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Hydrothermal synthesis of $Li_4Ti_5O_{12}$ microsphere with high capacity as anode material for lithium ion batteries

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Abstract

Lithium titanate ($Li_4Ti_5O_{12}$) microsphere has been successfully synthesized by a hydrothermal method. X-ray diffraction (XRD) and scanning electron microscope (SEM) are used to characterize the structure and morphology of the prepared $Li_4Ti_5O_{12}$ crystallites. The results show that the as-synthesized powders exhibit outstanding rate capacities and excellent cycling performance. The first discharge capacity at 0.1 C is 172.5 mAh g^{-1}, which is close to the theoretical capacity of 175 mAh/g. After 50 cycles, the efficiency of the synthesized $Li_4Ti_5O_{12}$ still retains up to 92.8% at 0.1 C and 95.2% at 0.5 C of its initial value, which present a promising applications as anode materials for lithium ion batteries in hybrid and plug-in hybrid electric vehicles.

Keywords: B. Surfaces; B. X-ray methods; C. Electrochemical properties; D. $Li_4Ti_5O_{12}$

1. Introduction

Lithium ion batteries that can perform high power operations and have long cycle lives are greatly needed for portable electronics, hybrid and plug-in hybrid electric vehicles. Recently, great effort has been made to promote their application in hybrid electric vehicles and dispersed energy storage systems, which demand light weight, small volume, high energy density and safety [1]. Spinel $Li_4Ti_5O_{12}$, as a promising anode material for lithium ion batteries, demonstrates many advantages compared to the conventional used graphite [2,3]. Graphite, a commonly used anode material, has small lithium diffusion coefficient and experiences large volume variation of 9% [4]. In addition, it has severe safety issues of dendritic lithium growth, due to its low operating voltage (below 0.2 V versus Li^+/Li) [5–7]. Spinel $Li_4Ti_5O_{12}$, however, is called "zero strain" material, because there is negligible change in the unit cell volume during lithium intercalation and deintercalation [8–10]. It also has a long and stable voltage plateau at approximately 1.5 V versus Li^+/Li [11], together with low cost, environmental friendliness and enhanced safety. Therefore, spinel $Li_4Ti_5O_{12}$ has a promising application as an alternative anode material to carbon-based materials.

The preparation of $Li_4Ti_5O_{12}$ by sol–gel and solid-state method need high temperature over 800 °C [12,15] and it is difficult to control the morphology of the product in the process. Compared with the above two methods, hydrothermal synthesis can decrease the activation energy of precursor, so we can obtain the $Li_4Ti_5O_{12}$ at 450–550 °C approximately. Meanwhile, the $Li_4Ti_5O_{12}$ with some special morphology also can be prepared by the hydrothermal method.

In this work, spinel $Li_4Ti_5O_{12}$ microsphere with large surface area was successfully synthesized via a simple hydrothermal method. We focused on the synthesis, structural characterization, and electrochemical properties of $Li_4Ti_5O_{12}$. The results demonstrated that the synthesized $Li_4Ti_5O_{12}$ had a large discharge capacity of 172.5 mAh g^{-1} at the first cycle. Meanwhile, it presented

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a great cycling performance and the 50th retention rate exceeded 92.8%, which could be a proper choice for the lithium ion batteries.

2. Experimental

2.1. Sample preparation

$Li_4Ti_5O_{12}$ was synthesized by a hydrothermal method. The stoichiometric amounts of lithium hydroxide monohydrate ($LiOH \cdot H_2O$) and tetrabutyl titanate ($Ti(OC_4H_9)_4$) were used as starting materials. The molar ratio of Li:Ti was 4:5, and the tetrabutyl titanate was mixed in ethylalcohol with stirring to form solution A, the volume ratio is 1:1. After that, 2 mol/L LiOH aqueous solution was dropwise added into the solution A with strong stirring for 0.5 h to get a white suspension B, and then transferred to stainless-steel autoclave at 180 °C for 24 h. The obtained precursor was calcinated at 500 °C for 10 h to get the final powders. The crystal structure of the powders was characterized by X-ray diffraction (XRD, Rigaku D/max-2000) using Cu-K_α radiation ($5 \le 2\theta \le 70^\circ$). The morphology was observed by scanning electron microscopy (SEM, S4800, Japan).

2.2. Electrode preparation and electrochemical test

Electrochemical measurements were performed using 2016-type coin cells assembled in an argon-filled glove box (German, M. Braun Co., $[O_2] < 1$ppm, $[H_2O] < 1$ppm). To fabricate the electrodes, a mixture of the synthesized $Li_4Ti_5O_{12}$, acetylene black, and polyvinylidene fluoride (PVDF) binder at a weight ratio of 80:10:10 was pasted on pure copper foil. Pure lithium foil was used as the counter electrode. The electrolyte consisted of a solution of 1 M LiPF6 in ethylene carbonate and dimethyl carbonate (EC+DMC, 1:1 in volume). The charge/discharge tests were carried out using a LAND Celltest 2001A (Wuhan, China) system between cutoff voltage of 2.5 and 1.0 V.

