Nanosized Spinel Li$_4$Ti$_5$O$_{12}$ Anode Material Prepared by Gel-polymer Method using Furfuryl Alcohol as Polymerizable Solvent

Chu-xiong Ding, Yao-cai Bai, Cong Wei, Chun-hua Chen*

CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China

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Nanosized Li$_4$Ti$_5$O$_{12}$ powders are synthesized by a polymerization-based method using titanium butoxide and lithium nitrate as precursors and furfuryl alcohol as a polymerizable solvent. The prepared samples are characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and Brunauer-Emmett-Teller (BET) analysis. The electrochemical performances of these Li$_4$Ti$_5$O$_{12}$ powders are also studied. The effect of different surfactants including citric acid, polyvinylpyrrolidone, and cetyltrimethyl ammonium bromide on the structure and properties is also investigated. It is found that pure spinel phase of Li$_4$Ti$_5$O$_{12}$ is obtained at an annealing temperature of 700 °C or higher. The use of surfactants can improve the powder morphology of nanosized particles with less agglomeration. With suitable annealing temperature and the addition of surfactant, Li$_4$Ti$_5$O$_{12}$ powders with high BET surface area and favorable electrochemical performance can be obtained.

Key words: Polymerization process, Lithium ion battery, Li$_4$Ti$_5$O$_{12}$, Nanoparticle, Rate performance

I. INTRODUCTION

The spinel Li$_4$Ti$_5$O$_{12}$, which shows a flat potential profile at about 1.55 V (versus Li$^+$/Li) and exhibits a theoretical capacity of 175 mAh/g, has been considered as a promising anode material for lithium-ion batteries [1–4]. Compared with the commercial carbonaceous anodes, Li$_4$Ti$_5$O$_{12}$ has several appealing advantages. Because its relatively high potential (1.55 V versus Li$^+$/Li) is above the reduction potential of common electrolyte solvents, the solvents would not be reduced to form a solid electrolyte interface (SEI) layer with high resistance on the surface of the electrode material [5, 6]. In addition, the spinel Li$_4$Ti$_5$O$_{12}$ is a zero-strain host compound for lithium insertion and extraction, which secures excellent reversibility and high structural stability in the charge-discharge process, leading to a super-long cycle life of the batteries [1, 2, 4, 7]. Furthermore, with a 3D-tunnel pathways for lithium ion transport in the spinel-type crystal structure, Li$_4$Ti$_5$O$_{12}$ has excellent lithium-ion mobility and thus high-rate performance for high power applications such as hybrid electric vehicles [4, 8]. Therefore, Li$_4$Ti$_5$O$_{12}$ is widely acknowledged as an anode material candidate with excellent cycling performance, high rate performance and safety.

On the other hand, Li$_4$Ti$_5$O$_{12}$ has a low electronic conductivity which may lead to poor rate performance and limit its wide practical applications [9, 10]. In order to improving the electrochemical performance, especially the high rate performance, several efforts have been devoted to improve the rate capability of Li$_4$Ti$_5$O$_{12}$. One approach is to synthesize nanosized Li$_4$Ti$_5$O$_{12}$ [11–18]. The nanosized particles can provide large contact surface area between the electrode material and electrolyte, and meanwhile shorten the distances for the diffusions of lithium ions and electrons. Another approach is to modify the lattice structure and microstructure of the Li$_4$Ti$_5$O$_{12}$ powder by doping [10, 11, 19–24] or surface coating with carbon [14, 15, 25–29] or noble metals [30].

Herewith, we present a novel polymerization-based method making use of polymerizable furfuryl alcohol (FA, C$_4$H$_9$OCH$_2$OH) to synthesize Li$_4$Ti$_5$O$_{12}$ nanosized particles. Poly(furfuryl alcohol) (PFA) has been used to synthesize carbon-based materials and polymers as adsorbents and separation membranes [31–34], and some unitary metal oxides such as TiO$_2$ [35]. However, it has not been applied to synthesize complex metal oxides such as Li$_4$Ti$_5$O$_{12}$. In this work, the PFA-based synthesis method for the important nanosized Li$_4$Ti$_5$O$_{12}$ is suitable. We also investigate the effect of adding a number of surfactants in order to solve the accompanying problem of particle agglomeration.

