

Preparation and characterization of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material from industrial titanyl sulfate solution

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Received 6 July 2009; accepted 30 December 2009

Abstract: Metatitanic acid was synthesized from industrial titanyl sulfate solution via controlling pH during hydrolyzing process. Inductively coupled plasma (ICP) analysis confirmed that a little Fe, Mg and Ca were deposited into precursor $\text{TiO}_2 \cdot \text{H}_2\text{O}$. Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared by sintering amorphous mixture at 800 °C for 16 h. The amorphous mixture was activated by ball-milling at room temperature, using the as-prepared $\text{TiO}_2 \cdot \text{H}_2\text{O}$ and Li_2CO_3 as raw materials. The sample was characterized by X-ray diffractometry, scanning electron microscopy and electrochemical charge and discharge test. The results show that spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is obtained, but it contains a few rutile TiO_2 impurities. The sample has fine particles with size of around 50 nm and homogenous size distribution. At room temperature, the initial reversible specific capacity of the sample is 136.9, 128.0, 119.2 and 96.3 $\text{mA} \cdot \text{h/g}$ at 0.1C, 1C, 2C and 5C, respectively, and the sample shows excellent cycling performance.

Key words: TiOSO_4 ; hydrolyzation; $\text{Li}_4\text{Ti}_5\text{O}_{12}$; anode material; electrochemical performance

1 Introduction

There are abundant titanic minerals in China, and Panzhihua ilmenite located in Sichuan Province is one of the largest titanium resources in the world and accounts for about 90% of the total resources in China[1]. Most of Panzhihua ilmenites associate with magnetite which has high-level CaO and MgO, therefore, almost 90% of TiO_2 are manufactured with the sulfate process[2], and most of TiO_2 are anatase. During sulfate process, ilmenite is firstly leached with concentrated sulphuric acid, and then the Ti-containing solution, which mostly contains TiOSO_4 , is purified and hydrolyzed. In general, the acid number of industrial titanyl sulfate solution is between 1.7 and 2.1. Concentrated industrial titanyl sulfate solution contains about 500 g/L sulphuric acid, 260 g/L TiO_2 and a few impurities such as Ni, Mg, Al, Mn, Ca, Na[3–4]. Therefore, in order to protect environment and enhance economy benefit, using resources synthetically attracts great attention in the world.

Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is viewed as one promising alternative to graphite to be an anode material in lithium ion batteries[5], because of having a spinel related structure, extremely flat discharge and charge plateaus at

about 1.55 V, excellent cycling ability and zero-strain insertion[6–8]. Generally, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders are mainly synthesized by solid-state reactions that involve mechanical mixing of oxides and carbonates, heating at higher temperature (800–1100 °C)[9–12] and sol-gel methods[13–16]. Three lithium ions per formula unit of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be reversibly inserted and extracted. As a consequence, a theoretical specific capacity of 175 $\text{mA} \cdot \text{h/g}$ is expected. This material has optimistic perspectives, and holds some promise of being used in power tools[17].

In this work, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared by heating the mixture of $\text{TiO}_2 \cdot \text{H}_2\text{O}$ and Li_2CO_3 . $\text{TiO}_2 \cdot \text{H}_2\text{O}$ was obtained by hydrolyzing industrial titanyl sulfate solution without crystal transformation and used as titanium precursor directly. Electrochemical properties were investigated as an anode material for lithium batteries.

2 Experimental

2.1 Preparation of samples

The precursor $\text{TiO}_2 \cdot \text{H}_2\text{O}$ was synthesized as the following procedure. The industrial titanyl sulfate solution was diluted in de-ionized water to obtain 2.5

mol/L Ti-containing solution; then $\text{NH}_3\cdot\text{H}_2\text{O}$ was dropped into the solution to control the $\text{pH}=5.0$, white precipitate was obtained immediately; after being stirred for 30 min, the precipitate was filtered and washed several times with de-ionized water until SO_4^{2-} was removed, and then dried in an oven at 80°C . Thus, $\text{TiO}_2\cdot\text{H}_2\text{O}$ powders were obtained.

Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared by heating the amorphous mixture of $\text{TiO}_2\cdot\text{H}_2\text{O}$ and Li_2CO_3 at 800°C for 16 h in air. The molar ratio of lithium and titanium was 4:5. The mixture was activated by ball-milling at room temperature firstly.

