

Preparation and characterization of high-density spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material for lithium secondary batteries

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Abstract

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a very promising anode material for lithium secondary batteries. A novel technique has been developed to prepare $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The spherical precursor is prepared via an “inner gel” method by TiCl_4 as the raw material. Spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders are synthesized by sintering the mixture of spherical precursor and Li_2CO_3 . The investigation of XRD, SEM and the determination of the electrochemical properties show that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders prepared by this method are spherical, and have high tap-density and excellent electrochemical performance. It is tested that the tap-density of the product is as high as 1.64 g cm^{-3} , which is remarkably higher than the non spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Between 1.0 and 3.0 V versus Li, a reversible capacity is as high as 161 mAh g^{-1} at a current density of 0.08 mA cm^{-2} . © 2005 Elsevier B.V. All rights reserved.

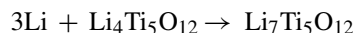
Keywords: Lithium secondary batteries; $\text{Li}_4\text{Ti}_5\text{O}_{12}$; High-density; Spherical

1. Introduction

Lithium-ion batteries, as one kind of the new-generation rechargeable batteries of excellent performance, are developed in the end of last century. The anode materials play an important role in the lithium-ion batteries. The spinel lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a so-called zero-strain insertion material as the negative-electrode material of lithium secondary batteries [1]. The structure does not vary with cycling. It shows a voltage flat of 1.56 V against a lithium electrode [2]. This material accommodates Li with a theoretical capacity of 175 mAh g^{-1} , and the actual discharge capacity is greater than 160 mAh g^{-1} [3]. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ does not react with electrolyte. It is cheap at price and easy to prepare. Compared with carbonaceous materials used as anode active materials in commercial lithium ion batteries, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has better electrochemical properties and higher safety. Compared with alloy-based anode, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is cheaper and easier to be synthesized. Therefore, this ma-

terial is regarded as one of the most promising anode materials.

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ does not offer Li^+ source. In principle, therefore, this material can be coupled with 4 V electrode as LiMn_2O_4 , LiNiO_2 or LiCoO_2 to provide a cell with an operating voltage of approximately 2.5 V, which is twice that of nickel–cadmium or nickel–metal hydride cell. Lithium reacts with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ according to the reaction



because lithium insertion into the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel displaces tetrahedrally coordinated lithium ion into octahedral sites with the formation of a rock-salt-type $\text{Li}_7\text{Ti}_5\text{O}_{12}$ product [4].

Recently, many authors [5–10] reported their study on spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, but there are still two major problems in the research and development of this anode material. One is the low conductivity and bad performance of charging–discharging in heavy current. The other is that the product has low density. Both problems are related to this material’s structure and electrode preparation process. At present, the preparation processes of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material are mostly solid state reaction method and traditional

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sol–gel method. Such processes are not very effective to improve the conductivity and the density. Therefore, a new preparation process is urgently needed.

What we should do is to prepare electrode materials with both high specific capacity and high tap-density. Actually, the tap-density of the powders is nearly related to the powders' particle morphology, particle size and particle size distribution, etc. For example, Ni(OH)₂ has been widely used as cathode material in the Ni–MH rechargeable batteries. The tap-density of the sheet Ni(OH)₂ powders is as low as 1.5–1.6 g cm⁻³. In comparison, the tap-density of the spherical Ni(OH)₂ powders without increasing the crystallinity and lowering the specific capacity is as high as 2.1–2.2 g cm⁻³. The power density of the Ni–MH rechargeable batteries using the spherical Ni(OH)₂ cathode material has been greatly improved. Spherical LiCoO₂, Li_{1+x}V₃O₈, LiNi_{0.8}Co_{0.2}O₂ and Li_{1-x}(Ni_{1-y-z}Co_yM_z)O₂ (M = Al, Mg) prepared by vary methods all have high tap-density and the power density of batteries using these material as electrode [11–14]. According to the fact, we can expect that the electrode materials with both high specific capacity and high tap-density are sure to be prepared by controlling the powders' particle morphology, particle size, and particle size distribution. It is expected that preparing spherical powders may be an effective way. Now, paper concerning preparation of spherical Li₄Ti₅O₁₂ material has not been found.

