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Effects of carbon sources on electrochemical performance of Li₄Ti₅O₁₂/C composite anode materials

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Abstract: Li₄Ti₅O₁₂/C composite materials were synthesized by two-step solid state reaction method with glucose, sucrose, and starch as carbon sources, respectively. The effects of carbon sources on the structure, morphology, and electrochemical performance of Li₄Ti₅O₁₂/C composite materials were investigated by SEM, XRD and electrochemical tests. The results indicate that carbon sources have almost no effect on the structure of Li₄Ti₅O₁₂/C composite materials. The initial discharge capacities of the Li₄Ti₅O₁₂/C composite materials are slightly lower than those of as-synthesized Li₄Ti₅O₁₂. However, Li₄Ti₅O₁₂/C composite materials show better electrochemical rate performance than the as-synthesized Li₄Ti₅O₁₂. The capacity retention (79%) of the Li₄Ti₅O₁₂/C composite materials with starch as carbon source, is higher than that of Li₄Ti₅O₁₂/C composite materials with glucose and sucrose as carbon source at current rate of 2.0*C*.

Key words: lithium-ion battery; anode material; Li₄Ti₅O₁₂; carbon; electrochemical performance

1 Introduction

Over the past few years, a surging demand for portable electronics and hybrid electric vehicles has increased the production of lithium-ion batteries and supercapacitors [1−2]. Spinel lithium titanate (Li₄Ti₅O₁₂) is demonstrated as the most potential candidate for the anode materials in high power lithium-ion batteries as well as hybrid supercapacitors. The active material has a great lithium-ion intercalation and deintercalation reversibility and exhibits several advantages as follows: (1) high columbic efficiency ($>$95% at 1.0*C*) close to the theoretical capacity of 175 mA·h/g; (2) the discharge plateau at 1.55 V vs Li/Li⁺; (3) zero-strain insertion that provides little volume change during charge-discharge; (4) little electrolyte decomposition (little solid electrolyte interface and little gas evolution); and (5) inexpensive raw materials [3−8].

However, the conventional Li₄Ti₅O₁₂ has a defect of poor electrochemical rate performance due to inherent poor Li⁺ diffusion coefficient ($<10^{-6}$ cm²/s) and low electronic conductivity ($< 10^{-13}$ S/cm). So far, two typical approaches have been developed to overcome this problem. One is to improve the intrinsic electronic conductivity by cation doping (V⁵⁺, Mn⁴⁺, Fe³⁺, and Ni²⁺) [9−11]. The other is to synthesize Li₄Ti₅O₁₂ with small particle size by adding conductive additives such as carbon and metal powders [12−14].

To improve the rate performance of Li₄Ti₅O₁₂ materials for lithium-ion batteries in the large-scale application for hybrid electric vehicles, carbon is considered a good electric conductor, which is widely used in lithium-ion batteries. Moreover, carbon can take part in the control of active material particle growth, thus enhancing its conductivity [15−16]. It is important to optimize carbon sources that can lead to excellent electrochemical properties of Li₄Ti₅O₁₂/C composite materials.

In this work, a simple solid-state reaction method was developed to synthesize the Li₄Ti₅O₁₂/C composite materials using three different cheap carbon sources, i.e., glucose, sucrose, and starch. The effects of carbon sources on the Li₄Ti₅O₁₂/C anode electrochemical performances were investigated by charge-discharge, and EIS electrochemical tests.

2 Experimental

The pristine Li₄Ti₅O₁₂ was prepared by solid-state reaction. Li₂CO₃ and TiO₂ powders with purities of 99.0% and 99.5% respectively, were used as the raw materials to synthesize Li₄Ti₅O₁₂. Li₂CO₃ and TiO₂ powders (the molar ratio of Li to Ti is 4.12:5.00) were mixed sufficiently in a rotary mill. After that, the mixtures were dried at 120 ℃ for 12 h in the vacuum oven. The powders were then pre-calcined at 650 ℃ for 8 h and continued to be treated at 800 ℃ for 6 h to form

the crystalline structure of $Li_4Ti_5O_{12}$ powders. The as-synthesized powder was denoted as LTO-P.

The $Li_4Ti_5O_{12}$/C composite materials were prepared as follows: LTO-P and 2% (mass fraction) carbon sources (glucose, sucrose, and starch) were mixed in ethanol solvent and ground in a rotary mill for 2 h. Then, the mixture was dried at 120 ℃ for 8 h. The obtained powders were placed in a tubular furnace and sintered at 800 ℃ for 6 h in N_2 atmosphere, and then cooled to the room temperature. The glucose-coated $Li_4Ti_5O_{12}$/C, sucrose-coated $Li_4Ti_5O_{12}$/C, and starch-coated $Li_4Ti_5O_{12}$/C composite powders were denoted as 4G2, 4S2 and 4F2, respectively.

