Preparation techniques of the submicron lithium titanate materials by electro-spinning

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Abstract. Combining sol-gel process and electro-spinning, the submicron lithium titanate materials are prepared with lithium acetate and titanium tetraisopropanolate respectively as the lithium and titanium sources, and polyvinylpyrrolidone (PVP) as the template. It’s found by scanning electron microscope(SEM )that, the prepared lithium titanate materials are characterized by the fiber diameter 150~200nm, a large number of irregular indentations in the surface, and the larger specific surface area than that before calcination. The lithium titanate cell receives charge-discharge test and cyclic voltammetry. The capacity of the submicron lithium titanate materials is up to 160mAh·g⁻¹ at the rate of 0.1C, and it’s revealed by cyclic voltammetry that the cell in the charge or discharge process undergoes a single redox reaction, but having good reversibility.

1. Introduction

The recently developed lithium titanate anode material has attracted widespread attention at home and abroad with its great strengths, such as long cycle life, structural stability among others.[1] There have been many lithium titanate preparation techniques over the world, mainly including solid phase method, sol-gel process, hydrothermal synthesis, templating, molten salt method, electro-spinning among others.[2], having great impacts on the materials properties to a varying degree.

Electro-spinning is an up-and-coming star among the preparation techniques of the fibers of different diameters. In the electric field formed by a high-voltage power supply, the precursor solution driven by the electric force is drawn into filaments, and such filaments eventually fall to a grounded collector. The fibers of different diameters can be obtained by adjusting different spinning parameters. Compared with solid phase method, electro-spinning has the submicron lithium titanate fibers of a smaller diameter prepared without agglomeration but having a larger surface area by which the specific capacity can be improved with a full contact with the electrolyte and the complete lithium intercalation/de-intercalation. In contrast with other techniques of preparing nano-materials, the water absorption of the sub-micron materials prepared by electro-spinning is significantly reduced, thereby effectively controlling the side reaction of any gas generated by the decomposition of water in the lithium titanate cell. [3,4]
2. Experiment scheme

2.1. Preparation of the lithium titanate fibers
The present experiment combines sol-gel process and electro-spinning, with lithium acetate and titanium Isopropoxide respectively as the lithium and the titanium source, the molar ratio of lithium to titanium of 0.82, polyvinyl pyrrolidone (PVP), a high molecular polymer, as the template for reaction and absolute ethyl alcohol as the solvent. Spinning parameter settings: 20kV, and 15cm(spinning distance). The preliminary experimental results show, a sufficient electric force is assured by 20kV, and combining with the given electro-spinning distance, the precursor of lithium titanate is stretched into submicron lithium titanate precursor filaments.

The prepared precursor filaments are placed into a muffle furnace, with the calcination conditions as follows: the temperature rises from room temperature to 600°C at the rate of 2°C·min⁻¹, and to 750°C at the same rate after constant temperature for 2h, and after constant temperature for 5h, lithium titanate filaments are finally obtained.

2.2. Morphological characterization
The filament morphology is observed by SEM(Hitachi X–650) before and after calcination.

2.3. Electrochemical test
The prepared lithium titanate, acetylene black and PVDF are evenly mixed by the mass ratio of 8:1:1, and uniformly coated on the copper foil, and the button cell is fabricated with a lithium metal sheet as the counter electrode. The cell is tested by cyclic voltammetry under the following conditions: under the open-circuit potential, the voltage range is 1-2.5V[5], and the scanning is 0.5mV·s⁻¹, with a total of 5 cycles. Then, at room temperature, the cell undergoes the charge-discharge test, with the aim of characterizing the electrochemical performance of lithium titanate fibers.

3. Results and discussions

3.1. Morphological characterization

![Figure 1. Original composite fibers](image1)

![Figure 2. composite fibers after calcination](image2)

Figure 1 & 2 are respectively the SEM image of the lithium titanate precursor fibers and that of the lithium titanate fibers obtained by calcination, and it's found that, the diameter of the lithium titanate fibers prepared by electro-spinning is 150~200nm. The lithium titanate precursor fibers before calcination is smooth silk-like under the electrostatic interaction and the bonding effect of the polymer, without agglomeration; however, after calcination, because lithium titanate is produced in the reaction between the lithium and titanium sources at high temperature and the polymer at a high temperature
generate gas while being calcined, thus forming surface irregularities which enlarge the specific surface area of the submicron lithium titanate materials. In contrast with nanometer materials, the submicron lithium titanate reduces the water absorption, thereby cut back the side reaction on the decomposition of water in the cell.

3.2. Electrochemical Test

Figure 3. cyclic voltammetry curves of the button cell of submicron lithium titanate

Figure 3 shows the cyclic voltammetry curves of the button cell of submicron lithium titanate, with a singlet oxidation peak and a singlet reduction peak, indicating there is no side reaction but intercalation/de-intercalation in the charge-discharge process; and, both the oxidation peak and the reduction peak are symmetric in the peak pattern, and the peak current ratio is approximately 1, which indicates the redox reaction is reversible.

Figure 4 is the cycle-capacity graph of the button cell of lithium titanate at 0.1, 0.5, 1 and 5 and 10C after being assembled, and it's observed that the specific capacity at low rate is about 160mAh·g⁻¹. As the rate increases, the intercalation/de-intercalation time is
shortened, and part of the sites for lithium ions lose their intercalation / de-intercalation abilities due to interfacial reaction rate is less than lithium ion transport rate, leading to a decline of the capacity. Figure 5 is the capacity-voltage graph of the button cell at 0.5C, the capacity retention rate in the charge-discharge process is relatively high, and the voltage difference between the charge platform and the discharge platform is smaller, indicating less polarization in the process.

4. Conclusions
In this paper, the submicron lithium titanate fibers were prepared by combining electro-spinning with certain calcination condition. Seen from the SEM images, the fibers with the diameter in the sub-micron level and free of aggregation, have a larger surface area. The specific capacity of the prepared button cell at low rate can reach 160mAh·g⁻¹. It's revealed by cyclic voltammetry that, the lithium titanate fibers in the intercalation/de-intercalation does not have any side reaction, but having high redox reversibility.

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