

Nitrogen doped CNT/Li₄Ti₅O₁₂ composite for the improved high-rate electrochemical performance of lithium-ion batteries

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Abstract. A novel Li₄Ti₅O₁₂ (LTO) composite with nitrogen doped multi-walled carbon nanotubes (CNTs), denoted N-C-LTO, was successfully prepared via simple thermal annealing of CNTs in the presence of melamine. For comparison, LTO, C-LTO (Li₄Ti₅O₁₂/CNT) were also synthesized. N-C-LTO demonstrated the best electrochemical performance among the samples. Even at a high charge/discharge rate of 20 C, the reversible capacity was maintained at the high level of 100 mAhg⁻¹. Moreover, after 150 cycles at 3.0 C, 90.7 % of the capacity was retained with negligible capacity fading. The excellent electrochemical performance was possibly due to the nitrogen in the doped CNTs, which maintained the benefits of the nitrogen as good electron donating.

1. Introduction

In the last decade, spinel Li₄Ti₅O₁₂ (LTO) has been considered as a promising anode material due to its outstanding safety performance and ultra-long lifetime [1-3]. Despite these advantages, drawbacks, such as poor electronic conductivity and sluggish Li-ion diffusion in the bulk, are still present [4-6]. To overcome these drawbacks, two typical approaches have been developed. The first approach is to synthesize nanostructured Li₄Ti₅O₁₂ materials with various morphologies to facilitate lithium-ion transport by shortening the diffusion path and to improve the intercalation kinetics by providing a large electrode/electrolyte contact area [7-9]. The other approach is to improve the electronic conductivity of Li₄Ti₅O₁₂ by doping with metal ions or through surface modification by coating or mixing with conductive species, such as Ag [10], carbon materials [11-13], etc. According to the literature, the synthesis of carbon-modified composites presents a simple but more effective way to improve the electronic conductivity. As a novel carbon material, carbon nanotubes (CNTs) are useful for improving the performance of Li₄Ti₅O₁₂ due to their high length/diameter ratio and unique conductivity. Several studies have demonstrated LTO/CNT composites with highly improved performance [14,15]. Therefore, a novel approach to modify LTO/CNT composites to further enhance the performance is highly desired.

The addition of dopants (N) in the CNT lattice affords a better electron transfer rate than that of ordinary CNTs. According to the literature, CNTs show enhanced conductivity upon nitrogen doping, as nitrogen atoms act as electron donors and decrease the band gap of the material [16,17]. To the best of our knowledge, LTO/ N-CNT composites have been rarely reported. Therefore, we examined the



effect of N-CNT on the electrochemical properties of LTO. In this paper, we successfully prepared the LTO/N-CNT composite and obtained excellent electrochemical performance. The effects of N doping was studied. In addition, characterizations of the LTO/ N-CNT composite, such as the electrochemical performance, phase purity, morphology, are also discussed in this paper.

2. Experimental section

2.1 Preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) was prepared from TiO_2 (anatase structure) and Li_2CO_3 via a solid-state method. The starting materials, TiO_2 and Li_2CO_3 in a Li:Ti molar ratio of 0.85:1, were mixed in water and ball-milled for 6 h. The obtained binary precursor slurry was treated by the spray-drying method to form a dry powder. The dry powder was then calcinated at 750 °C for 12 h under air atmosphere with a temperature ramp rate of 5 °C/min.

2.2 Preparation of N-CNT

A commercial multi-walled carbon nanotube (CNT) sample (Cnano Technology 9100) was used as the starting material. According to the supplier, these nanotubes had an average diameter of 10-15 nm and a carbon purity higher than 97%. For the preparation of N-CNT, 1 g of the CNT sample was mixed with 0.075 g of N using melamine as the nitrogen precursor (5 wt% of N in N-CNT), and the mixture was ball-milled for 4 h. Then, the resulting material was heated under N_2 flow to 600 °C and subjected to thermal treatment at this temperature for 2 h.

2.3 Preparation of LTO/CNT, LTO/N-CNT

Then, 4 g LTO (300 mesh) and 0.2 g CNT, N-CNT were mixed, and the mixture was then ball-milled for 5 h and finally dried at 60 °C for 12 h. After that, the dried mixture was calcined at 500 °C for 5 h under nitrogen flow to obtain LTO/CNT, LTO/N-CNT. The corresponding products are denoted C-LTO (LTO/CNT), N,C-LTO (LTO/N-CNT)

2.4 Electrochemical measurements

The electrochemical properties of all samples were measured using a CR2032 coin-type half-cell in which the cathode and Li metal anode were separated by a porous polypropylene film (Celgard 2400, Celgard Inc., USA). The cathode slurry was prepared by the homogeneous mixing of the active material (LTO material), Super-P, and polyvinylidene fluoride (PVDF) in a mass ratio of 85:10:5 in N-methyl-2-pyrrolidone (NMP). The resulting slurry was cast onto Cu foil and dried under vacuum for 12 h at 90 °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 cells were assembled in an argon-filled glove box. The electrolyte (Capchem Technology (Shenzhen) Co., Ltd.) was a 1 mol L^{-1} solution of LiPF_6 in ethylene carbonate, dimethyl carbonate, and diethyl carbonate (volume ratio = 1:1:1).

