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Short Communication **Microwave-Assisted Sol-Gel Modification of Al- or C-doped** Li₄Ti₅O₁₂ Samples as Anode Materials for Li-ion Batteries

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Pure Li₄Ti₅O₁₂ and Al- or C-doped Li₄Ti₅O₁₂ samples were synthesized by a microwave-assisted solgel method. The structural characterization was performed by X-ray diffraction. The surface morphology was analyzed by scanning electron microscopy. The electrochemical properties were studied by galvanostatic charge and discharge measurements. The results show that after a microwave treatment at 800 °C for 4 h, the size of the particles was 60–70 nm. The crystal structure of Li₄Ti₅O₁₂ was unchanged and the Ti atom position in the sample was replaced by Al or C, and the dispersion of the doped samples was better than the original sample, which is beneficial for the intercalation and deintercalation of Li⁺. The measured electrochemical properties indicated that the discharge capacity of the all samples was stable, with the first discharge capacity of the Al- and C-doped sample higher than the original sample. The first discharge capacity of Li₄Ti₅O₁₂/C was 162 mAh/g, which was closer to the theoretical capacity of Li₄Ti₅O₁₂ (175 mAh/g). After 40 cycle life tests, the discharge capacity could be maintained at 136 mAh/g. The discharge rate capability tests showed that the reversible capacity of Li₄Ti₅O₁₂/C is restored to 150 mAh/g, with a current density loss of 12 mAh/g compared to the initial discharge capacity, indicating its better structural stability.

Keywords: Li₄Ti₅O₁₂; sol-gel method; microwave heating; electrochemical property

1. INTRODUCTION

 $Li_4Ti_5O_{12}$ has received significant attention as an anode material in Li-ion batteries since Ohzuku [1] identified it as a "zero-strain" anode material. $Li_4Ti_5O_{12}$ has good cycling performance, very flat charge/discharge curves and the potential for Li insertion is ~1.55 V [2]. $Li_4Ti_5O_{12}$ has a wide charge/discharge platform of ~1.55 V (vs. Li/Li^+), which avoids the formation of a solid electrolyte interface film and inhibits the deposition of lithium dendrites [3]. This anode material is a likely alternative to carbon for safety reasons [4].

However, $Li_4Ti_5O_{12}$ suffers from poor electrical conductivity and a low lithium diffusion coefficient [5], with a capacity much lower than the carbon anode material [6]. In order to improve the conductivity and increase the capacity, doping with aliovalent metal ions at the Li [7], Ti [8] or O [9] sites is common, as is the incorporation of a second phase with high electronic conductivity [10,11]. The sol-gel method is a mature homogeneous mixing technology [12,13] for preparation of the material with high purity, good uniformity, small particles and so on. The microwave heat treatment method uses the energy provided by an electromagnetic field to cause polarization of the heat-treated material to produce friction, the material temperature rises and causes chemical reactions [14,15]. This technique has the advantages of a short reaction time, low energy consumption, high synthesis efficiency and particle uniformity [16].

In this study, the addition of sucrose and aluminum nitrate to $Li_4Ti_5O_{12}$ is studied by a microwave heating-assisted sol-gel method. The influence of doping on the electrochemical properties of $Li_4Ti_5O_{12}$ is analyzed. The results show that the prepared $Li_4Ti_5O_{12}/C$ presents an improved conductivity, capacity, excellent rate capability and cycling performance.

2. EXPERIMENTAL

2.1. Synthesis

 $Li_4Ti_5O_{12}$ was prepared using a sol-gel method. Typically, 5 ml of butyl titanate was dissolved in 25 ml ethanol, and 2 ml of acetylacetone was added into the solution with a continuous stirring for 10 min. Then, a certain amount of LiNO₃ was dissolved in 30 ml of deionized water and dropped into the above suspension slowly to form a sol. A ratio of n(Li)/n(Ti) = 4:5 was used in the sol, with Li salt over 4% to make up for the high temperature volatilization and continued stirring for 1 h until a gel was formed. After drying and grinding, the precursor dry gel was obtained and placed in a graphite crucible in a microwave field (frequency of 2.45 GHz and power of 1350 W) generated by an LG-2M285 magnetron, and in an air atmosphere heating from 600–850 °C, holding for 20–60 min and the heat treatment product was grinded by a planetary mill to obtain the samples.