In the synthesis procedure of Li$_4$Ti$_5$O$_{12}$, the chemical
The chemical reactions of the preparation of the Li$_4$Ti$_5$O$_{12}$ nanosized powders.

Scheme 1 The chemical reactions of the preparation of the Li$_4$Ti$_5$O$_{12}$ nanosized powders.

Reactions are presented in Scheme 1. FA is an excellent solvent for titanate precursors (e.g., Ti(OC$_4$H$_9$)$_4$), which can also be stabilized by FA through an alcohol-exchange reaction. PFA is formed via thermal polymerization of FA and the water produced by FA polymerization initiates the sol-gel process of titanate precursors. PFA serves as the temporary barrier in the confined crystallization of mesoporous titanate precursors frameworks. The titanate precursors with uniformly dispersibility in PFA are obtained after FA polymerization is complete [34]. At last, the PFA is burnt off in air and uniform Li$_4$Ti$_5$O$_{12}$ nanosized particles are obtained. The synthesis and characterizations of the nanosized Li$_4$Ti$_5$O$_{12}$ are detailed in this work.

II. EXPERIMENTS

15 g of FA, 3 g of Ti(OC$_4$H$_9$)$_4$ and 0.5 g of lithium nitrate dissolved in 5 mL of ethanol were mixed with stirring. In order to investigate the effect of different kinds of surfactants, i.e. citric acid (CA, 0.1 g), polyvinylpyrrolidone (PVP, 0.5 g) (K-30, Sinopharm Chemical Reagent Co., Ltd) or cetyltrimethyl ammonium bromide (CTAB, 0.5 g) dissolved in 10 mL of ethanol was added into the solution. The resulting solution was stirred at room temperature for 4 h, followed by a heat-treatment at 150 °C for 24 h to polymerize FA. The obtained black composites were calcined at 500 °C for 6 h to produce white powders, which were further annealed at 650, 700, 750 and 800 °C in air for 12 h to obtain spinel Li$_4$Ti$_5$O$_{12}$ powders.

The crystalline structures of the samples were characterized by X-ray diffraction (XRD) using an X-ray diffractometer (Philips X'Pert Pro Super, Cu Kα radiation). The diffraction patterns were recorded at room temperature in the 2θ range from 10° to 70°. Scanning electron microscopy (SEM, JSM-6390 LA, JEOL) and transmission electron microscopy (TEM, Tecnai F20, FEI) were performed to analyze the particle morphologies of the powders. Their specific surface areas were determined by the Brunauer-Emmett-Teller (BET) method (SA3100, BECKMAN COULTER).

The electrochemical properties of the Li$_4$Ti$_5$O$_{12}$ powders were measured with Li$_4$Ti$_5$O$_{12}$/Li half cells. The Li$_4$Ti$_5$O$_{12}$ electrode laminates were prepared by coating 80%Li$_4$Ti$_5$O$_{12}$, 10%carbon black and 10%PVDF on copper foil. The electrolyte was a solution of 1.0 mol/L LiPF$_6$ dissolved in EC/DEC (1:1), and lithium metal was chosen as the counter electrode. The coin-cells (CR2032 size) were fabricated in an argon-filled glove box (MBraun Labmaster 130) with a porous polypropylene membrane (Celgard 2400) as the separator. The weight of active material of Li$_4$Ti$_5$O$_{12}$ was loaded to roughly 3.0 mg/cm$^2$. The cells were galvanostatically cycled with different current densities between the cutoff voltages of 1.0 and 2.5 V on a multi-channel battery cycler (Neware BTS 610) at 25 °C. The AC impedance spectroscopy of the cells was performed on a CHI 604B Electrochemical Workstation. The cells were fully charged after 5 cycles at 35 mAh/g, and measured with an AC voltage amplitude of 5.0 mV and a frequency range from 10 mHz to 100 kHz.

