



# Nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ anode material with ultrafast charge/discharge capability for lithium ion batteries



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## ABSTRACT

Nano-structured  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  crystals coated with carbon layer are in situ synthesized via one-step liquid process taking advantage of low-cost sucrose as carbon source in this work. The as-prepared LTO/C particles present much larger specific surface area ( $58 \text{ m}^2 \text{ g}^{-1}$ ) relative to the value of pure LTO, with a size around 13 nm in average. Its electronic conductivity of  $6.56 \times 10^{-4} \text{ S cm}^{-1}$  is over three orders of magnitude higher than the pure one. The composite anode displays a distinguished electrochemical charge/discharge performance, especially, quite high rate capability along with a stable cyclability. It delivers the initial discharge specific capacities of 156.7 and 142.1  $\text{mA h g}^{-1}$  at 40C and 60C respectively, and remains the values of 114.2 and 98.1  $\text{mA h g}^{-1}$  after 200 cycles. Furthermore, a capacity of 132.8  $\text{mA h g}^{-1}$  is delivered even at an 80C rate and the value of 82.7  $\text{mA h g}^{-1}$  can be maintained after 200 cycles. The ultrafast charge/discharge capability may be attributed to the shorten  $\text{Li}^+$  transport path in the nanosized composite and the enlarged access area with electrolyte. Additionally, the carbon coating may provide an effective conductive network among the particles promoting charge transfer.

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## 1. Introduction

Nowadays, with the fast development of electric vehicles (EV) and hybrid electric vehicles (HEV), the study on high-performance secondary batteries has attracted more and more attention. Lithium ion batteries (LIBs) are considered as the most promising candidates for their high energy density and long cyclic performance [1–4]. As a commonly-used commercial anode for LIBs, graphite material exhibits low electrode potential, high coulombic efficiency and high energy density and so on. But it also encounters several serious shortages when used in LIBs, such as poor rate performance, solid electrolyte interface (SEI) formation and lithium dendrite deposition during charge process [5–7]. Many efforts have been made to pursue high performance alternatives for the anode material [8,9]. Spinel lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , LTO) shows the potential as a candidate because of its excellent safety performance, outstanding reversibility, stable crystal structure [10–12]. The

voltage plateau around 1.55 V (vs  $\text{Li}/\text{Li}^+$ ) of LTO electrode is higher than the reduction potentials of electrolyte solvents in general, thus it is possible to prevent the formation of SEI due to solvent decomposition, and avoid lithium dendrite deposition on the surface of the anode material. In addition, as a kind of “zero-strain” material, the lattice parameters and the volume of LTO crystal almost have no change during the process of lithium insertion/extraction [13–15]. In spite of the charming merits, LTO hasn't been utilized widely as the anode material for LIBs yet because of its low rate capability led by the poor electronic conductivity ( $10^{-9} \text{ S cm}^{-1}$ ). The factor tends to cause serious polarization so that the charge/discharge may be retarded when proceeded under a high current density [16–18].

In order to conquer the main obstacles and improve the power performance of the LTO anode, many approaches have been put forward [19–21]. One choice is to create suitable micro-nanostructure [22,23]. Sun et al. designed mesoporous LTO nanocluster material whose capacity could reach 132  $\text{mA h g}^{-1}$  at 5C, and its retention was about 86.3% after 100 cycles. Besides, doping with metal ions or metallic oxides is also an effective method to modify the LTO material [24,25]. Zhang et al. [26] reported a kind of

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Gd-doped LTO composite, which could deliver a discharge capacity of  $110.8 \text{ mA h g}^{-1}$  at 20C after 100 cycles. Another commonly-used method is to introduce conductive agents to LTO, especially conducting carbonaceous materials. Graphene is such a choice due to its good electronic conductivity and large specific surface area. Ni et al. [16] adopted reduced graphene oxide as incorporating conductive agent for LTO. The capacities of the electrode could reach  $154 \text{ mA h g}^{-1}$  at 10C and  $149 \text{ mA h g}^{-1}$  at 20C. Nevertheless, the preparation of graphene is generally complex and high cost in energy and time consuming [27], it hasn't been large-scale used as carbon source to modify LTO but limited in the laboratory [28–30].

In this work, sucrose was incorporated into LTO as carbon source not only because of its rich yield, low price, but also due to the wide application in the electrode materials for LIBs [31,32]. More importantly, the LTO/C composite could be in situ synthesized with a facile preparation process taking use of the sucrose as carbon source. Herein, one step liquid synthesis method was adopted to prepare target product under room temperature. In this process, no any additional heating was necessarily requested like hydrothermal process, as well as no any other additives except sucrose. The dispersed sucrose molecule in reaction solution might have effect on the nucleus formation and the growth of precursor products. Carbon coating was in situ attainable around LTO particles via subsequent high temperature calcination, during which the size of the crystals was constrained. As a result, a nanosized hybrid of LTO/C was synthesized in an average size about 13 nm. Its structure and morphology were examined in detail, as well as the impact on the electrochemical performance. The composite electrode exhibited an outstanding lithium storage properties, in particular the ultra-fast charging/discharging rate performance. The work may present a promising scale-up approach for the preparation of LTO/C anode material.

