



Improving the lithium storage properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes by facile two-phase formation and nanostructure engineering strategy



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ABSTRACT

The main issues spinel lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) anodes suffered from are poor electrical conductivity and low theoretical capacity, which impede the practical application of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes in power lithium-ion batteries. Herein, the improvement in rate capability and specific capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes has been achieved by facile two-phase formation and nanostructure engineering strategy. When evaluated as anode material for lithium-ion batteries, the as-prepared TiO_2 *in-situ* decorated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanobelts exhibit impressive performance, delivering a high reversible specific capacity of 185.1 and 161.2 mAh g^{-1} at 20 and 200 mA g^{-1} after 250 and 2000 cycles, respectively. More importantly, a capacity of 135.6 mAh g^{-1} could be retained at a high rate of 2000 mA g^{-1} even after 5000 cycles, showing excellent rate property and cycle life. Thus excellent performance may make them a promising anode material for advanced lithium-ion batteries.

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1. Introduction

Search and development of new anode materials is one of the current research hotspots in lithium-ion batteries (LIBs) due to the predominantly used graphite cannot meet the urgent need of next generation LIBs for high power density and safety [1–5]. With the intrinsic characteristics of zero strain and safe operation potential, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (denoted as LTO) has attracted extensive research interest as a promisingly alternative anode material for high power LIBs [6–14]. However, its practical application is yet impeded by poor electrical conductivity and low theoretical capacity of 175 mAh g^{-1} [15–21]. To promote the development of LTO, great efforts have been devoted to design and explore effective strategies to improve the electrical conductivity and lithium storage of LTO anodes.

It has been demonstrated that LTO anodes with high performance can be achieved by fabrication of proper nanostructures, because the elaborate low-dimensional nanostructure active materials have larger contact area with electrolyte, shorter diffusion distance of lithium-ions and electrons and special excess near-

surface lithium storage when compared with bulk LTO anodes [22–25]. Thus, design and preparation of nanoscale LTO materials with novel nanostructures had been regarded as an effective strategy for improving electrochemical performance of LTO anodes and, at the same time, became a hot research topic in LIBs anode field. For example, lots of low-dimensional nanostructure LTO materials have been reported, such as LTO nanowires [26], LTO nanotubes [27], LTO nanosheets [28], and so on. As a result, all of them exhibited higher lithium storage and better rate than pristine bulk LTO materials. Currently, it was found that engineering nanoscale grain boundaries by introduction of trace second phase TiO_2 into desirable nanostructure LTO to form dual-phase LTO- TiO_2 nanostructures could further enhance the electronic transport properties and lithium storage of electrodes due to the two aspects: one hand, the LTO- TiO_2 nanostructures could reserve the characteristics of nanostructure LTO, namely large contact surface area with electrolyte, shorten diffusion path of ions and electrons and excess near-surface lithium storage; on the other hand, the generated grain boundaries between two phases would act as channels to transport electrons in the active materials, as well as provide more sites for lithium storage [29–32]. This was demonstrated in a number of studies that the electrochemical performance of LTO electrodes with dual-phase LTO- TiO_2 nanostructures, in term of capacities and rate capabilities in particular, was significantly

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improved compared with the pure LTO electrodes, such as mesoporous spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2$ [33], hierarchical carambola-like $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2$ composites [34], high grain boundary density $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{anatase-TiO}_2$ nanocomposites [35], Ag quantum dots promoted $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2$ nanosheets [36], porous $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2$ nanosheet arrays [37], copper-doped dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2$ nanosheets [38], and petal-like $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2$ nanosheets [30]. Thus, fabrication of two-phase LTO- TiO_2 nanostructures with abundant grain boundaries is a wise strategy for effectively overcoming the issues LTO materials suffered from. However, facile preparation of LTO-based materials with proper dual-phase nanostructures is still a challenge.

Herein, we present a facile approach for preparing TiO_2 *in-situ* decorated LTO nanobelts (denoted as T-LTO NBs) by ionic exchange and followed by calcination in air. The as-prepared T-LTO NBs would have two main merits when used as anode material for LIBs: (1) The nanobelt structures have shortened diffusion distance of lithium-ions and electrons, increased contact interface with electrolyte and abundant surface lithium storage sites (pseudocapacitance or excess near-surface lithium storage); (2) the abundant grain boundaries between TiO_2 and LTO would act as channels to transport electrons in the active materials to enhance electronic transport properties and lithium storage of electrodes. In consequence, the as-prepared T-LTO NBs exhibits impressive performance, delivering a high reversible specific capacity of 185.1 and 161.2 mAh g^{-1} at 20 and 200 mA g^{-1} after 250 and 2000 cycles, respectively. More importantly, a capacity of 135.6 mAh g^{-1} could be retained at a high rate of 2000 mA g^{-1} even after 5000 cycles, showing excellent rate property and cycle life. Thus excellent performance may make T-LTO NBs a promising anode material for advanced LIBs.

