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Solid-state synthesis of $Li_4Ti_5O_{12}$ whiskers from TiO_2-B

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ABSTRACT

In this work, $Li_4Ti_5O_{12}$ (LTO) was synthesized from the precursors of TiO_2-B and anatase whiskers, respectively. The synthesized LTO whiskers from TiO_2-B whiskers via a solid state reaction at 650 °C have a high degree of crystallinity with an average diameter of 300 nm. However, when anatase whiskers were used as the precursor, only particle morphology LTO was produced at 750 °C. The further analysis of the precursors, the intermediate products and the final products reveal that the crystal structure of the anatase hinders the diffusion of lithium, leading to a typical reaction–diffusion process. Under this condition, only particle morphology LTO can be produced. However, the crystal structure of the TiO_2-B is easy for lithium diffusion and the process is performed in two separated steps (i.e., diffusion and reaction), which makes it possible to decrease the solid-state reaction temperature down to 650 °C and then maintain the morphologies of whiskers.

1. Introduction

The solid-state reaction is the most widely used method for the preparation of crystalline solids from a mixture of solid materials. However, the traditional solid-state synthesis is generally diffusion-controlled and high-temperature is required for calcinations, which often results in inhomogeneous and impure products, such as non-uniform, irregular morphology and large-size particles.

$Li_4Ti_5O_{12}$ (LTO) spinel has been proven as one of the most promising electrode materials for high power density of lithium-ion batteries because it has extremely small volume expansion during lithium insertion and extraction processes [1–20]. Many methods have been used to prepare LTO, such as solid-state synthesis [2–8], sol–gel [9–11], spray drying [12–16], flux method [17,18] and hydrothermal [19,20]. Among them, the solid-state synthesis of LTO is conventionally prepared from TiO_2 and Li_2CO_3 (or LiOH) with sintering temperatures of 800–1000 °C for 12–24 h [2–8], but the synthesized products are generally large particles (from submicron to micron) with impurities. Recently, one-dimensional LTO was synthesized with an ingenious carbon pre-coating process by Cheng [21]. Li developed successfully a brand-new carbon pre-coating method to prepare nanostructured LTO spinel materials with nanorod morphologies [22]. The synthesized LTO rods with the carbon pre-coating method showed high rate-capability and stability for lithium-ion intercalation [21,22]. However, previous work showed that only the carbon-coated nanostructured LTO maintained the initial rod morphology during the solid-state reaction process. To the best of our knowledge, how to synthesize the LTO spinel with uniform whisker morphology has not yet been reported, especially at low temperatures (below 700 °C).

TiO_2 is the precursor for the solid-state synthesis of LTO. TiO_2 has mainly four polymorphs in nature: anatase, rutile, brookite, and TiO_2-B. Electrochemical studies have shown that both anatase and TiO_2-B are promising to be used as electrode materials in solid-state lithium intercalation [23–25], which means that the lithium can be easily diffused in the crystal structures of anatase and TiO_2-B. In our previous work [26,27], the anatase and TiO_2-B crystalline whiskers have been synthesized from the layered $K_2Ti_2O_5$ whiskers via ion-exchange and air calcination methods. Meanwhile, $K_2Ti_2O_5$ fibers were prepared from amorphous titania and K_2CO_3 at low temperatures by solid-state reaction method, and the morphologies and microstructures of $K_2Ti_2O_5$ fibers were controlled successfully by separating the process into reaction and crystallization steps [28]. It is expected that the similar ideas can be used to synthesize LTO with target morphology.

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Therefore, this work aimed to synthesize LTO with uniform whisker morphology and single crystal structure via a solid-state reaction, in which anatase and TiO_2-B whiskers were used as Ti-precursor materials, respectively. The micro-structural and phase transformation of the products during the synthesis process as well as the precursors were characterized, and the mechanism of forming LTO whiskers was discussed.

2. Experiments

2.1. Material synthesis

2.1.1. Preparation of TiO_2-B

$K_2Ti_2O_5$ was prepared by sintering the mixture of K_2CO_3 (reagent grade) and $TiO_2{\cdot}nH_2O$ with a proper TiO_2/K_2O molar ratio [29]. After that 2 g $K_2Ti_2O_5$ and 20 mL deionized water were sealed in a Teflon-lined autoclave and placed in an oven at the temperature of 180 °C to conduct hydration treatment for 12 h. The intermediate product was sampled and used to perform the ion-exchange in 0.1 mol/L HCl solutions with vigorously stirred until K ion was completely exchanged. The sample after the ion-exchange was filtered and washed with distilled water and then dried in an oven at 80 °C. Calcinations of the dried samples were performed in a muffle oven at 500 °C in air for 2 h, and the products were denoted as TiO_2-B.

2.1.2. Preparation of anatase TiO_2

$K_2Ti_2O_5$ was hydrated by adding water into the powders and then ion-exchange was carried out with HCl aqueous solution (0.5 mol/L) to form hydrated titanate ($H_2Ti_2O_5$). The product was filtered and washed with distilled water and dried in an oven at 60 °C under vacuum. The residual K^+ in the final product that should be less than 0.2 wt% was detected by inductively coupled plasma-mass spectrometry (ICP-MS). The $H_2Ti_2O_5$ was calcined in a muffle oven at 500 °C for 2 h to obtain anatase TiO_2.