The main steps of the Al-doped $Li_4Ti_5O_{12}$ sample were basically the same as for the pure phase $Li_4Ti_5O_{12}$ preparation, a certain amount of Al(NO₃) was added after LiNO₃, the ratio of Ti and Al solution is x:5-x (x = 0.1, 0.2 or 0.3). The sample was stirred for 1 h until gel formation. Drying and grinding was carried out to obtain a precursor dry gel, heating by microwave, heating in the air atmosphere to 600–850 °C, holding for 20–60 minutes and the heat treatment product was grinded using a planetary mill to obtain $Li_4Al_xTi_{5-x}O_{12}$.

For the C-doped $Li_4Ti_5O_{12}$ solution preparation, the main steps were consistent with the preparation of pure $Li_4Ti_5O_{12}$. A certain amount of sucrose was added to the anhydrous ethanol solution of butyl titanate as a carbon source. The ratios of C to $Li_4Ti_5O_{12}$ were 1:17, 1:18, 1:19 and

1:20, and the precursor was heat treated in the microwave oven under the protection of an argon atmosphere. The $C/Li_4Ti_5O_{12}$ sample was obtained after ball milling.

2.2. Materials characterization

The phase structure of the samples was analyzed by X-ray diffraction (XRD). The test conditions were a Cu K α line, a tube voltage of 40 kV, a tube current of 40 mA, a step width of 0.5° and a diffraction angle of $10^{\circ} \le 2\theta \le 80^{\circ}$. The morphology of the powder samples was observed using scanning electron microscopy (SEM).

2.3. Electrochemical measurements

The electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Al}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ were investigated in CR2025 coin-type cells. The working electrodes were composed of an active material, carbon black and polyvinylidenefluoride (8:1:1 in weight) on Cu foil. They were vacuum-dried at 80 °C for 12 h. Battery assemblies were conducted in an argon-filled glove box using a metallic lithium foil as the counter electrode, a Celgard 2400 polypropylene film as the separator and 1 M LiPF₆ in ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate (1:1:1 in volume) as the electrolyte. The charge/discharge properties were tested using a CT-3008 battery test system (Shenzhen Newware Electronics, Ltd.) at room temperature. The tested voltage window and current densities were 1.0–3.0 V and 0.1–2.0 C, respectively.

3. RESULTS AND DISCUSSION

3.1. Optimization of $Li_4Ti_5O_{12}$ synthesis conditions

Figure 1 shows the XRD patterns of the dry gel after 600, 650, 700, 750, 800 and 850 °C, and a holding time of 20 min. They are compared to the standard PDF card (49-0207) of Li₄Ti₅O₁₂ and the standard PDF card for TiO₂ (21-1272) in the ICDD/JCPDS database. After the heat treatment, most of the samples were composed of Li₄Ti₅O₁₂. It can be seen from Figure 1 that when the heat treatment temperature is lower than 750 °C, the diffraction peak intensity is not strong. The diffraction peaks are wide because the heat treatment temperature did not provide sufficient energy to complete the precursor reaction, meaning the product crystallinity is low. When the temperature increases to 800 °C, the line is smooth and sharp, indicating that the crystal is complete, but a weak diffraction peak appears at $2\theta = 27.48^{\circ}$, which is the characteristic peak of rutile TiO₂. The contributor for this phase is in order to maintain the electronic balance and a certain amount of Ti⁴⁺/Ti³⁺ mixed valence states [17]. Ti³⁺ is oxidized to Ti⁴⁺. At the same time, with a Ti element excess, rutile TiO₂ is generated [18].



Figure 1. XRD patterns of Li₄Ti₅O₁₂ synthesized at 600–850 °C.

When the temperature rises to 850 °C, rutile TiO_2 is obviously increased, because when the temperature is higher than 850 °C, Li_2O will volatilize [19]. If the temperature is too high, the atomic counting ratio will undergo a significant change, prone to heterogeneous TiO_2 [20]. It was found that the optimum heat treatment temperature of the sample was 800 °C.

Figure 2 shows the XRD patterns of different microwave heat treatment time synthesis products. It can be seen from Fig. 2 that the main crystal phases of the three different holding time samples are $Li_4Ti_5O_{12}$, including 20, 40 and 60 min. The heat temperature chosen was 800 °C. When the sample was kept for 20 min, the diffraction peak of rutile TiO₂ appeared, which indicated that the holding time was not sufficient and the reaction was not yet complete. When the incubation time was 40 min, no miscellaneous peak appeared, indicating pure phase $Li_4Ti_5O_{12}$. When the time extended to 60 min, a trace of rutile was generated [21], which is because the temperature is higher than 700 °C and Li_2O volatilizes [22]. If the holding time is too long, the sample atomic ratio will change as it is prone to many hybrids. Through the above analysis, we can see that the best holding time of the sample is 40 min.



