



Facile preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AB}/\text{MWCNTs}$ composite with high-rate performance for lithium ion battery

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ABSTRACT

$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AB}/\text{MWCNTs}$ material was fabricated through a facile solid-state reaction. The structure and morphology of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AB}/\text{MWCNTs}$ material were determined by XRD and SEM. The electrical conductivity of the composite is improved by imbedding $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles into the conductive AB/MWCNTs network. The electrochemical properties of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AB}/\text{MWCNTs}$ composite was measured by charge–discharge tests, cyclic voltammogram (CV) and electrochemical impedance spectroscopy (EIS). Compared with the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AB}/\text{MWCNTs}$ material exhibits an excellent high rate performance and cycling performance, which is due to the decrease of particle size and the increase of electrical conductivity of the material. The discharge capacities were 116 and 102 mAh g^{-1} at the charge–discharge rates of 20 and 30 C, respectively. After 1000 cycles at 2 C, the discharge capacity of the composite maintained 163 mAh g^{-1} .

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1. Introduction

Compared to other rechargeable batteries Li-ion battery has a higher capacity density and energy level per unit weight and it has therefore been widely used as the main power source for portable electronic devices such as camera, vidicon, mobile phone, etc. [1,2]. Recent researches indicate that Li-ion battery will become an important green energy for next generation electric vehicles and hybrid electric vehicles [3]. However, there exists some technical bottlenecks to be solved before Li-ion battery can be used in the automobile industry. The production cost is high for current Li-ion battery and the lifespan is limited, especially at low temperature. More importantly, safety is a concern when Li-ion battery is charged or discharged at high current. The safety property is mainly determined by the carbon material which serves as the anode material [4]. Therefore, it is very important to find cheap and safe electrode materials with excellent electrochemical performance for the large-scale industrial production.

As one of the most excellent Li-ion battery anode materials, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has been widely studied in recent years. LTO is cheap and environmentally benign which has high reversible capacity [5,6]. It has a spinel structure with space group of $Fd-3m$, providing three-dimensional diffusion paths for Li ions [7,8]. The diffusion coefficient is $2 \times 10^{-8} \text{ cm}^2/\text{s}$ and is one order of magnitude higher than that of the usual commercial graphite anode material

[9]. When used as anode material in Li-ion batteries, an extremely small structural change (zero-strain) occurs during lithium insertion/extraction process [10,11]. These properties of LTO endow it with a good structural stability and excellent cycling performances and the reversibility of the lithium insertion/extraction process in a long cycling life. Furthermore, LTO provides a steady working voltage (1.55 V vs. Li^+/Li) [12], this working voltage is far from the electric potential at which Li ions precipitate out. This prevents electrolytes from electrolysis and the formation of SEI (usually occurring below 1.0 V Li^+/Li) [13]. Both safety and reliability are improved. Hence, LTO is a very promising anode material for rechargeable lithium ion batteries and can be used as electric power battery.

However, LTO has poor electronic conductivity, which results in poor electrochemical properties, especially at high rate [13]. This is closely related to the manufacturing process, crystal structure and particle sizes. Various synthetic and processing approaches have been employed to solve this problem including sol–gel, doped compounds, nanotechnology, conductive coatings and introducing conductive additives (AB, CNT, CNF), etc. [14–22]. The rate performance of LTO and LTO/C nanostructured materials can be improved due to good electronic conductivity and short lithium-ion diffusion path [23–25]. However, there are several disadvantages: (1) the manufacturing process is very complex; (2) the cost is high; (3) the process is strongly affected by temperature; (4) the process is rigorous. Recent researches show that electrode materials and mesoporous structure can effectively decrease the polarization and enhance the rate performance [26,27]. The high temperature dependency and high mobility which exist in nanosized particles

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are reduced by large particle sizes. However, most of the processes are either complex or have to be performed at high cost.

In the present study, we describe a facile, inexpensive and industrially scalable solid-state reaction route to fabricate LTO/AB/MWCNTs material. The synthetic process was involved with sintering of TiO_2 and Li_2CO_3 by using acetylene black (AB) and multi-wall carbon nanotubes (MWCNTs) as additive at 800°C in an inert environment. AB and MWCNT are chosen as a conductive additive to form a well connected conductive network and present a much better electrochemical performance than LTO, including an excellent rate capability and capacity.

2. Experimental

2.1. Preparation of materials

Pristine LTO and LTO/AB/MWCNTs composites were prepared by solid-state reaction. Sample A: TiO_2 -anatase and Li_2CO_3 ($n_{\text{Li}}:n_{\text{Ti}}=4.32:5$ by mole) the starting materials were first mixed using a planetary high energy ballmilling machine (Fritsch pulverisette 7) in acetone. The ball and initial material mass ratio are 6:1, the volume of acetone is 1.5 times than initial materials, the ball milling is 6 h with the speed of 400 rpm. The obtained binary precursor slurry was treated at 80°C , and became dried powder. The dried powder was then calcinated at 800°C for 10 h in Ar atmosphere ($10^\circ\text{C min}^{-1}$) to obtain well-crystallized LTO.

