) was added to compensate for the volatilization of Li during the calcined process.

Graphene (Qingdao hi tech Polytron Technologies Inc) and carbon nanotubes (Beijing Cnano Technology Limited) powders were purchased for this study. For fabricating LTO/carbon nanotubes/graphene composite: 5% wt. graphene and 5% wt. carbon nanotubes were dispersed in anhydrous ethanol with sonication for 0.5 h. Then, the carbon nanotubes and graphene suspension and LTO powders were mixed by ball milling (the weight percentage ratio of the total carbon nanotubes and graphene to LTO is 10%) at 500 rpm for 5 h. Subsequently, the mixture was dried at 85°C for 4 h, followed by calcining at 500°C for 5 h under N$_2$ atmosphere to obtain the homogeneous LTO/carbon nanotubes/graphene composite (abbreviated for LTO-CNT-G). For comparison, a LTO/graphene composite (the weight percentage ratio of graphene to LTO is 10%) was also prepared by the same process. This composite was abbreviated LTO-G.

Powder XRD (Ultima IV, Riguku) with Cu K$_\alpha$ radiation was used to identify the phase composition of all samples. The diffraction patterns were collected at room temperature by scanning stepwise in the range of 10–90° at a scanning rate of 0.02° per 10 s. The morphology of the materials was characterized by SEM (Tescan Maia3 MHL).

2.2 Electrochemical measurements

The electrochemical properties of all samples were tested by adopting a CR2032 coin-type half-cell with Li foil as the counter electrode. The cathode slurry was prepared by homogeneously mixing the active materials, Super-P, and polyvinylidene fluoride (PVDF) in a mass ratio of 85:10:5 in N-methyl-2-pyrrolidone (NMP) solvent. Then, the slurry was cast onto a Cu foil and dried for 12 h in vacuum at 105°C. Finally, the electrode laminate was punched into disks (10 mm in diameter) and dried in a vacuum oven at 105°C for 24 h. The coin cell was assembled entirely in an argon-filled glovebox. The loading density of the active materials on each electrode was about 1.52 mg cm^{-2}. The separator was Celgard 2400 (Celgard Inc., USA), and the electrolyte (Capchem Technology (Shenzhen) Co., Ltd.) was a solution of 1 mol L^{-1} LiPF$_6$ in ethylene carbonate, dimethyl carbonate, and diethyl carbonate (1:1:1, volume ratio).

Galvanostatic charge-discharge tests were carried out on an automatic galvanostatic charge-discharge unit (Land 2001A, Wuhan, China) between 1 and 3 V at C-rates of 0.2 C, 0.5 C, 1 C, 3 C, 5 C and 10 C (1 C = 250 mAh g^{-1}) at 25 °C.

3. Results and discussion

3.1 Material characterization

Figure1 shows the XRD patterns of pure LTO, LTO-G, and LTO-CNT-G composites. All the XRD patterns are indexed to the standard spinel structure of LTO (card NO. 49-0207) with *Fd*-3m space

group. The absence of graphite diffraction peaks from LTO-G and LTO-CNT-G composites may be ascribe to the low quantity and amorphous structure. The XRD patterns prove that the structures of LTO-G and LTO-CNT-G composites are not destroyed after the graphene and carbon nanotubes incorporated with LTO particles.

Figure 2 shows the SEM images of pure LTO, LTO-G, and LTO-CNT-G composites. It can be seen that the LTO particles are well dispersed and wrapped in the graphene sheets with cross-linked carbon nanotubes to form 3D conducting networks, which can offer more conductive pathways for electron transfer during the charge/discharge process.
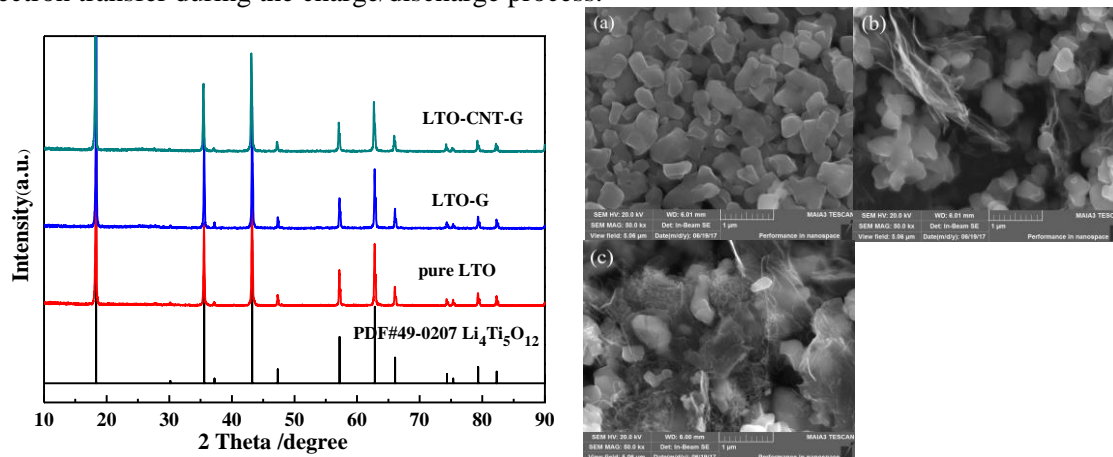

Figure 1: XRD patterns of pure LTO, LTO-G composite, LTO-CNT-G composites and the standard XRD patterns of LTO.

