Electrospinning synthesis of spinel Li$_4$Ti$_5$O$_{12}$ and its characterization

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Abstract. The electrode material Li$_4$Ti$_5$O$_{12}$ (LTO) with excellent electrochemical properties was synthesized by an electrospinning method using Ti(OCH(CH$_3$)$_2$)$_4$ and CH$_3$COOLi as raw materials. The effects of the solution viscosity and calcination conditions on the structure and electrochemical performance of LTO were investigated by scanning electron microscopy (SEM), X-ray diffractometry (XRD) and charge-discharge test. The optimal synthesis condition is 11 cP for the viscosity of the precursor solution, 800 ℃ for 12h with the heating rate of 1 ℃ · min$^{-1}$ for the calcination of precursor filaments. The product has a narrow diameter distribution and small amounts of impurities. The discharge capacity of LTO sample is 199.51 mAh g$^{-1}$.

1. Introduction
Lithium-ion batteries (LIBs) are widely used in small mobile electronic devices for its high energy density, high power density and other characteristics. Currently, people focus on the superior LIBs which are suitable for electric vehicles and smart grid [1]. As a new anode material, spinel Li$_4$Ti$_5$O$_{12}$ (LTO) has a very flat charge-discharge plateau at ~1.55V (vs Li$^+$/Li) [2], which prevents the growth of lithium dendrites and thereby improves the safety of LIBs. Moreover, it has the “zero-strain” characteristic during Li$^+$ insertion/extraction process, thus makes it has a good stability in the long-term cyclic usage. Therefore, it becomes one of the most promising anode materials [3]. Different methods are used for synthesizing LTO, such as solid-state method, sol-gel method and hydrothermal method, etc. The hard agglomeration is a problem of easy occurring in LTO powders, which leads to the increase of preparation cost. As a new method for preparing submicron- or nano- materials, electrospinning is simple and efficient. Materials prepared by electrospinning don not easily form hard agglomerates due to electrostatic repulsion effect. In this paper, LTO submicron fibers were synthesized by an electrospinning method, and the effect of synthesis conditions on the structure of LTO and its electrochemical performance were investigated.

2. Experimental details
2.1. Synthesis of the spine LTO
The precursor solution for electrospinning was prepared from lithium acetate, tetraisopropyl titanate, acetic acid and different doses of polyvinyl pyrrolidone (PVP) (1 g, 2 g, 3 g and 4 g). The viscosities of the resulting solution were 11cP, 38cP, 74cP and 117cP with different doses of PVP (Brookfield viscometer at a temperature of 21°C using spindle No. 3 at 100 rpm). A certain amount of the solution was loaded into a plastic syringe and subjected to electrospinning. The flow rate was 1.5 ml•h⁻¹ and the distance between the tip of the needle and collector was 10 cm, the collector drum speed was 800~1000 rpm, experiment voltages was 12 kV [4]. Then LTO samples were obtained under different calcination conditions. LTO samples with the PVP dosage of 1 g, 2 g, 3 g and 4 g were marked for LTO-11cP, LTO-38cP, LTO-74cP and LTO-117cP, respectively.

2.2. Morphology and structure
X-ray diffractometry (XRD) measurements were performed on a Rigaku UltimaIV instrument with Cu Ka radiation (10°<2θ<90°). The surface morphologies of the fibers were studied by scanning electron microscopy (Hitachi X−650).

2.3. Preparation of electrode films and the button cell assembly
The electrodes were prepared by mixing 80 wt.% active materials with 10 wt.% carbon black (CB) and 10 wt.% polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP) onto a Cu foil. The slurry was coated on a copper current collector and dried for 12 h at 80°C in order to remove the NMP solvent. The resulting electrode foil was rollpressed and punched to a circular disc. The electrode films were preserved in argon-filled dry box (Unilab, MB 200B) in which oxygen and moisture contents were maintained less than 1 ppm. The coin cells were fabricated with LTO, metallic lithium anode, 1 M LiPF₆ in 1:1 ethylene carbonate (EC) and diethylene carbonate (DEC) electrolyte, and Celgard polypropylene separator.

2.4. Electrochemical measurements
The cell was cycled between 1.0 and 2.5 V [5] versus Li/Li⁺ electrode at 24°C. The charge–discharge test was performed by using a multichannel cell cycling system (Maccor S4000).

![Figure 1. SEM image of (a) LTO-11cP, (b) LTO-38cP, (c) LTO-74cP, and (d) LTO-117cP.](image-url)
3. Results and discussion

3.1. Morphology and structure

Figure 1 shows the SEM images of LTO submicron fibers obtained after the calcination of electrospun precursor at 800 °C for 12 h in air. As shown in figure 1, the fiber diameters of LTO-11cP, 38cP, 74cP and 117cP were about 0.17–0.23 μm, 0.23–0.30 μm, 0.36–0.41 μm and 0.44–0.58 μm, which indicating that the viscosity of LTO precursor solution dramatically affects the morphology of LTO submicron fiber. When the viscosity of the solution increases, it tends to resist the bending-instability occurring in the solution injection process, thereby reducing the spinning paths. It means the tensile force of the solution decreases which causes the formation of thicker fibers.

Figure 2. XRD patterns of LTO samples at (a) different calcination temperature, (b) different heating rates.

Figure 2 shows the XRD patterns of samples which were obtained under different calcination conditions. The sharp diffraction peaks of LTO samples are consistent with the spinel LTO (JCPDS PDF 49-0207), which means it is a single-phase cubic material with an Fd3m space group. From figure 2, it can be seen that there are some diffraction peaks that corresponds to the existence of rutile TiO2 (JCPDS PDF 26-1198) for samples at the calcination temperature of 600, 700 °C (figure 2(a)) as well as the heating rates of 3, 5 °C·min⁻¹ at 800 °C (figure 2(b)). In addition, the peak intensities of LTO sample at 1 °C·min⁻¹ are obviously stronger than those of LTO samples at 3, 5 °C·min⁻¹ in the figure 2(b). In summary, the optimum calcination conditions are 1 °C·min⁻¹ heating rate, 800 °C, holding time 12 h.

Figure 3. The charge-discharge curves of (a) LTO-11cP, (b) LTO-38cP, (c) LTO-74cP, and (d) LTO-117cP at 0.1, 0.2, 0.5, and 1.0 C rate.

3.2. Electrochemical test

Figure 3(a) shows the charge-discharge curves of LTO samples at different rates. The LTO samples have the c.a. 1.55 V voltage platform and the discharge capacities of LTO-11cP, LTO-38cP and LTO-74cP samples at 0.1C rate are 199.51, 192.79, 182.51, and 178.51 mAh·g⁻¹, respectively. Figure 3(b)
reveals the obvious influence of LTO fiber diameter on the rate capability of LTO samples. The rate capability of LTO-11Cp (c.a. 0.17~0.23 μm) is comparatively better than other LTO samples which can be seen in figure 3 (b), its specific capacity retention reaches 75% at 1.0 C discharge rate.

4. Conclusion

In the paper, LTO precursor fiber was prepared by an electrospinning technology and then LTO submicron fiber was synthesized by solid state sintered method. The proper viscosity of LTO precursor solution was 11 cP and the optimum conditions are heating rate of 1 °C·min⁻¹, calcination temperature of 800 °C, calcination time of 12 h. The discharge capacity of LTO-11Cp is 199.51 mAh·g⁻¹ at 0.1C rate and it possesses good rate capability.

Acknowledgment

The work was financially by the science and technology project of State Grid Corporation of China (DG71-13-037).

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