Sample B: the LTO/AB/MWCNTs hybrid material was also prepared by similar solid-state reaction method mentioned above. Firstly, MWCNTs and AB were mixed and dispersed in acetone with sufficient ultrasonication for 2 h to form a homogeneous slurry. After that, TiO_2 and Li_2CO_3 ($n_{\text{Li}}:n_{\text{Ti}}=4.32:5$) were added and ball-milled for 12 h to obtain a uniform mixture followed by drying at 80°C . Finally, the obtained powder was placed in tubular furnace and heated at the rate of $10^\circ\text{C min}^{-1}$ to 800°C , and sintered under 800°C for 10 h in Ar atmosphere. After cooling to room temperature, LTO/AB/MWCNTs composite was obtained for later use.

2.2. Measurements

The crystal structures of pure LTO and LTO/AB/MWCNTs powders were analyzed using X-ray diffract meter (XRD, Rigaku D/max- γB). The morphologies of the as-prepared powders were observed using a scanning electron microscope (SEM, Hitachi S4800) and a transmission electron microscope (TEM, Hitachi H-7650). The amount of AB and CNTs in LTO/AB/MWCNTs composite was measured by thermogravimetry (TG, Netzsch STA449F3). Raman spectroscopy (JY, Labram HR800) using 457.9 nm excited laser.

The electrochemical characterizations were conducted by means of two-electrode coin-type half cells (CR2025). The cell is composed of a lithium metal negative electrode and active material powder positive electrode that were separated by a microporous polypropylene film, and 1 mol L^{-1} solution of LiPF_6 in a mixed solvent of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) with 1:1:1 in volume ratio was used as the electrolyte. The anodes were made of the pristine LTO materials with an acetylene black conducting agent and a polyvinylidene fluorid (PVDF) binder, with a weight ratio of 80:10:10. After these materials were thoroughly mixed in N-methyl-2-pyrrolidone (NMP) solution and stirred for 4–6 h, the slurry was coated uniformly on Cu foil. However LTO/AB/MWCNTs positive electrode (95 wt.% active material, 5 wt.% PVDF binder), only stirring for 20 min. The prepared slurry was coated on Cu foil to a thickness of approximately 60 μm . The anode was punched

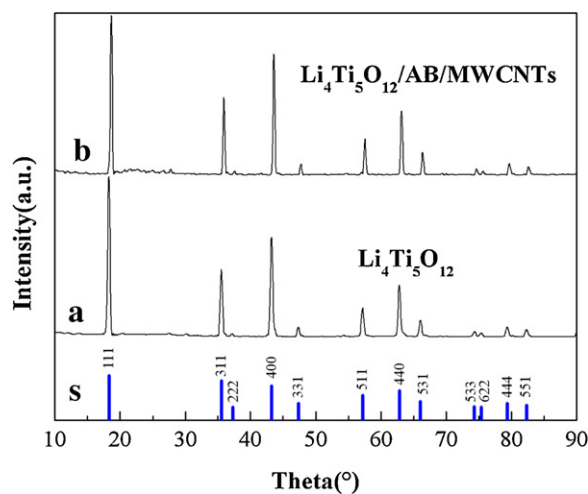


Fig. 1. XRD diffraction patterns of: LTO (JCPDS Card No. 26-1198, noted as S) and synthesized LTO (a) and LTO/AB/MWCNTs (b) samples.

into circular discs. Finally, the electrode was dried under vacuum at 120°C for 10 h. The cells were assembled in a glove box filled with high purity argon gas. The cells were charged and discharged between 1.0 and 3.0 V by applying various current densities at 25°C .

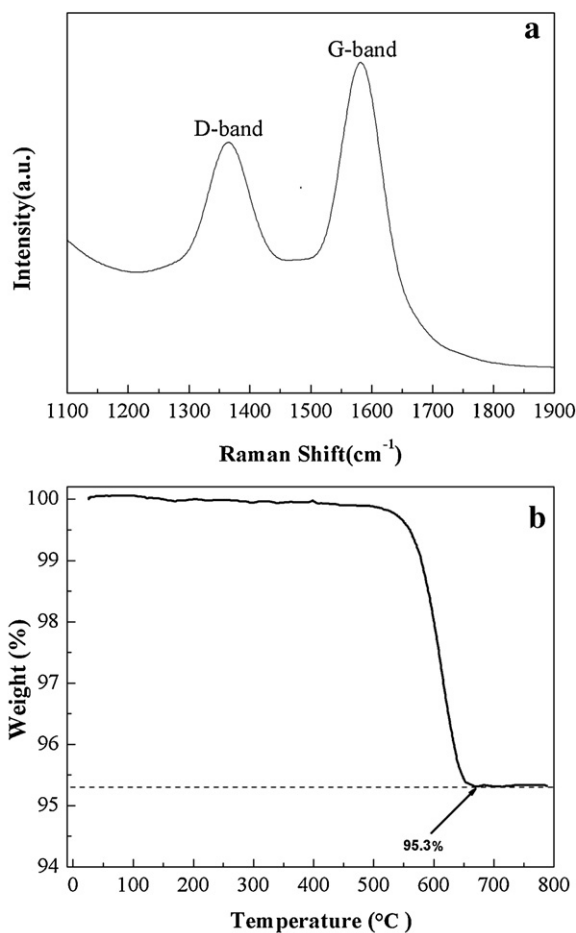


Fig. 2. (a) Raman spectrum of LTO/AB/MWCNTs sample. (b) TG curve of LTO/AB/MWCNTs composite from 25 to 800°C in air at a heating rate of $10^\circ\text{C min}^{-1}$. The residual weight ratio corresponds to the content of LTO in composite.

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