In this work, the authors develop the “inner gel” process to prepare spherical Li₄Ti₅O₁₂ material. The spherical particles can improve the density of product. The structure, the morphology, and the electrochemical performance of the spherical Li₄Ti₅O₁₂ powders have been investigated in detail.

2. Experimental

The spherical precursor was prepared by an “inner gel” method. Titanium tetrachloride (TiCl₄) was dissolved in deionized water. Then this solution was mixed with a certain quantity of hexamethylene-tetramine ((CH₂)₆N₄) and carbamide (CO(NH₂)₂) by stirring at <10 °C temperature. The mixed solution was dripped into coal oil by stirring, having a volume water/oil ratio of 1:10. After this, the mixed slurry was heated at 70 °C for about ten minutes and the spherical gel precursor deposited. Then the dried spherical gel precursor and Li₂CO₃, in a certain molar ratio of Li:Ti, were mixed uniformly. The spherical Li₄Ti₅O₁₂ powders are synthesized by sintering the mixture at 800 °C for 16 h in an air atmosphere.

Powder X-ray diffraction (XRD, D/max-rB) using Cu Kα radiation was used to identify the crystalline phase and crystal lattice parameters of the powders. The particle morphology, particle size and particle size distribution of the powders were observed using a scanning electron microscopy (SEM, JSM6301F).

Experimental test cells for measurements used the cathode with the composition of 80 wt.% Li₄Ti₅O₁₂, 10 wt.% car-

bon black and 10 wt.% PTFE. The separator was a Celguard 2400 microporous polypropylene membrane. The electrolyte was 1 M LiPF₆ EC + DEC (1:1, v/v). A lithium metal anode was used in this study. The cells were assembled in a glove box filled with argon gas. The discharge–charge cycling was galvanostatically performed at different current density of 0.08–0.32 mA cm⁻² with cut-off voltages of 1.0–3.0 V (versus Li/Li⁺) at 20 °C.

3. Results and discussion

Fig. 1 shows the morphology of the precursor powders and the Li₄Ti₅O₁₂ powders obtained by sintering the mixture of the precursor powders and Li₂CO₃ powders at 800 °C for 16 h in an air atmosphere. Fig. 1(a) shows the particles of the precursor are spherical with the particle size of about 2–10 μm. The surface of every spherical particle is smooth as shown in Fig. 1(b). It is tested that the tap-density of the precursor arrives 1.21 g cm⁻³. In contrast to the precursor, there is obvious difference of particle morphology, particle size, particle size distribution, crystalline phase, and tap-density among the sample obtained after thermal treatment with Li₂CO₃. Fig. 1(c and d) shows the morphology of the Li₄Ti₅O₁₂ powders obtained after thermal treatment. It can be found in Fig. 1(c and d) that the spherical particles are shrank after sintering and the surface of the spheres is not smooth. The particle size of these samples are about 2–6 μm and mostly are around 4 μm. It is tested that the tap-density of this sample is as high as 1.64 g cm⁻³ because of the close structure. The crystalline grains have grown to be much larger on the surface of every particle and each of the spherical particles is made up of a large number of fine nanocrystalline grains, as shown in Fig. 1(d). Kavan and Gratzel [15,16] reported that nanocrystalline Li₄Ti₅O₁₂ prepared via a sol–gel route exhibited excellent activity toward Li insertion and the average particle sizes varied from 1 μm to 9 nm. But the Li-diffusion coefficients decreased by orders of magnitude if the average particle size drops from 1 μm to 9 nm. Especially, the nanoparticle should result in the low tap-density of the product. The spherical particles prepared via an “inner gel” route in this paper make up of large nanocrystalline grains. So, the product shows good electrochemical performance and high tap-density.

The X-ray diffraction patterns of the precursor powders, the experiment sample and the pure Li₄Ti₅O₁₂ powders are shown in Fig. 2. It can be observed that there are few weak diffraction lines on the XRD pattern of the precursor powders, as shown in Fig. 2(a). These lines were not assigned to anyone of already known titanium oxides. Thus, the precursor sample is in an amorphous state. After heated at 800 °C for 16 h with Li₂CO₃, however, there are a lot of obvious diffraction lines on the XRD pattern, and all of them are attributed to Li₄Ti₅O₁₂, and the relative intensities of the experiment sample are almost same as those of the standard pattern of Li₄Ti₅O₁₂, as shown in Fig. 2(b and c).