Figure 2. XRD patterns of Li₄Ti₅O₁₂ synthesized at 800 °C with different sintering times of 20, 40 and 60 min.

3.2. Doping ratio optimization of Al and C

Figure 3 shows the XRD patterns of different Al-doped samples. The ratio of the Ti and Al solution is x:5-x (x = 0.1, 0.2 or 0.3). The three XRD patterns are very similar. $Li_4Ti_5O_{12}$, which is a pure phase after heat treatment, shows that Al is not changed in the $Li_4Ti_5O_{12}$ structure. Since the Ti ion radius is closer to the Al ion radius than the Li⁺ radius, and the Li⁺ radius is small, the Al ion replaces part of the Ti ion to form the solid solution $Li_4Al_xTi_{5-x}O_{12}$. The unit cell parameters of the Al-doped samples are 0.8348, 0.8341 and 0.8356 nm, respectively, which are lower than the standard value of 0.8359 nm, when x = 0.1, 0.2 and 0.3 are calculated by the Scherrer formula:

$$D = \frac{K\gamma}{B \cdot \cos\theta}$$

where *K* is the Scherrer constant, *D* is the average thickness of the crystal grains perpendicular to the crystal plane direction, *B* is the diffraction half peak width of the measured sample, θ is the diffraction angle and γ is the X-ray wavelength with a value of 0.15 nm.

With the increase of the amount of aluminum incorporated, the parameters of the sample cell were reduced, since the radius of the aluminum ions (0.0535 nm) is less than the radius of the titanium ions (0.0605 nm), leading to lattice distortion.



Figure 3. XRD patterns of $Li_4Al_XTi_{5-X}O_{12}$ with different amount of x = 0.1, 0.2 or 0.3, respectively.

Figure 4 shows the XRD patterns of samples doped with different amounts of C. It can be seen that the diffraction peaks of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ appear in the XRD patterns of the four different C doping amounts, and there are no miscellaneous peaks. It is known that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ retains the spinel-type structure after mixing with C [23]. When the mass ratio of C and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is 1:17 or 1:18, the first strong peak of C appears at $2\theta = 26.508^\circ$. However, the peak of C disappeared when the mass ratio of C and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is 1:19 or 1:20. This may be because the doping concentration is too small.



Figure 4. XRD patterns of different doped ratios of C:Li₄Ti₅O₁₂ (1:17, 1:18, 1:19 and 1:20).

3.3. Microstructural characterization

Figure 5 shows the SEM images of different samples obtained by the microwave heat treatment at 800 °C for 40 min. Fig. 5a is pure Li₄Ti₅O₁₂, Fig. 5b is Li₄Al_{0.3}Ti_{4.7}O₁₂ and Fig. 5c is Li₄Ti₅O₁₂ doped with C at 1:17. It can be seen that the particle size of the three samples is less than 100 nm. The shape of the pure Li₄Ti₅O₁₂ particle is not obviously because of the reunion. However, it makes a significant difference after doping. The edge of the particle becomes white, this is because the electron beam gather at the edge of the particle. This phenomenon indicates that the agglomeration of the sample particle is improved. The partial magnification is from the high magnification field emission electron microscopy. It can be seen from Fig. 5 that the size of the sample particles is ~60-70 nm, which is better than that reported [24–27], such as a conventional solid state reaction with a doping Al particle size of 0.3–0.4 μ m [28]. Li₄Ti₅O₁₂ was prepared through a sol-gel method with Li₄Ti₅O₁₂ particle sizes of 400–700 nm [29]. The hybrid microwave synthesis of Li₄Ti₅O₁₂ produced connected grains and their average size was $\sim 1 \ \mu m$ [30]. In this study, we use sol-gel synthesis for the precursor, which effectively reduces the initial grain size. Furthermore, the microwave method was used for heat treatment. Compared with ordinary methods, shortening the heating time limits the growth of particles. Therefore, the size of the particles prepared by the microwave-assisted sol-gel method used in this study is much smaller than others.

The undoped samples show a certain degree of agglomeration. This phenomenon is also observed in ref. [31] and the distribution of the particles of Al and C is better, indicating that the doping makes the distribution of particles more uniform. The dispersion of the particles is better and the structure is loose, which is beneficial to the intercalation and deintercalation of Li⁺, thus improving the electrochemical performance of Li₄Ti₅O₁₂ [32–34].



