



Self-assembled synthesis of nanoflower-like $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for ultrahigh rate lithium-ion batteries

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HIGHLIGHTS

- ▶ The morphology reveals nanoflower-like shape with nanoplates crosslink.
- ▶ The thickness of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoplates was around 10 nm
- ▶ Nanoplates shorten lithium transportation path and facilitate rate capability.
- ▶ Nanoflower-like spinel lithium titanate shows an outstanding cycling behavior.

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ABSTRACT

Nanoflower-like spinel lithium titanate is synthesized through combining sol/gel and hydrothermal process. The role of hydrothermally treating amorphous TiO_2 beads under the additive of LiOH precursor can derive nanocrystalline spinel lithium titanate with nanoflower-like shape. Afterward, calcination helps the formation of nanoflower-like spinel lithium titanate. The crystalline structure and morphological observation of the as-synthesized nanoflower-like $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The nanoflower-like structure can be revealed through the N_2 adsorption/desorption isotherm. It is demonstrated that the electrochemical performance is significantly improved by the architecture control. The nanoflower-like spinel lithium titanate shows outstanding cycling behavior of 148, 143, 141, 138, 133, 126, 118 mA h g^{-1} at 0.5, 1, 3, 5, 10, 20, 30 °C, respectively. The reversible capacity at 30 °C even remains over 80% of that at 0.5 °C. The superior C-rate performance is associated with the nanoflower-like structure, facilitating lithium transportation ability during cycling. It is believed that the novel self-assembled synthesis for nanoflower-like lithium titanate can exhibit an excellent cycling performance and can be a good candidate for the next-generation anode material of ultrahigh rate Li-ion batteries for the application of electric vehicles.

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1. Introduction

As energy storage devices, lithium-ion batteries are the dominant power source for portable consumer electronics, such as mobile phones and notebook computers. Besides, to meet the environmental concern for global issue, lithium-ion batteries have been used for electric vehicle and hybrid electric vehicle to save oil and to decrease exhaust emissions. The increasing demands for high-energy density and high-power density of batteries have attracted investigators to develop new materials for lithium-ion batteries. In present commercial lithium-ion batteries, graphite is

a widely used as anode material [1]. However, graphite cannot satisfactorily meet the safety and rate performance requirements for future applications in EV and HEV. The theoretical capacity of graphite is only 372 mA h g^{-1} . Consequently, Sn-based materials have attracted particular interest as negative electrodes, due to their higher theoretical lithium storage capacities, higher lithium packing density and proper operating voltage [2]. Nevertheless, the most critical problem is the severe volume changes during lithium alloy and dealloy, causing electrode disintegration, reducing battery life, and finally limiting the possibility of commercialization [3,4].

Recently, spinel lithium titanate, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, has attracted great interest as anode material for rechargeable lithium-ion batteries, due to its unique characteristics, including the zero-strain feature and the flat Li insertion voltage at about 1.55 V versus Li [5–7]. It is revealed that spinel host has an excellent structural stability and

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a very small volume change during cycling. The space group of the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is $Fd3m$. One part of lithium ions is located at (8a) sites, the other part of lithium ions and all titanium ions at (16d) sites, and oxygen ions at (32e) sites [8]. During cycling, 3 mol of lithium ions in tetrahedral sites (8a) are capable of inserting into the octahedral sites (16c) of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ lattices, forming $\text{Li}_7\text{Ti}_5\text{O}_{12}$ rocksalt structure [7,9]. It accommodates Li-ions to have a theoretical capacity of 175 mA h g^{-1} with excellent cyclability and displays a discharge platform around 1.55 V vs. Li/Li^+ , suppressing the reduction of electrolyte, thus reducing the impedance of cell and making batteries more safe. Nevertheless, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a poor electrical conductor with a conductivity of only $10^{-13} \text{ S cm}^{-1}$ at room temperature [10]. Currently, new strategy is to design porous spinel lithium titanate anode materials [11–17]. Accordingly, porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode materials give an ideal approach for the efficient transport of lithium ions at high cycling rates [11–17]. Thus, porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is indeed a potential candidate material for high-rate lithium-ion batteries. Recently, mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been synthesized via acidized carbon black as templates under hydrothermal condition [13]. It was demonstrated that the cycling stability could be significantly enhanced by mesoporous incorporation, especially at high cycling rate. Consequently, to further reduce the cost for fabrication without templates additive, the present work aims to develop a novel self-assembled synthesis for nanoflower-like spinel lithium titanate anode materials.