## 2. Experiment

### 2.1. Material preparation

Initially, 12.8 g of tetrabutyl titanate (TBT) was added into 20 ml anhydrous ethanol at room temperature with stirring until it dissolved completely. The solution was marked as A. 12.3 g lithium hydroxide monohydrate ( $\text{LiOH} \cdot \text{H}_2\text{O}$ ) and 1.7 g sucrose were added into 13 ml deionized water to make solution B under stirring for 30 min. Then, solution A was added dropwise to solution B by peristaltic pump (flow rate is about  $300 \mu\text{l} \cdot \text{min}^{-1}$ ) accompanying with vigorous stirring. After the titration the stirring still lasted for 2 h, and then a cream-like mixture was obtained and kept in a vacuum oven at  $100^\circ\text{C}$  for 24 h to get precursor substance. Subsequently, the precursor product was calcined at the temperature of  $800^\circ\text{C}$  for 5 h at a heating rate of  $5^\circ\text{C min}^{-1}$  under argon atmosphere, then cooled down to room temperature naturally. The synthesis procedures for LTO phase were identical to the steps above except the introduction of sucrose to solution B.

### 2.2. Material characterization

The morphologies of the as-prepared LTO/C and LTO particles were characterized by field emitting scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscopy (TEM, Tecnai G12). The crystal structure of the sample was analyzed by X-ray powder diffraction (XRD, Rigaku UltimaIV-185) with  $\text{Cu-K}\alpha$  radiation at scanning rate of  $8^\circ \text{ min}^{-1}$ , and the diffraction patterns were recorded in the angle ( $2\theta$ ) range from  $10^\circ$  to  $90^\circ$ . Raman spectra were measured by a Renishaw inVia Reflex Raman Microscope using laser excitation at 514.5 nm from an argon ion laser source. Thermogravimetric analysis (TGA) was performed on a

thermal analysis instrument (NETZSCH STA449F3) between  $30^\circ\text{C}$  and  $900^\circ\text{C}$  at a heating rate of  $10^\circ\text{C/min}$  in air. BET surface area of the sample was estimated through nitrogen adsorption/desorption on a Gold APP V-sorb 2800P surface analyzer. As for electronic conductivity measurement, the material was pressed into an identical cylinder (with a pressure of 20 Mpa). Then, the resistance of the cylinder was measured based on the applied voltage and the corresponding current. Thus, the electronic conductivity was obtained to make the comparison between the samples.

### 2.3. Electrochemical measurement

CR2025-type coin cells were assembled in an argon-filled glovebox in which both oxygen and water concentrations were less than 1 ppm. In the cell, pure lithium sheet acted as the reference and counter electrode. The working electrode was composed of active material, acetylene black as conducting agent, polyvinylidene fluoride (PVDF) as binder dissolved in N-methyl pyrrolidinone (NMP) and the mass ratio of the three matters was 80:10:10. The mixture was grinded in a carnelian mortar for 30 min to be a slurry substance. Then it was pasted on copper foil homogeneously and dried under vacuum at  $80^\circ\text{C}$  for 12 h, finally the electrode sheet was punched to disks in a diameter of 11 mm. The mass density of the active material in the electrode sheet was between  $1.4$  and  $1.7 \text{ mg cm}^{-2}$ . The electrolyte used in the cell was of 1 M  $\text{LiPF}_6$  in a mixing solvent of dimethyl carbonate (DMC), ethylene carbonate (EC) and ethyl methyl carbonate (EMC) by the volume ratio of 1:1:1. The galvanostatic charge–discharge measurement was conducted on Land battery test system (LAND CT2001A) and Arbin battery cyler (BT2000) under different current densities with the voltage range from 1 to 3 V at room temperature. Cyclic voltammogram was performed between 1 V and 3 V on CHI608C electrochemical workstation at various scan rates, the electrochemical impedance spectroscopy (EIS) was also recorded using the same electrochemical workstation in the frequency range of  $0.01$ – $10^5 \text{ Hz}$  with perturbation signal amplitude of 5 mV. The potential/voltage mentioned in this study referred to  $\text{Li/Li}^+$  redox couple.

## 3. Results and discussion

### 3.1. Material characterization

Scheme 1 shows the synthetic process of LTO/C composite. The TBT hydrolyzes and the corresponding resultants react with lithium ions to form precursor products during the process. The homogeneously dispersed sucrose in the solution may facilitate the nucleation and limit the dimensional growth of the precursor. It would be transformed into spinel structure LTO through subsequent high temperature calcination. Meanwhile, carbon coating may be formed via the pyrolysis of the sucrose surrounding the precursor.

Fig. 1a exhibits the XRD patterns of the as-prepared LTO/C and LTO materials. As shown in the figure, all diffraction peaks of both samples correspond well with the standard pattern of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (JCPDS card No. 49-0207), which proves the formation of LTO phase with high purity. But, no significant carbon peak could be detectable in the pattern. Herein, Raman spectrum of LTO/C has been collected to analyze the carbon species from sucrose decomposition, as shown in Fig. 1b. Two peaks evidently locating at  $1350$  and  $1595 \text{ cm}^{-1}$  can be assigned to D-band and G-band, respectively, which are the extremely distinct symbols for carbon materials. As well known that G-band corresponds to the  $\text{E}_{2g}$  mode (stretching vibrations) in the basal of the crystalline graphite, while D-band relates to structural disorder and the degree of anti-graphitization

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