The structures of the products were determined by an X-ray diffractometer (XRD, D/max-r A type Cu $K_{\alpha1}$, 40 kV, 300 mA, 10°−85°, Japan). The morphologies of the products were observed by a scanning electron microscope (SEM, JEOL JSM−6360LV).

The anode was prepared by mixing 80% (mass fraction) active material, 10% carbon black and 10% polyvinylidene fluoride (PVDF). The mixture was made into slurry by milling using N-methyl-2 pyrrolidene (NMP) as the solvent. The electrodes were formed by coating the slurry onto Cu foils. After drying at overnight 393 K in a vacuum oven, the 2025 coin-type cells were assembled with the as-prepared anode, lithium metal and Celgard 2400 film in an ultrapure argon-filled glove box. The electrolyte was 1 mol/L $LiPF_6$ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1, in mass ratio). The electro-chemical measurements were performed by LAND CT2001A test system between 2.5 and 0.8 V at room temperature. And the EIS measurement at a constant potential of 1.55 V against Li metal electrode, was performed by an electrochemical workstation M273 with the amplitude of an alternating current signal of 5 mV and the frequencies ranging from 100 kHz to 10 mHz.

3 Results and discussion

3.1 XRD analysis

Fig.1 shows the XRD patterns of the $Li_4Ti_5O_{12}$ and $Li_4Ti_5O_{12}$/C composite materials. The XRD results are in good agreement with JCPDS file (card No.49−0207), confirming that pure $Li_4Ti_5O_{12}$ was formed. The diffraction peaks can be indexed on the spinel structure $Li_4Ti_5O_{12}$ with the space group $Fd3m$ and without any impurity phase peaks. No diffraction response of carbon in the XRD patterns is observed since it is in low content and amorphous state [12]. The carbon sources have no effect on the spinel structure of $Li_4Ti_5O_{12}$ during the sintering reaction. The results indicate that carbon is in amorphous form, which is not incorporated in the $Li_4Ti_5O_{12}$ crystal lattice.
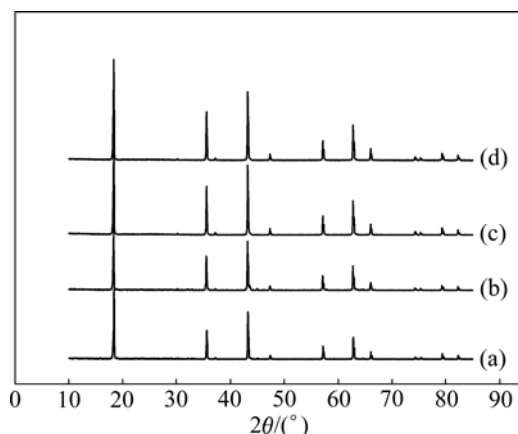

Fig.1 XRD patterns of different samples: (a) LTO-P; (b) 4G2; (c) 4S2; (d) 4F2

3.2 Morphology

The as-synthesized LTO-P has a very white color without any different color dots, while the $Li_4Ti_5O_{12}$/C composite powders are deep gray or black in visual inspection. Scanning electronic micrographs (SEM) of the prepared products are shown in Fig.2. The surface of the as-synthesized LTO-P composite powders is inclined to be smooth, since they agglomerate from independent sphere-like micro particles. However, the surface of $Li_4Ti_5O_{12}$/C composite powders is coarse and the particles of the $Li_4Ti_5O_{12}$/C composite materials appear to be finer because of the existence of carbon. The carbon can exist in the place among the $Li_4Ti_5O_{12}$ particles and the surface of $Li_4Ti_5O_{12}$ particles. Such a carbon network can lead to electrical interparticle connection, which results in improving the electronic conductivity. However, it can be seen that the SEM images of $Li_4Ti_5O_{12}$/C composite materials from glucose, sucrose, and starch have no distinct difference. Further investigation will be performed by TEM analysis.

3.3 Electrochemical performance

The electrochemical performance in terms of initial charge−discharge of $Li_4Ti_5O_{12}$ and $Li_4Ti_5O_{12}$/C composite materials are shown in Fig.3. It can be seen that the charge-discharge plateau is quite flat. The discharge plateau potential and charge potential are about 1.53 and 1.57 V, respectively. Moreover, it can be seen that the coulomb efficiency of all the products are close to 100%, which suggests that the products have good reversibilty. In addition, the initial discharge capacity of $Li_4Ti_5O_{12}$ is 168.7 mA·h/g, slightly higher than that of $Li_4Ti_5O_{12}$/C composite materials. The initial discharge capacities of 4G2, 4S2, and 4F2 are 154.3, 158.6, and 159.0 mA·h/g, respectively.