In general, spinel lithium titanate could be synthesized through solid-state reaction between lithium salts and titanium sources under high calcination temperature [18–20]. Various shapes of TiO_2 as titanium sources could be also reacted with lithium salts to obtain spinel lithium titanate. However, the final $\text{Li}_4\text{Ti}_5\text{O}_{12}$ hardly retained the original structure of TiO_2 precursors, owing to the high sintering temperature requirement for the formation of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, causing the grain coarsening and agglomeration of powders. One approach is to decrease the annealing temperature and time to alleviate the possibility of grain growth, possibly worsening the crystallinity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, even affecting the battery performance [20]. Hereafter, this study aims to develop newly self-assembled synthesis of spinel lithium titanate with crosslink of nanoplates, so-called nanoflower-like structure. This research tends to employ LiOH as starting material to obtain layered hydrous lithium titanate precursor under hydrothermal process without the formation of TiO_2 , greatly reducing the calcination temperature without sacrificing the crystallinity [21]. According to the phase diagram between Li_2O and TiO_2 , once TiO_2 is formed, it is necessary to obtain spinel lithium titanate by reacting with lithium salts at high temperature for a long time [22]. Consequently, nanoflower-like structure of spinel lithium titanate under the assistance of LiOH precursor could be successfully derived. It is predicted that the thickness of nanoplates in nanoflower-like structure is short enough to enable lithium ions to be penetrated even under ultra-high cycling rates, inspiring the novel anode materials for high-rate and high-power Li-ion batteries.

2. Experimental section

2.1. Material preparation

The chemicals used in the study were titanium(IV) isopropoxide (TTIP, 97%, Sigma–Aldrich), hexadecylamine (HDA, 90%, Sigma–Aldrich), absolute ethanol (99.5% Merck), lithium hydroxide (LiOH, Sigma–Aldrich). A general synthesis of amorphous TiO_2 submicron spheres was as follows. 1.58 g HDA was dissolved in 500 mL absolute ethanol. After dissolution, 20 mL TTIP was added under vigorous stirring at room temperature. The resulting white TiO_2 precipitation was aged at room temperature for 24 h, then TiO_2

beads were collected by centrifugation and washed with ethanol for at least three times, finally drying in air at room temperature.

In a typical synthesis of nanoflower-like $\text{Li}_4\text{Ti}_5\text{O}_{12}$, a stoichiometric amount of LiOH and as-synthesized TiO_2 submicron spheres ($\text{Li/Ti} = 4:5$) were mixed in 180 mL of ethanol solvent and stirred at room temperature, transferring to a Teflon-lined stainless steel autoclave (225 mL in volume) and then reacting in an air-flow electric oven at 180 °C for 6 h. After cooling down naturally, the precipitate was harvested by centrifugation and washed thoroughly with ethanol for at least three times. The products were further dried at 50 °C for 1 day. Eventually, the powder was calcined at 600 °C for 3 h to obtain nanoflower-like $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

2.2. Materials characterization

The phase of as-synthesized powder was identified with an X-ray diffractometer (XRD, LabX XRD-6000, Shimadzu, Japan) operated at 30 kV and 20 mA using $\text{Cu K}\alpha$ with a wavelength of 1.5406 Å. Morphological observation was carried out via field-emission scanning electron microscope (SEM; JSM-7600F, JEOL, Japan). The BET specific surface area was obtained from the N_2 adsorption/desorption isotherms at 77 K (Autosorb-1, Quantachrome).

2.3. Electrochemical measurement

Electrochemical tests were performed by using two-electrode of 2032 type coin cells (20 mm in diameter and 3.2 mm thick). The cells contained anode electrode, metallic lithium, polypropylene separator, and electrolyte of 1.0 M LiPF_6 in EC/DMC (1:1, vol.%), and were assembled in an argon glove box where both moisture and oxygen content were less than 1 ppm. The cells were cycled between 1 V and 2.5 V versus Li/Li^+ . The C-rate capability test was performed at the charge/discharge rate of 0.5, 1, 3, 5, 10, 20, and 30 C. The electrochemical impedance spectroscopy (EIS) measurements were carried out with a potentiostat (PAR model 263A, EG&G). The sinusoidal excitation voltage applied to the cells was 10 mV rms with a frequency range of between 100 kHz and 10 mHz.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) pattern of powders after hydrothermal process and calcination. The structure of the products after hydrothermal process is close to layered hydrous lithium titanate with a C-based centered orthorhombic structure (JCPDS Card No. 47-0123). It was worth noting that the peak at $\sim 10.5^\circ$ indicated the layered structure. After calcination, all the diffraction peaks can be indexed on the basis of a cubic spinel lithium titanate, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (JCPDS Card No. 26-1198). That is to say, the layered hydrous lithium titanate was completely converted to spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ without the presence of impurity. It was revealed that high purity $\text{Li}_4\text{Ti}_5\text{O}_{12}$ could be prepared by calcinating layered hydrous lithium titanate precursors under relatively low temperature, say, 600 °C. Furthermore, no impurity could be detected through X-ray diffraction pattern of spinel lithium titanate. It was demonstrated that the self-assembled synthesis of spinel lithium titanate did not cause the impurity.

The SEM images of amorphous TiO_2 submicron spheres, layered hydrous lithium titanate after hydrothermal process, and spinel lithium titanate after calcination are revealed in Fig. 2. The SEM image of amorphous TiO_2 precursors is shown in Fig. 2a. The diameter of monodispersed TiO_2 precursors was around 400 nm with smooth surface. With the addition of HDA as a structure-directing agent, the solvation force between nanoclusters strengthened the formation of amorphous TiO_2 spheres. Besides, the agglomeration of TiO_2 beads could be avoided by the HDA

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