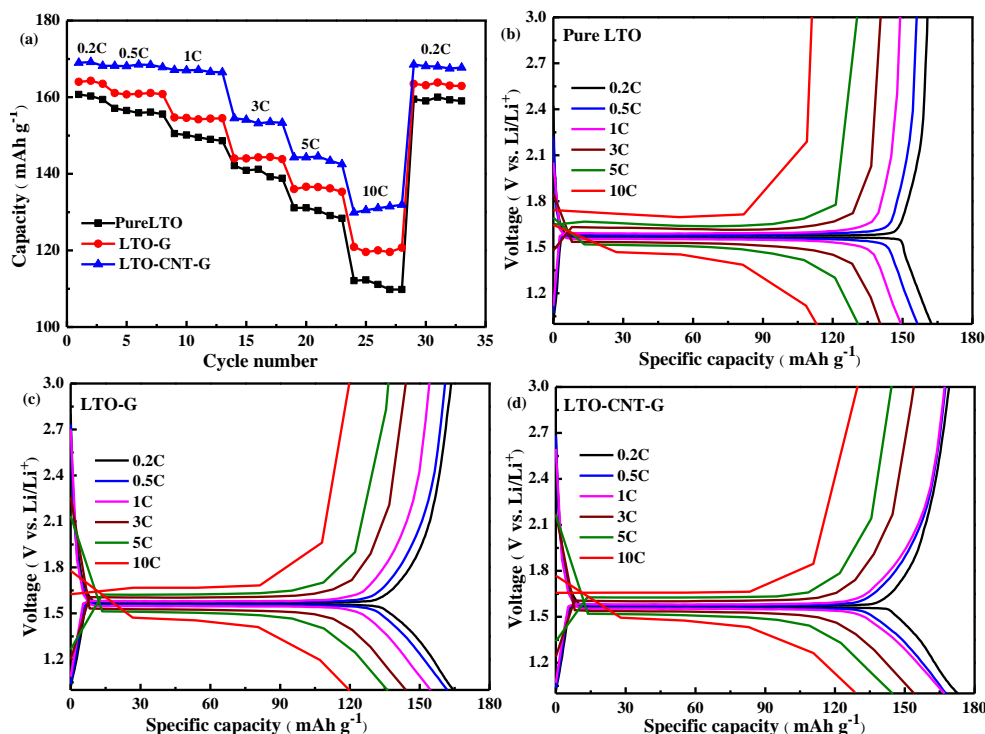Figure 2: SEM images of (a) pure LTO, (b) LTO-G and (c) LTO-CNT-G composites.

Figure 3: (a) Rate capacity of pure LTO, LTO-G and LTO-CNT-G composites from 0.2 C to 10 C, and (b-d) galvanostatic charge-discharge curves at different C-rates for pure LTO, LTO-G composite, LTO-CNT-G composites between 1 and 3 V (1 C = 160 mAh g^{-1}).

3.2 Electrochemical properties

Figure 3a displays the rate capacity of pure LTO, LTO-G, and LTO-CNT-G composites at C-rates from 0.2–10 C in the range of 1 and 3 V. The LTO-CNT-G composite shows a superior rate capacity than LTO-G composite and pure LTO. The galvanostatic charge-discharge curves of pure LTO, LTO-G and LTO-CNT-G composites are shown in Figure 3b–d, respectively. The LTO-CNT-G composite exhibits a smallest potential difference between the charge and discharge platforms compared with LTO-G composite and pure LTO at high C-rates. This is attributed to that LTO particles incorporated with graphene and carbon nanotubes could improve electronic conductivity and reduce electrode polarization , thereby enhancing the rate capacity of LTO. The charge capacity values of the LTO-CNT-G composite are 169.0, 168.5, 167.1, 153.2, 144.5, 131.5 mAh g^{-1} at 0.2, 0.5, 1, 3, 5 and 10 C, (1 C = 160 mAh g^{-1}), respectively. However, the charge capacity values of the LTO-G composite are 164.3, 160.9, 154.6, 144.3, 136.2, 120.0 mAh g^{-1}, respectively, and the charge capacity values of pure LTO are 160.3, 155.9, 149.5, 139.2, 130.4, 111.1 mAh g^{-1}, respectively.

4. Conclusions

In summary, the LTO-CNT-G composite has been successfully synthesized by a solid-state method. The characterization results show that LTO particles are well dispersed and wrapped in the graphene sheets with cross-linked carbon nanotube. The electrochemical results indicate that the LTO-CNT-G composite displays a superior rate capability than the LTO-G composite and pure LTO, which may be attributed to that the synergistic effect of graphene and carbon nanotubes could enhance the electronic conductivity and reduce electrode polarization. Therefore, the LTO-CNT-G composite is a promising anode material for lithium ion batteries.

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