Galvanostatic charge-discharge tests were carried out using an automatic galvanostatic charge-discharge unit (Land 2001A, Wuhan, China) between 1 and 3 V at C-rates of 0.2, 1, 3, 10 and 20 C (1 C = 250 mAh g^{-1}) at 25 °C. Electrochemical impedance spectroscopy (EIS) was performed between 10 mHz and 100 kHz before and after the cycling tests using an electrochemical workstation (Interface 1000, Gamry, USA).

2.5 Characterization of the materials

Powder X-ray diffraction (XRD, Ultima IV, Rigaku) utilizing Cu-K α radiation was used to characterize the phases and crystal structures of all samples. The diffraction patterns were collected at room temperature by step scanning over a range of 10-90° at a scanning rate of 5°/min. The morphologies of the materials were characterized by scanning electron microscopy (SEM, Hitachi S-4800, Japan) and transmission electron microscopy (TEM, JEOL, JEM-2010F). The surface

compositions of the LTO materials were examined by X-ray photoelectron spectroscopy (XPS, PHI5600 Physical Electronics).

3. Results AND Discussion

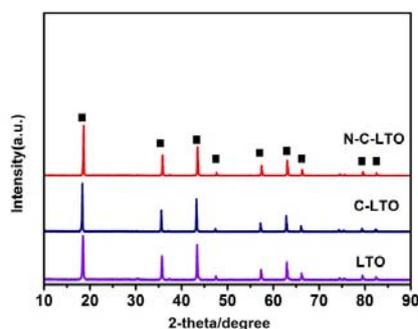


Fig. 1 XRD patterns of LTO, C-LTO, N,C-LTO.

Fig. 1 shows the XRD patterns of LTO, C-LTO, N,C-LTO. The five as-prepared materials show intense, sharp peaks that can be assigned to spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with good crystallinity in accordance with JCPDS card no. 49-0207. No extra phases are detected, confirming the high phase purity. Additionally, no diffraction peaks corresponding to carbon are present, presumably due to the low CNT content in these composite materials.

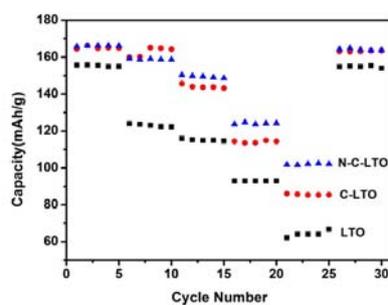


Fig. 2 Cyclic performances of the LTO, C-LTO, B,C-LTO, N,C-LTO, and N-B-C-LTO samples at different

rates: 1st–5th cycles at 0.2 C, 6th–10th at 1C, 11th–15th at 3 C, 16th–20th at 10C, and 21th–25th at 20 C.

Fig. 2 shows the cyclic performances of the LTO, C-LTO, N,C-LTO samples over 5 cycles at different rates of 0.2, 1.0, 3.0, 10 and 20 C. As shown in Fig. 4, the discharge capacity of all the samples gradually decreased with increased rate. However, the two CNT-LTO composite samples manifested a higher reversible capacity than LTO at all rates, and both the CNT-LTO composite samples showed almost the same reversible capacities at 0.2, 1 and 3 C. However, at the higher rate of 20 C, the capacity of the doped CNT-LTO composite showed a much higher reversible capacity than the non-doped CNT-LTO composite. N-C-LTO demonstrated the highest capacity at 20 C. These results indicate that the N -C-LTO composite exhibits the best rate capability among the samples of LTO, C-LTO, N,C-LTO possibly due to the CNTs show enhanced conductivity upon nitrogen doping, as nitrogen atoms act as electron donors and decrease the band gap of the material.

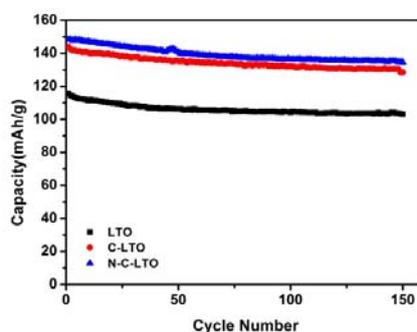


Fig. 3 The cycling performance of LTO, C-LTO, N,C-LTO over 150 cycles at 3 C.

The cycling performance of various samples at 3 C is shown in Fig. 5. In the initial cycle, the discharge capacity of LTO, C-LTO, N,C-LTO is 115.8, 141.8, 148.4 mAh/g, respectively. The discharge capacity decreases to 103.2, 128.5, 137.5mAh/g after 150 cycles of charging/discharging, maintaining 89.5%, 90.7%, 92.7% of the capacity relative to the initial cycle. The N-C-LTO sample exhibits superior electrochemical performance. As shown above, N-doping of the CNTs not only improved the discharge capacity at high C-rates but also enhanced the cycling stability.

4. Conclusion

We successfully synthesized N doped CNT-LTO composite materials using a simple ball-milling process followed by calcination. The results show that the electronic conductivity and the electrochemical performance can be improved through nitrogen doping. The N-B-C-LTO demonstrated a much better electrochemical performance. At a high charge/discharge rate of 20 C, the reversible capacity reached the high level of 100 mAhg⁻¹. Moreover, after 150 cycles at 3.0 C, 92.7% of the capacity was retained with negligible capacity fading.

Acknowledgments

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