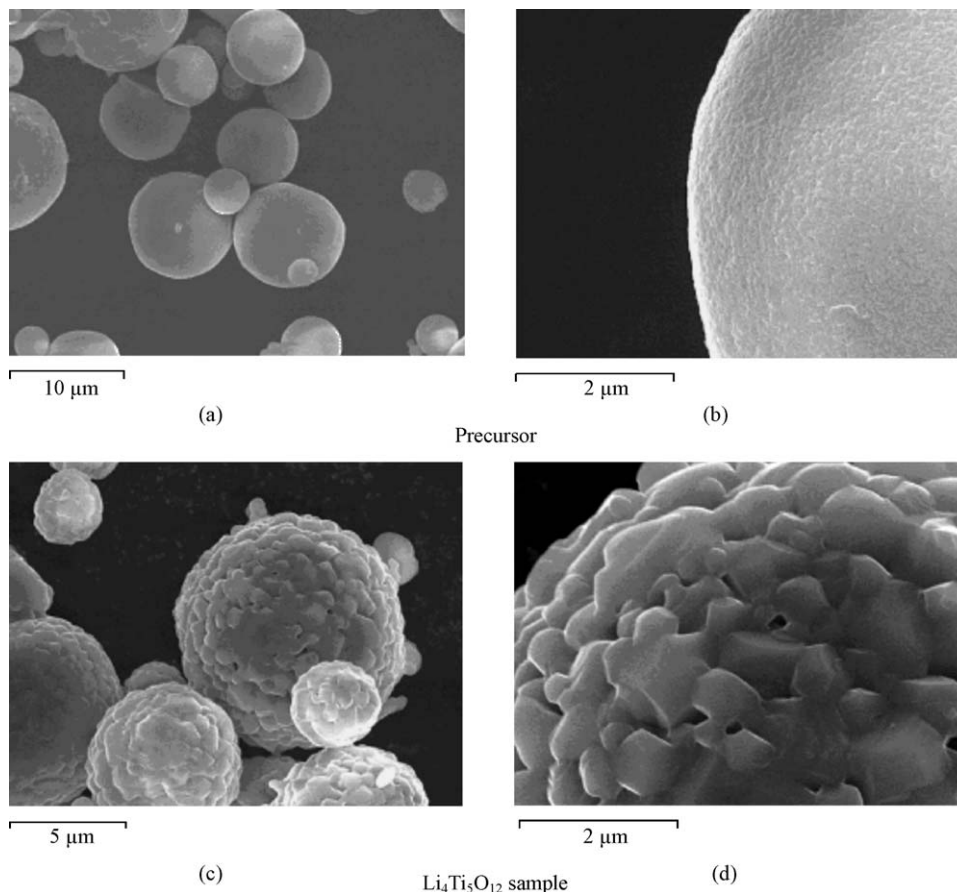


Fig. 1. SEM images of the precursor powders and the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders.

The spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material has high specific capacity and good cycling stability. We tested the model cells using the spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders prepared in this work as the cathode material. Fig. 3 shows the first discharge–charge curves of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different current densities. As shown in Fig. 3(a), the sample has a first cycle

discharge capacity of 161 mAh g^{-1} at a constant current density of 0.08 mA cm^{-2} . However, the sample has a first cycle discharge capacity of 156 mAh g^{-1} at a constant current density of 0.16 mA cm^{-2} and that is only 121.5 mAh g^{-1} at a constant current density of 0.32 mA cm^{-2} , as shown in Fig. 3(b and c). Furthermore, at discharge–charge current

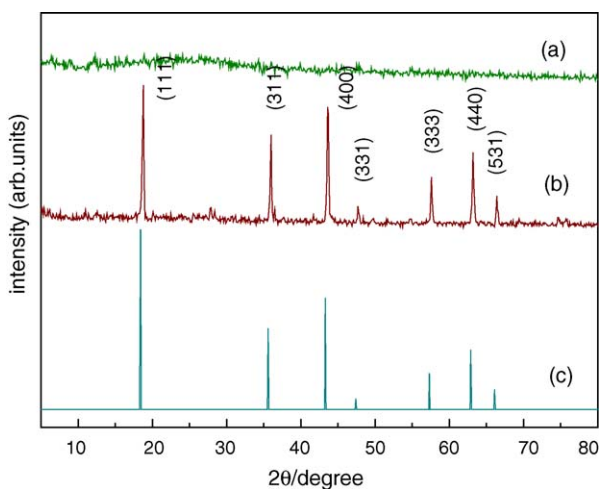


Fig. 2. X-ray diffraction patterns of (a) the precursor; (b) the experiment sample; (c) the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders.