Figure 5. SEM images of the different samples: (a) $Li_4Ti_5O_{12}$; (b) $Li_4Ti_5O_{12}$ /Al and (c) $Li_4Ti_5O_{12}/C$.

3.4. Electrochemical performance



Figure 6. First galvanostatic charge and discharge curves of different samples.

Figure 6 shows the first charge and discharge curves of the samples microwave heat-treated at 800 °C for 40 min. The current density is 0.2 mA/cm^2 and the voltage range is 1–3 V. It can be seen from the figure that the three samples have a relatively stable voltage platform. Their charge voltage platform is ~1.6 V and the discharge voltage platform is ~1.5 V. This is consistent with the

characteristic of $Li_4Ti_5O_{12}$. It is worth noting that the discharge capacity of C-doped $Li_4Ti_5O_{12}$ is 152 mAh/g, which is better than that of the pure material (135 mAh/g) and Al-doped samples (138 mAh/g). The rising capacity of the C-doped sample can be explained by more Li being embedded than others sample. However, it is unusual that the capacity of the Al-doped samples is also rising, which has not been found in previous studies.

Figure 7 shows the cycling performance of the different samples. The initial discharge capacity of the undoped sample is 138 mAh/g, lower than the theoretical value of 175 mAh/g. The first Coulomb efficiency is 90.2%. The initial discharge capacity of the Al-doped sample is 140 mAh/g and the first Coulomb efficiency is 92.3%. The initial discharge capacity of the C sample is 162 mAh/g and the first Coulomb efficiency is 94.5%. All three samples show a stable discharge capacity during cycling. It is noticed that the discharge capacity of Li₄Ti₅O₁₂/Al is almost the same as the pure sample after 40 cycles. However, in similar works [29, 35], it was found that the discharge capacity of Li₄Ti₅O₁₂ after Al doping is reduced. This significant difference may be the result of the smaller particle size in our work. In general, doping improves the initial charge-discharge capacity and Coulomb efficiency of Li₄Ti₅O₁₂, and the microwave-assisted sol-gel modification shows a great advantage in particle size control.



Figure 7. Discharge capacity and cycle life for different samples.

Figure 8 shows the rate performance of the different samples. The charge-discharge current density of all samples is 33.5 mA/g (0.1 C). The current rate is 0.1, 0.2, 0.5, 1 and 2 C, respectively. Charge-discharge cycles under each current density are five times, and finally, charge-discharge cycle five times under a low current density at 0.1 C. As the current rate increased, the discharge capacities of the three samples decreased gradually. The discharge capacities of Al-doped $Li_4Ti_5O_{12}$ are better than pure samples, second only to C-doped $Li_4Ti_5O_{12}$. According to the size effect of nanomaterials, a small size can bring a small diffusion activation energy [19]. That means the microwave-assisted solgel modification can not only reduce the particle size, but also improve the diffusion process of Li ions.



Figure 8. Rate capability of different samples at different current densities (1 C = 335 mA/g).

4. CONCLUSIONS

1) Al and C are doped into $Li_4Ti_5O_{12}$ by a microwave assisted sol-gel method. The phase composition and grain size at different process parameters were compared through X-ray diffraction. In this work, the best process parameters of heat treatment are 40 min and 800 °C. The best doping ratios of Al and C are 0.3:5 and 1:18, respectively.

2) The $Li_4Ti_5O_{12}$ sample shows good crystallinity after doping and the particles size is ~60–70 nm. It is indicated that the microwave-assisted heating inhibit the growth of the particles effectively. The crystal structure of $Li_4Ti_5O_{12}$ is unchanged and the dispersion of the doped Al or C sample is better than the original sample, which may be beneficial to the intercalation and deintercalation of Li^+ .

3) The electrochemical performance of the $Li_4Ti_5O_{12}/C$ sample was better than Al-doped and pure $Li_4Ti_5O_{12}$. The first discharge capacity of the $Li_4Ti_5O_{12}/C$ was 162 mAh/g, which was closer to the theoretical capacity of $Li_4Ti_5O_{12}$ (175 mAh/g). After 40 cycles, the discharge capacity can be maintained at 136 mAh/g. The rate capability tests shows that the reversible capacity of the $Li_4Ti_5O_{12}/C$ is restored to 150 mAh/g, and it has a loss current density of 12 mAh/g compared to the initial discharge capacity, indicating that it has better structural stability.

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