III. RESULTS AND DISCUSSION

The X-ray diffraction patterns of the Li$_4$Ti$_5$O$_{12}$ powders annealed at the temperatures from 650 °C to 800 °C for 12 h in air are shown in Fig.1. It is noticed that some impurity peaks corresponding to rutile TiO$_2$ are observed for the sample annealed at 650 °C [13, 16]. But the powders annealed at the temperatures over 650 °C show the single phase of spinel Li$_4$Ti$_5$O$_{12}$. All the diffraction peaks can be indexed based on a face-centered cubic structure with an Fd3m space group (JCPDS card No.26-1198).

Figure 2 shows the SEM images of the Li$_4$Ti$_5$O$_{12}$ powders annealed at the temperatures from 650 °C to 800 °C for 12 h. It can be seen that the average parti-
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FIG. 1 Powder X-ray diffraction patterns of Li$_4$Ti$_5$O$_{12}$ powders annealed at temperatures from 650 to 800 °C for 12 h.

FIG. 2 SEM images of Li$_4$Ti$_5$O$_{12}$ powders annealed at different temperatures for 12 h. (a) 650 °C, (b) 700 °C, (c) 750 °C, and (d) 800 °C.

FIG. 3 SEM images of Li$_4$Ti$_5$O$_{12}$ powders prepared at 700 °C with different surfactants. (a) No surfactant, (b) 0.1 g CA, (c) 0.5 g PVP, and (d) 0.5 g CTAB.

The BET surface areas of the Li$_4$Ti$_5$O$_{12}$ powders synthesized without any surfactant are 22.82, 14.11, 10.25, and 5.68 m$^2$/g for the samples annealed at 650, 700, 750, and 800 °C, respectively. Obviously, bigger particle size leads to the decrease in the BET surface area. The sample annealed at 800 °C has much bigger average particle size, which is about 300 nm. In addition, there exist large agglomerates in all of the four Li$_4$Ti$_5$O$_{12}$ samples.

The SEM images of the Li$_4$Ti$_5$O$_{12}$ powders prepared with different surfactants and annealed at 700 °C for 12 h are shown in Fig.3. It can be seen that there is...
FIG. 4 TEM images of Li$_4$Ti$_5$O$_{12}$ powders prepared at 700 °C with different surfactants. (a) No surfactant, (b) 0.1 g CA, (c) 0.5 g PVP, and (d) 0.5 g CTAB.

less degree of agglomeration and the addition of surfactant results in more uniform morphology and smaller secondary particle sizes. The TEM images shown in Fig.4 indicate that the Li$_4$Ti$_5$O$_{12}$ particles are composed of nanosized primary particles with sizes ranging from 40 nm to 200 nm. With the use of the surfactants, the BET surface areas of the Li$_4$Ti$_5$O$_{12}$ powders annealed at 700 °C are 17.21, 19.94 and 20.55 m$^2$/g for the samples synthesized with CA, PVP and CTAB, respectively. Obviously, smaller secondary particle size and the less degree of agglomeration lead to the increase in the BET surface area.

The electrochemical properties of the Li$_4$Ti$_5$O$_{12}$ powders prepared at 700 °C with different surfactants are shown in Fig.5. The cells are first cycled at 0.2 C rate for 5 cycles, and then they are further charged-discharged at 1 C rate for 100 cycles. We can see that these Li$_4$Ti$_5$O$_{12}$ samples prepared with surfactants show higher charge capacity and better cycling performance than those prepared without surfactants. Specifically, the Li$_4$Ti$_5$O$_{12}$ prepared with CA gives a charge capacity of 165.5 mAh/g at 0.2 C and 156.6 mAh/g at 1 C. After 100 cycles at 1 C, the capacity retention is 96.8%. The Li$_4$Ti$_5$O$_{12}$ prepared with PVP shows a charge capacity of 170.7 mAh/g at 0.2 C. When the current density increases to 1 C, the charge capacity is 161.7 mAh/g and the capacity retention is 97% after 100 cycles. It is worth mentioning that the Li$_4$Ti$_5$O$_{12}$ prepared with CTAB exhibits the best electrochemical performance with a specific charge capacity of 173.4 mAh/g at 0.2 C, 165.5 mAh/g at 1 C with the capacity retention of 97.9% after 100 cycles. It can be concluded that the additions of the surfactants result in higher reversible capacity and better cycling performance, which is in good agreement with the SEM analysis and the BET measurement of these samples.