2.2 Detection methods

Elements contained in samples were investigated by inductively coupled plasma (ICP, Thermo Electron Corporation). The powder X-ray diffraction (XRD, Rint-2000, Rigaku) measurement using $\text{Cu K}\alpha$ radiation was employed to identify the crystalline phase of the synthesized materials and the data was recorded at room temperature. The particle size and morphology of the prepared powders were observed by scanning electron microscopy (JEOL, JSM-6380LV) with an accelerating voltage of 20 kV.

2.3 Electrochemical measurements

The electrochemical characterizations were performed using CR2430 coin-type cell. For positive electrode fabrication, the prepared powders were mixed with 10% (mass fraction) acetylene black as conducting agent, and 10% (mass fraction) polyvinylidene fluorides as binder in N-methyl pyrrolidinone. And then, the blended slurries were pasted onto a copper current collector, and the electrode was dried at 120°C for 6 h. The test cell consisted of the positive electrode and lithium foil negative electrode was separated by a porous polypropylene film, and 1 mol/L LiPF_6 in EC:EMC:DMC (1:1:1 in volume) as the electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box. The cells were charged and discharged over a voltage range of 1.0 to 2.5 V versus Li/Li^+ electrode at the rate of 0.1C, 1C (160 mA/g), 2C and 5C at room temperature. Cyclic voltammogram (CV) test was performed on a CHI660A electrochemical workstation in voltage range of 0.5 to 2.5 V versus Li/Li^+ electrode at the scanning rate of 0.1, 0.5, 1 mV/s.

3 Results and discussion

3.1 Characterization of precursor $\text{TiO}_2\cdot\text{H}_2\text{O}$

Fig.1 shows a SEM image of the precursor $\text{TiO}_2\cdot\text{H}_2\text{O}$ synthesized by hydrolyzing industrial titanyl sulfate solution. The sample exhibits a uniform fine-grained microstructure, which is conducive to the

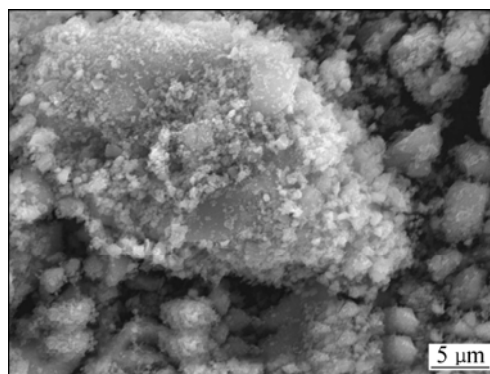


Fig.1 SEM image of precursor $\text{TiO}_2\cdot\text{H}_2\text{O}$

synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ fine powders.

The ICP results of the industrial titanyl sulfate solution (2.5 mol/L Ti) and the solution after hydrolyzing are given in Table 1. 25.0%Fe, 76.0%Mg and 24.3%Ca are deposited into the precursor $\text{TiO}_2\cdot\text{H}_2\text{O}$; however, Al and Mn are absent. It is reported that a little Mg and Al doping could improve the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [9].

Table 1 Impurity contents in raw material and solution after hydrolyzing (mass fraction, 10^{-6})

Solution	Fe	Mg	Ca	Al	Mn
Industrial TiOSO_4 solution	52	25	37	14	7
Solution after hydrolyzing	39	6	28	14	7

3.2 Characterization of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$

3.2.1 Structure and morphology analysis

Fig.2 shows the XRD pattern of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared by sintering at 800°C for 16 h in air. The diffraction peaks of the sample can be indexed as spinel lithium titanium oxide (cubic phase, space group $Fd\bar{3}m$) in accordance with spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (JCPDS Card No. 49-0207). The crystal lattice parameter, a , calculated by using the software WinPLOTR, is $8.359\text{ \AA}$, which shows good agreement to that reported in Ref.[5]. As shown in