3. Results and discussion

3.1. Characterization of materials

Powder X-ray patterns of the samples obtained before and after calcination at 500 °C for 10 h are shown in Fig. 1. Fig. 1a is the pattern of the precursor powders and indicates that the precursor is orthorhombic $Li_{1.81}H_{0.19}Ti_2O_5 \cdot 2H_2O$ (JCPDS No.47-0123). The result shows that the hydrothermal process cannot synthesize the lithium titanate directly, but the precursor can be transformed to spinel $Li_4Ti_5O_{12}$ after heat treatment [13]. Fig. 1b shows that all the precursor can be transformed to lithium titanate(JCPDS No. 49-0207) after calcination at 500 °C without obvious impurity and the lattice parameters have been determined to be $a=8.357$ Å, which is consistent with the reported $a=8.36$ Å. Furthermore, the heat treatment temperature is much lower and the time is much shorter than those obtained at 800 °C for 24 h by sol–gel and solid state method [14,15].

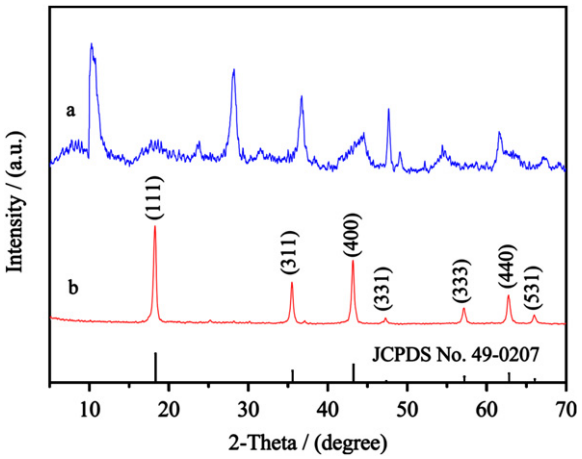

Fig. 1. XRD patterns of the products by hydrothermal process before (a) and after calcination (b).

The SEM images of the precursor and the $Li_4Ti_5O_{12}$ prepared at 500 °C are shown in Fig. 2. The result shows that both the precursor and the $Li_4Ti_5O_{12}$ are assembled by many sheets. It can be seen that the precursor has an anomalous surface, which is just constituted by the sheets disorderly. However, it is obviously found that the $Li_4Ti_5O_{12}$ has a spheroidic morphology with the diameter of 1–5 μm. The thickness of the sheets is about several nanometers. It is well known that the morphology and particle size have an important effect on the electrochemical properties of $Li_4Ti_5O_{12}$. The microsphere can highly increase the specific surface area of the $Li_4Ti_5O_{12}$, which can provide more transport channels and surface storage for lithium to insert into the electrode material. Meanwhile, it also increases the contact between the electrolyte and the prepared products, which can decrease the irreversible capacity loss caused by the concentration polarization when the current density enhanced [13]. And the small nano-sheets may shorten the diffusion distance of lithium ions. Thus, the microsphere assembled by nanosheets will make improvement of electrochemical properties of $Li_4Ti_5O_{12}$ such as specific capacities and cycling performances.

3.2. Electrochemical properties test

The electrochemical properties of $Li_4Ti_5O_{12}$ were studied using $Li_4Ti_5O_{12}$/Li half cells. The initial charge-discharge curves at different rates are shown in Fig. 3. Fig. 3a shows that a high discharge capacity of 172.5 mAh g^{-1} is achieved at a rate of 0.1 C for the first cycle. It is approximately 10–15 mAh g^{-1} higher than those prepared by sol–gel and solid state method at high temperature [14,15]. This may be caused by the microsphere morphology, which can increase the Li surface storage.

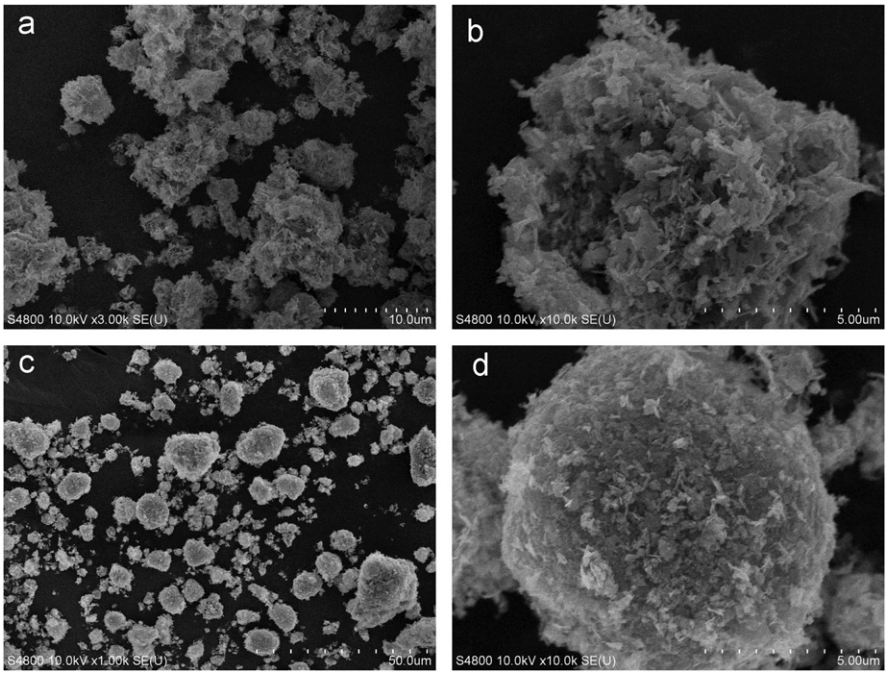

Fig. 2. SEM images of precursor (a: × 3000; b: × 10,000) and $Li_4Ti_5O_{12}$ prepared at 500 °C (c: × 1000; d: × 10,000).