2.1.3. Synthesis of LTO

The molar ratio of TiO_2 to $CH_3COOLi{\cdot}2H_2O$ was fixed at 1:1.05. A certain amount of $CH_3COOLi{\cdot}2H_2O$ was dissolved in distilled water where the mass ratio of solid to liquid was set to be 1:3. Anatase TiO_2 whiskers were added into $CH_3COOLi{\cdot}2H_2O$ solutions with a magnetic stirring for 30 min. After the ultrasonic dispersion for 10 min, the mixed slurry was dried at 80 °C for 12 h. The prepared mixture was labelled as MA. The mixture of MB was prepared by using TiO_2-B whiskers as the Ti-source with the same process as MA. Calcinations of MA or MB were performed in a muffle furnace at a heating rate of 5 °C/min. The heating temperatures were chosen based on the results from the thermogravimetric analysis as described in the following section. The heating time was last up to 5 h. The heated samples were quenched by quickly removing them from the furnace and immediately cooling them down to the room temperature.

2.2. Characterizations

The crystalline structure of the synthesized LTO was characterized by X-ray diffraction (XRD) using a Rigaku D/Max 2500 powder diffractometer with Cu Kα radiation (λ = 1.5406 Å). The textural properties were studied by N_2 adsorption–desorption measurements (ASAP 2020 M) at a liquid nitrogen temperature of 77 K (−196 °C). The specific surface area and the pore volume were measured using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH), respectively. The phase transition temperatures were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) (NETZSCH STA 449C, Germany), and the determinations were carried out on the dried powders with a flowing nitrogen of 30 mL/min and a heating rate of 10 °C/min at a temperature ranging from 40 to 900 °C. The morphology of the sample was observed by field emission scanning electron microscopy (FESEM; Hitachi-S4800, Japan). The transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) analysis were conducted with a JEM-2100F field emission transmission electron microscope operated at 200 kV.

3. Results and discussion

3.1. Characterization of TiO_2-B and anatase TiO_2

The XRD patterns of the prepared TiO_2-B and anatase TiO_2 are shown in Fig. 1(a). The XRD results reveal that these two samples have monoclinic TiO_2-B phase (JCPDS no. 46-1237) and tetragonal anatase phase (JCPDS no. 21-1272), respectively.

N_2 adsorption–desorption isothermal measurements were carried out for determining the BET surface area and pore sizes. Fig. 1(b) shows the isotherm curves for the prepared TiO_2-B and anatase TiO_2, and all these curves present as typical type IV isotherms representing mesoporous structure. The textural

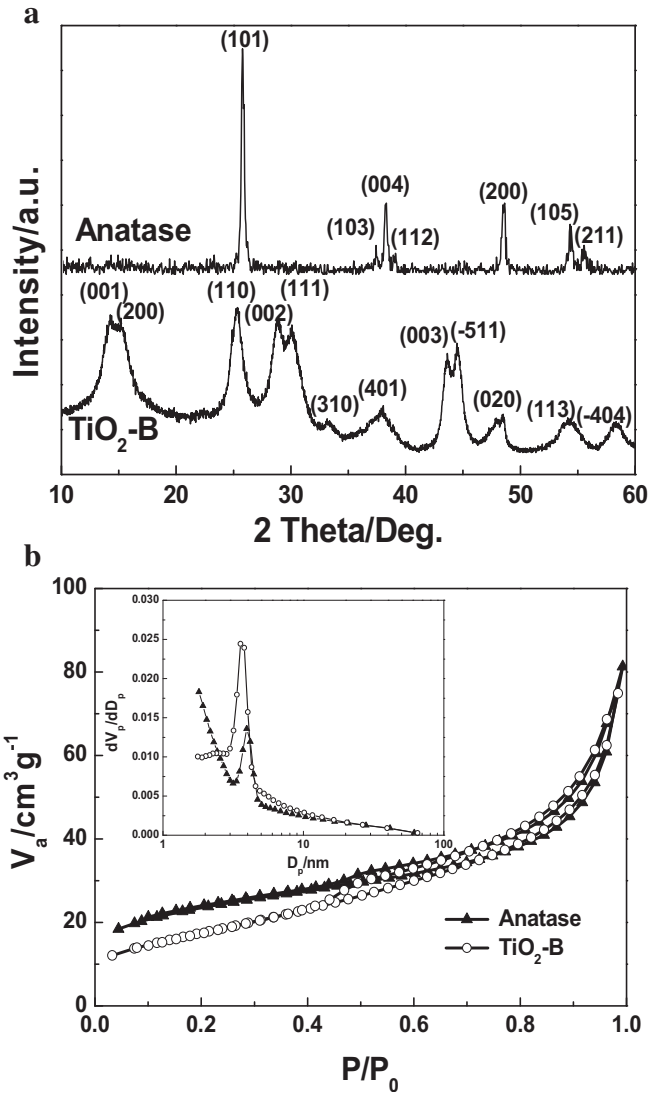

Fig. 1. (a) XRD patterns and (b) N_2 adsorption-desorption isotherms (the inset pore size distribution curves) of Anatase and TiO_2-B.