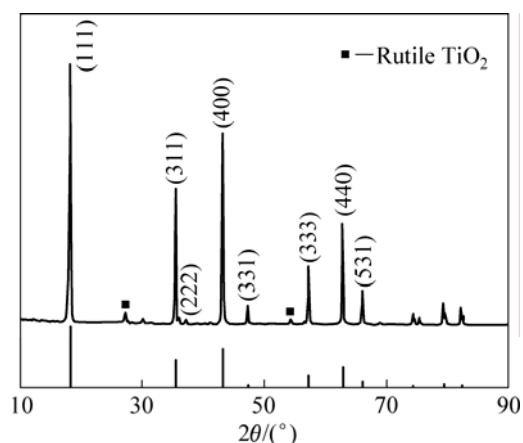


Fig.2 XRD pattern of prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Fig.2, besides the peaks of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, two extra weak diffraction peaks are also observed at $2\theta=27.4^\circ$ and 54.3° , which are attributed to a secondary phase of rutile TiO_2 . The presence of impurity phase is due to the loss of lithium at high temperature, thus the precursor $\text{TiO}_2\cdot\text{H}_2\text{O}$ is transformed to anatase TiO_2 , and then transformed to rutile TiO_2 .

The SEM image of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is shown in Fig.3. It can be seen that the dried powder sample show aggregated nanoparticles with homogeneous distribution. The size of the primary particles is around 50 nm.

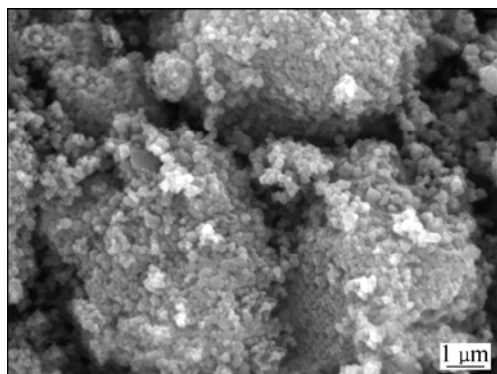


Fig.3 SEM image of prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$

3.2.2 Electrochemical analysis

Fig.4 shows the initial charge/discharge profiles of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different rates (0.1C, 1C, 2C and 5C) in the voltage range of 1.0–2.5 V. The flat charge and discharge curves, intrinsic electrochemical properties of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel-based anode based on two-phase mechanism, are observed at 1.53 and 1.51 V versus Li/Li^+ , respectively, and indicate little polarization even up to 5C. As seen in Fig.4, the charge and discharge property is reversible, but the capacity is low.

The initial reversible specific capacity of the sample is 136.9 $\text{mA}\cdot\text{h/g}$ at 0.1C (1C=160 mA/g). By increasing the rate, the utilization of the active material decreases,

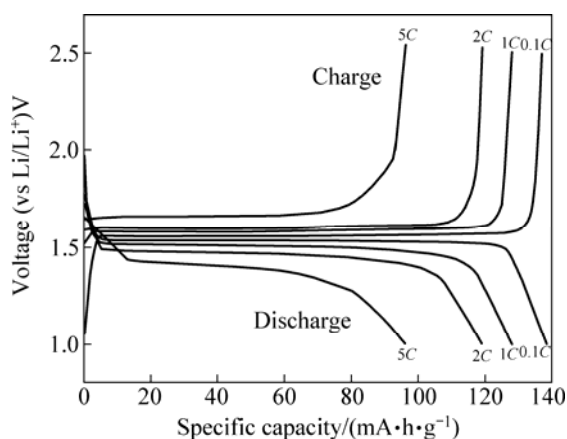


Fig.4 Initial charge/discharge curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different rates in voltage range of 1.0–2.5 V

128.0, 119.2, and 96.3 $\text{mA}\cdot\text{h/g}$ at 1C, 2C and 5C rate, respectively. In addition, it can be seen that the coulomb efficiency of the sample is very close to 100%[6]. Thus, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is often called as a zero-strain material with a promising cycling ability[15].