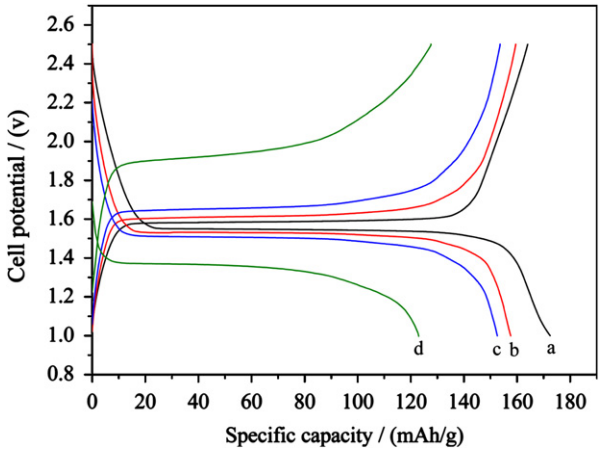

Fig. 3. Charge/discharge curves of the $Li_4Ti_5O_{12}$. (a) 0.1 C, (b) 0.5 C, (c) 1.0 C, (d) 5 C.

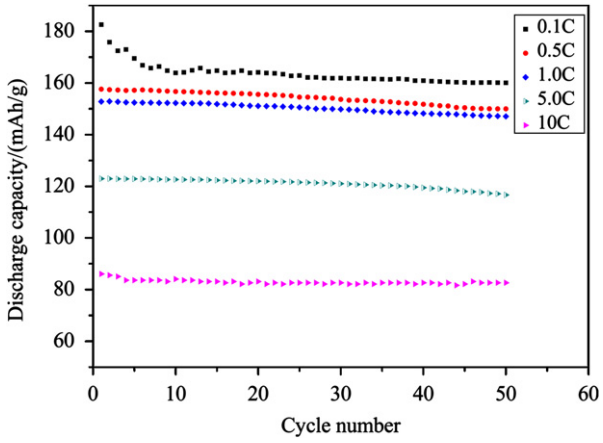

Fig. 4. Cycling performances of the $Li_4Ti_5O_{12}$ at different rates.

It is clear in Fig. 3 that there is a long and smooth voltage plateau between 1.5 and 1.7 V/Li during the initial cycle, which is a common phenomenon related to the decrease in particle and crystallite size for nanomaterials. After 50 cycles, the capacity retention is still excellent and exceeds 92%, meaning that there is only about 0.25 mAh g^{-1} capacity decrease for each charge-discharge process. Therefore, the $Li_4Ti_5O_{12}$ exhibits a great cycling performance, which may be attributed to the spheroidic microstructure and tiny nano-sheets. When the rates are enhanced to 0.5 C, 1 C and 10 C, the capacities are 157.6 mAh g^{-1}, 152.7 mAh g^{-1}, 82.2 mAh g^{-1} respectively. There is a large potential difference between the charge and discharge plateaus at the rate of 10 C. This is because the reaction is controlled by the diffusion of lithium between the phase surface of $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ in the charge/discharge process. With the discharging current increased, it will lead to a concentration polarization, which can reduce the reversible capacity.

Cycling performances of $Li_4Ti_5O_{12}$ at the rates of 0.1–10C are shown in Fig. 4. After the initial 10 cycles, the performances tend to be stable at the rate of 0.1 C. The 50th discharge capacity is 160 mAh g^{-1} and the retention is 92.8% compared to the first discharge capacity. When the current density enhanced to 0.5 C and 1.0 C, the specific capacity retention are 95.2% and 96.7% after 50 cycles. With the density increased to 10 C, only 82.6 mAh g^{-1} of the discharge capacity is obtained, but the curves present excellent performances on the cycle stabilities. It indicates that the microsphere morphology of $Li_4Ti_5O_{12}$ will make qthe active materials contact with the electrolyte solution sufficiently enough, which can decrease the concentration

polarization significantly. Meanwhile, the tiny crystallite size of nano-sheets can shorten the diffusion distance of lithium and electrons.

4. Conclusions

In summary, we have synthesized microsphere spinel $Li_4Ti_5O_{12}$ crystallites by a simple hydrothermal method. The $Li_4Ti_5O_{12}$ is prepared at a low temperature and has a large rate capacity of 172.5 mAh g^{-1} and an excellent cycling performance. Meanwhile the tiny crystallite size of nanosheets can promote the surface area and decrease the polarization.

Acknowledgements

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