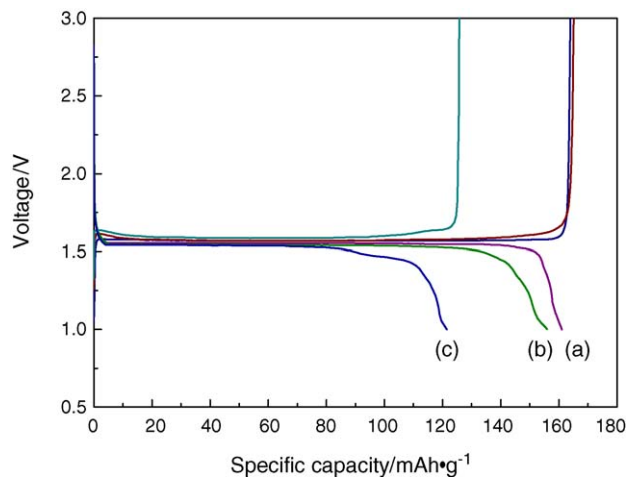


Fig. 3. First discharge–charge curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different current densities: (a) 0.08 mA cm^{-2} ; (b) 0.16 mA cm^{-2} ; (c) 0.32 mA cm^{-2} .

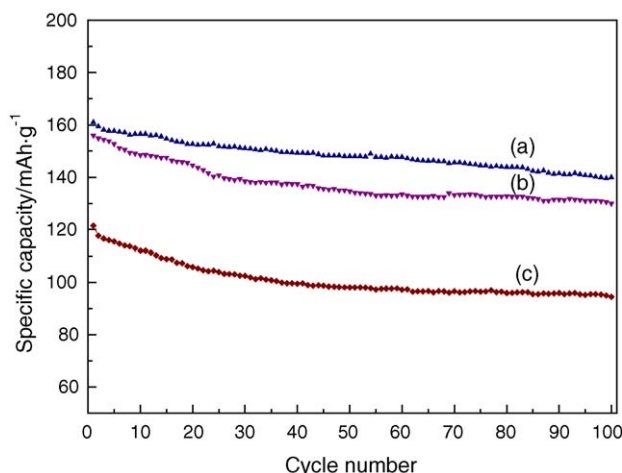


Fig. 4. Specific discharge capacity dependence on cycle number of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different current densities: (a) 0.08 mA cm^{-2} ; (b) 0.16 mA cm^{-2} ; (c) 0.32 mA cm^{-2} .

density of 0.08 mA cm^{-2} , a plateau appears clearly near 1.56 V in the discharge curve and the region of the plateau is so wide, as shown in Fig. 3(a). The plateau looks much narrower in the discharge curve along with the increasing of the current density, as shown in Fig. 3(b and c).

Fig. 4 shows the cycle performance at the discussed three kinds of current density. The initial reversible specific capacity of the sample is 161 mAh g^{-1} at current density of 0.08 mA cm^{-2} , and after 100 cycles it is still 140 mAh g^{-1} . When the current density is 0.16 and 0.32 mA cm^{-2} , the sample still keep the excellent cycle performance. But the initial specific capacity at large current is much low, especially at 0.32 mA cm^{-2} .

The problem of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders' tap-density has been solved satisfactorily in this work. We improve the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders' tap-density by controlling the powders' particle morphology, particle size, and particle size distribution. Now, some measures are being taken to improve the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material's conductivity in our laboratory, such as doping carbon in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles and doping other metal elements to substitute the element of Ti.

4. Conclusion

The spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders with high specific capacity and excellent cycle performance have been synthesized via a novel technique in this work. The sample prepared at 800°C for 16 h results the attainment of both higher discharge capacity (161 mAh g^{-1}) and a better cycle performance. The products possess good morphology, small particle size, good particle size distribution. The excellent electrochemical performance of the spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material is partly attributed to the advanced preparation. This preparation technique should be a suitable method to synthesize spherical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material, and is significant to be further studied.

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