The cycling performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different rates is shown in Fig.5. The cell cycled 10 times at 0.1C, then cycled 20 times at 1C, 2C and 5C in turn, and at last cycled 10 times at 0.1C again. It shows that the capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ retains 70.3% at 5C, compared with that at 0.1C. After cycling, the reversible specific capacities at 0.1C, 1C, 2C and 5C are 134.9, 121.9, 113.0 and 86.8 $\text{mA}\cdot\text{h/g}$, respectively, and retain 98.5%, 95.2%, 94.8% and 90.1% of their initial reversible specific capacity, respectively. Finally, the capacity can be recovered to 137.9 $\text{mA}\cdot\text{h/g}$ at 0.1C. That is to say, the structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is not destroyed during the charge/discharge cycling. The loss of capacity fluctuation on the capacity-cycle profile at this high current rate also suggests that Li^+ insertion/extraction only takes place in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ grains at or near the outer surface of the highly aggregated particles. The capacity is much low at high current rates, and needs to be improved.

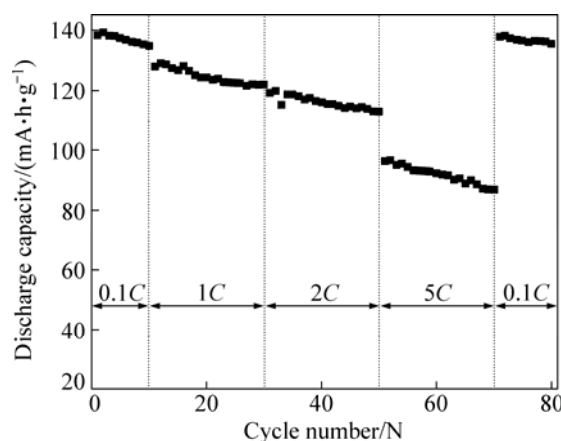


Fig.5 Cycling performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different rates

Fig.6 shows the cyclic voltammograms of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different scanning rates (0.1, 0.5 and 1 mV/s). At any scanning rate, a pair of reversible redox peaks can be clearly seen, corresponding to a cathodic and anodic process. The cathodic peak located around 1.50 V at 0.1 mV/s corresponds to the voltage plateau of the first cycle discharge process, in which Li intercalates into the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, moves steadily to the lower voltage with the increase of scanning rate. Meanwhile, the anodic peak located at 1.66 V corresponds to the voltage plateau of the first cycle charge process, in which Li de-intercalates from the spinel $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$, moves steadily to the higher voltage with the increase of scanning rate[14, 18]. Moreover, it can be seen that there is a small peak among the cathodic peaks at higher scanning rates in

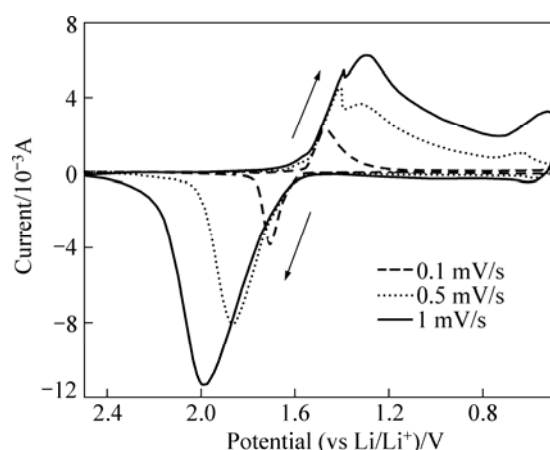


Fig.6 Cyclic voltammograms of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different scanning rates

consequence of impurity phase.

4 Conclusions

1) The precursor $\text{TiO}_2 \cdot \text{H}_2\text{O}$ is obtained by hydrolyzing industrial titanyl sulfate solution at $\text{pH}=5.0$. The sample exhibits a uniform fine-grained microstructure. The ICP results show that 25.0% Fe, 76.0% Mg and 24.3% Ca are deposited into the precursor; however, Al and Mn are not precipitated.

2) In order to cut down the cost and simplify the synthesis technology, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is prepared by heating the amorphous mixture of the as-prepared precursor $\text{TiO}_2 \cdot \text{H}_2\text{O}$ and Li_2CO_3 at 800 °C for 16 h in air.

3) XRD analysis shows that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has cubic spinel structure with the impurity rutile TiO_2 ; SEM image shows that the particle is about 50 nm in size together with homogeneous distribution. The initial reversible specific capacity of the sample is 136.9, 128.0, 119.2, 96.3 $\text{mA} \cdot \text{h/g}$ at 0.1C, 1C, 2C and 5C, respectively. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ shows excellent cycling performance.

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(Edited by LIU Hua-sen)