2. Experimental section

2.1. Preparation of T-LTO NBs sample

First, the nanobelt precursor was prepared by hydrothermal reaction and subsequent proton exchange. Typically, a 3 mL of tetrabutyl titanate (TBT) was slowly dropped into 60 mL of 10 M NaOH aqueous solution. After continuously stirred for 30 min, the as-prepared white suspension was transferred into a Teflon-lined stainless steel autoclave, and then placed in an oven at 180 °C for 24 h. After cooled down to room temperature naturally, the white product was collected by centrifugation, washed with deionized water and ethanol thoroughly, followed by dispersed in 50 mL of 0.1 M HCl and stirred for 24 h to exchange Na^+ by H^+ completely. Then, the precursor obtained after ion exchange was collected by centrifugation, washed with deionized water and ethanol thoroughly, and dried in an oven at 60 °C under vacuum overnight. Finally, the T-LTO NBs was prepared by second ionic exchange

during hydrothermal process and subsequent washed with one time of anhydrous ethanol and two times of deionized water orderly, and finally calcination at air: 0.5 g of as-prepared nanobelt precursor was dispersed in 50 mL of 0.63 M LiOH by ultrasound for 0.5 h. The suspension was transferred into a Teflon-lined stainless steel autoclave, and then placed in an oven at 100 °C for 24 h. After cooled down to room temperature naturally, the as-prepared white product was collected by centrifugation, washed with one time of anhydrous ethanol and two times of deionized water orderly, and dried in an oven at 60 °C under vacuum overnight. Finally, the T-LTO NBs was obtained via second ionic exchange product calcination at 500 °C for 2 h under a ramping rate of 3 °C min^{-1} in air.

2.2. Materials characterizations

The field emission scanning electron microscopy (FE-SEM, JEOL JSM-7401F) and transmission electron microscopy (TEM, JEOL JEM-2010) coupled with a selected area electron diffraction measurement (SAED) were applied to observe the microstructures of as-prepared T-LTO NBs. The X-ray diffraction measurement (XRD, Rigaku, D/max-Rb using Cu K radiation) and X-ray photoelectron spectroscopy (XPS, carried out on an AXIS ULTRA DLD instrument with using aluminum K X-ray radiation) were used to measure the crystal structure and surface chemical states of T-LTO NBs samples. The nitrogen (N_2) adsorption/desorption isotherms (Micromeritics ASAP 2010 instrument) were adopted to study the specific surface area of T-LTO NBs.

2.3. Electrochemical characterization

The 2016-type coin cells, assembled in an argon-filled glove box (German, M. Braun Co., $[\text{O}_2] < 1 \text{ ppm}$, $[\text{H}_2\text{O}] < 1 \text{ ppm}$), were used to evaluate the electrochemical performances of as-prepared T-LTO NBs samples. The working electrodes were prepared via fully mixing active material (T-LTO NBs), conductive material (acetylene black, AB), and binder (sodium carboxymethyl cellulose, CMC) in a weight ratio of active material/AB/CMC = 70/20/10 in right amount of deionized water, and then pasting the mixture on Cu foil to dry in a vacuum oven at 110 °C overnight. The counter electrode and separator respectively used pure lithium disc and Cellgard 2400 membrane. The electrolyte used in this work is composed of a solution of LiPF_6 (1 M) in dimethyl carbonate (DMC) and ethylene carbonate (EC) (1:1 by volume). The CT2001a cell test instrument (LAND Electronic Co.) was used to test the galvanostatic discharge/charge cycling performance of cells with a voltage range of 1.0–3.0 V at room temperature. The CHI660D electrochemical workstation was applied to record Cyclic Voltammograms (CVs) of cells at a certain scan rate between 1.0 and 3.0 V.

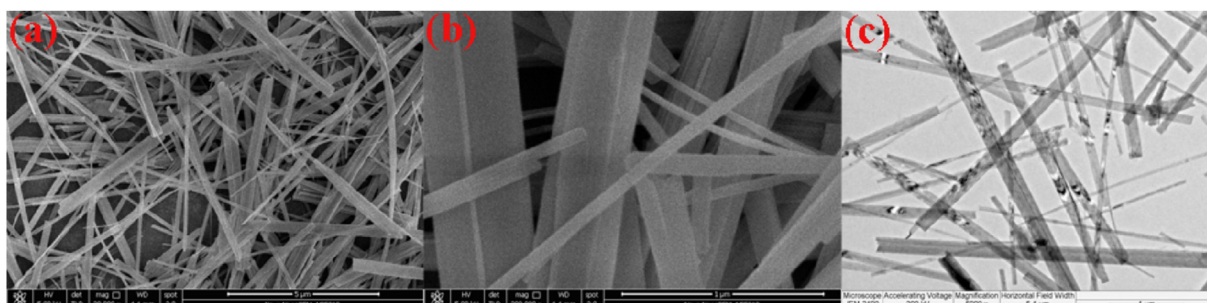


Fig. 1. (a, b) SEM and (c) TEM images of the as-prepared precursor.

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