To evaluate the rate capability of the samples prepared with different surfactants, the cells were charged and discharged at 0.2 C for the initial 5 cycles, and then cycled at different charge current densities from 1 C to 10 C and discharged with 1 C. The results are shown in Fig.6. The specific charge capacities of
the sample prepared without any surfactant is around 153.3, 137.6, 126.0, 107.6, and 79.3 mAh/g at the current densities of 0.2, 1, 2, 5, and 10 C. Clearly, the capacity decreases rapidly with the increasing current density. However, the samples synthesized with CA, PVP, and CTAB manifest higher reversible capacity, especially at high current density. For example, the specific charge capacity of the sample obtained with CTAB is 173.4 mAh/g at 0.2 C, which is slightly reduced to 167.4, 164.8, 161.7, and 156.7 mAh/g at 1, 2, 5, and 10 C, respectively. When returning to 1 C after the progressive rate tests, these four samples can recover their initial capacity, which suggests that there is virtually no volume change during the Li\(^+\) intercalation and de-intercalation process. From Fig.6(b), we can see that the capacity retention of the samples prepared with the surfactants is much higher than that of the pristine sample. The capacity retention of the sample obtained with CTAB is 96.5%, 95%, 93.3%, and 90.4% at 1, 2, 5 and 10 C, respectively, which is the highest of the four samples. It can be concluded that the rate capability of the Li\(_4\)Ti\(_5\)O\(_{12}\) samples prepared with a surfactant is obviously better than that of pristine Li\(_4\)Ti\(_5\)O\(_{12}\) sample. As mentioned earlier, the larger surface area introduced by the more uniform morphology and smaller particle size provides the possibility of faster transfer of electrons and lithium ions, resulting in excellent rate performance.

To further demonstrate the effect of the surfactants on the electrochemical performance of the Li\(_4\)Ti\(_5\)O\(_{12}\) electrodes, the AC impedance spectra of different Li\(_4\)Ti\(_5\)O\(_{12}\) cells that were fully charged after 5 cycles were measured. As shown in Fig.7, the pristine Li\(_4\)Ti\(_5\)O\(_{12}\) sample exhibits the highest charge transfer resistance and the Li\(_4\)Ti\(_5\)O\(_{12}\) obtained with CTAB has the lowest resistance, which is consistent with the difference in reversible capacities. The difference in the resistance can be ascribed to the difference in the BET surface areas among three Li\(_4\)Ti\(_5\)O\(_{12}\) electrodes. A higher BET surface area of the active material (here Li\(_4\)Ti\(_5\)O\(_{12}\)) of the electrodes would lead to a greater contact surfaces among the active material particles, the conductive additive (acetylene black here), and the electrolyte. Hence, a lower resistance can be achieved [12, 14, 29].

IV. CONCLUSION

Nanosized spinel Li\(_4\)Ti\(_5\)O\(_{12}\) powders have been synthesized by a polymerization based method using furfuryl alcohol as polymerizable solvent. The pure spinel phase of Li\(_4\)Ti\(_5\)O\(_{12}\) can be obtained at an annealing temperature of 700 °C or higher. The optimal annealing temperature for such a Li\(_4\)Ti\(_5\)O\(_{12}\) powder is 700 °C. The addition of surfactant helps to result in more uniform morphology of the synthesized powders. The optimized synthesis conditions can result in a Li\(_4\)Ti\(_5\)O\(_{12}\) powder with high reversible capacity, high capacity retention and good rate performance.

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