Fig.4 shows the cycling performance of $Li_4Ti_5O_{12}$ and $Li_4Ti_5O_{12}$/C composite materials at various charge−discharge current rates of 0.1, 0.2, 0.5, 1.0 and 2.0C. This
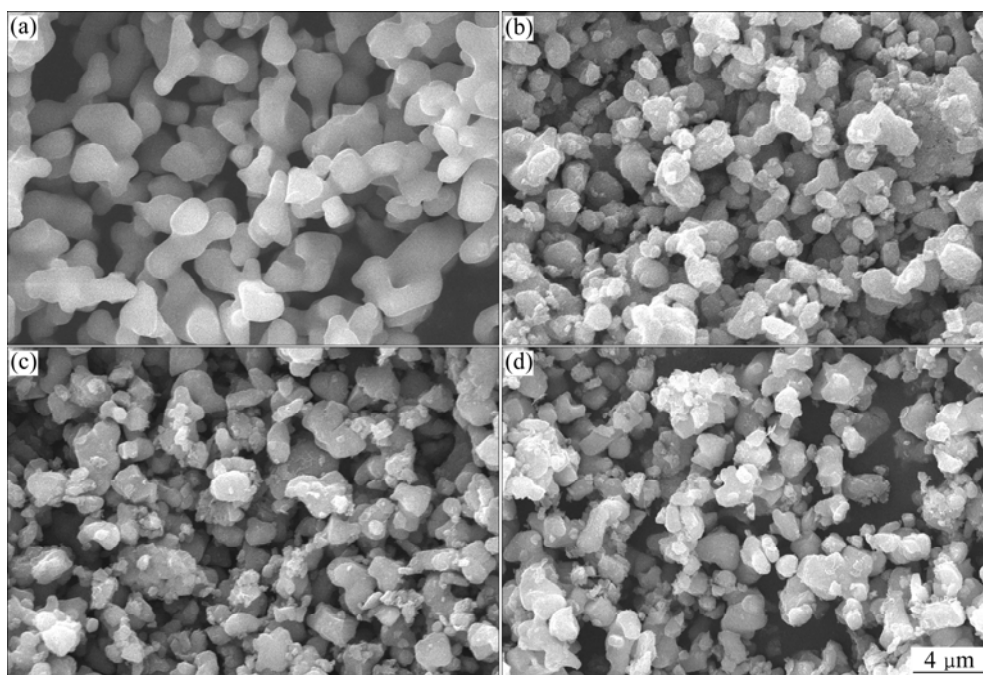
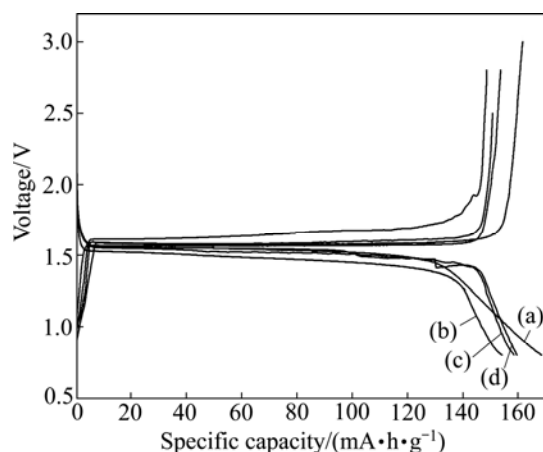**Fig.2** SEM images of different samples: (a) LTO-P; (b) 4G2; (c) 4S2; (d) 4F2

Fig.3 Charge−discharge profiles of $Li_4Ti_5O_{12}$ and $Li_4Ti_5O_{12}/C$ composite materials: (a) LTO-P; (b) 4G2; (c) 4S2; (d) 4F2
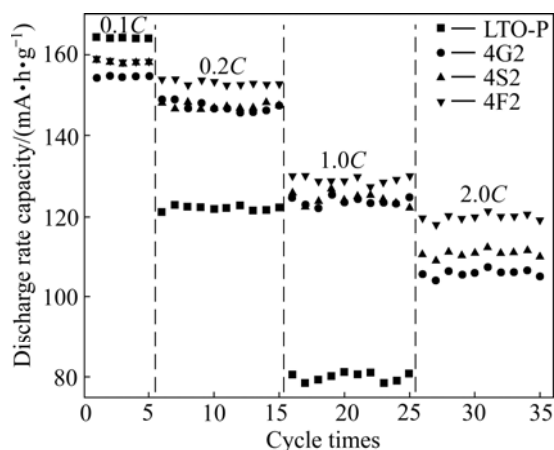
Fig.4 Cycling behaviors of $Li_4Ti_5O_{12}$ and $Li_4Ti_5O_{12}/C$ composite materials at different discharge current rates: (a) LTO-P; (b) 4G2; (c) 4S2; (d) 4F2

result shows high discharge rate capability and good cycling stability of the $Li_4Ti_5O_{12}/C$ composite material. It is related to the high electrical conductivity of $Li_4Ti_5O_{12}/C$ composite materials [12, 15]. When the charge−discharge current rate is $0.1C$, the discharge capacity of $Li_4Ti_5O_{12}/C$ composite materials is lower than that of $Li_4Ti_5O_{12}$. With the increase of the discharge current rate, when the current rate exceeds $0.2C$, the discharge capacity of $Li_4Ti_5O_{12}/C$ composites is superior to that of $Li_4Ti_5O_{12}$. Among the $Li_4Ti_5O_{12}/C$ composite materials, it can be seen that the capacity retentions of 4G2, 4S2, and 4F2 are almost equal. However, when the discharge current rate is $2C$, 4F2 shows the highest capacity retention of 79%. The capacity retentions of 4G2 and 4S2 are 68% and 72%, respectively.

To further investigate the difference of electrochemical performances of the three $Li_4Ti_5O_{12}/C$ composite materials and understand the carbon coating effect in more detail, EIS measurements were carried out in order to compare the conductivity of the three $Li_4Ti_5O_{12}/C$ composite materials. The Nyquist plots of 4G2, 4S2, and 4F2 are depicted in Fig.5. An intercept in Re Z axis in high frequency corresponds to the ohmic resistance (R_Ω), which represents the resistance of the electrolyte. The depressed semicircle in the high frequency range is related to the Li-ion migration resistance (R_{ct-C}) through carbon layer formed on the anode surface. The second semicircle in the middle frequency range indicates the charge transfer resistance (R_{ct}). The inclined line in the lower frequency represents the Warburg impedance, which is associated with Li-ion
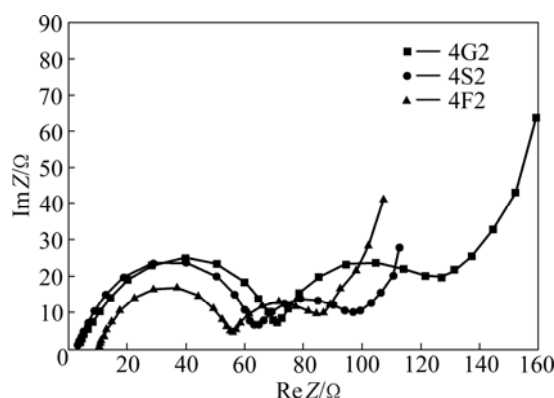
Fig.5 Nyquist plots for different samples (Z is impedance of sample): (a) 4G2; (b) 4S2; (c) 4F2

diffusion in the $Li_4Ti_5O_{12}$ particles. It is found that the migration resistance (R_{ct-C}) through carbon layer and charge transfer resistance of 4F2 are smaller than those of the 4S2 and 4G2.

This indicates that the coating layer obtained from the starch enhances the electrical contacts between $Li_4Ti_5O_{12}$ particles better than glucose and sucrose. Considering the resistance, the $Li_4Ti_5O_{12}/C$ composite materials from starch show the lowest resistance, suggesting that the carbon greatly improves the performance of the active materials.

Therefore, the $Li_4Ti_5O_{12}/C$ composite materials from starch show high initial capacity, good rate capability indicating the promising anode material for lithium-ion battery.

4 Conclusions

(1) Using glucose, sucrose, and starch as carbon sources, $Li_4Ti_5O_{12}/C$ composite materials are obtained by heating the mixture of carbon sources and the spinel $Li_4Ti_5O_{12}$ firstly synthesized by a solid-state reaction method with two-step calcination.

(2) The XRD results show that $Li_4Ti_5O_{12}/C$ composite materials show the spinel structure and carbon have almost no effect on the structure of $Li_4Ti_5O_{12}/C$ composite materials.

(3) The initial discharge capacity of the $Li_4Ti_5O_{12}/C$ composite materials is slightly lower than that of the as-synthesized $Li_4Ti_5O_{12}$. The initial discharge capacities of 4G2, 4S2, 4F2 are 154.3, 158.6, and 159.0 mA·h/g, respectively.

(4) $Li_4Ti_5O_{12}/C$ composite materials show better electrochemical rate performance than as-synthesized $Li_4Ti_5O_{12}$. The capacity retention (79%) of the $Li_4Ti_5O_{12}/C$ composite materials using the starch is higher than that of glucose and sucrose under $2.0C$ rate, indicating the promising anode material for lithium-ion battery.

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