Research Article

Electrochemical Characterization of Li$_4$Ti$_5$O$_{12}$/C Anode Material Prepared by Starch-Sol-Assisted Rheological Phase Method for Li-Ion Battery

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1. Introduction

Lithium ion batteries have been promising to be used in electric vehicle (EV) or hybrid electric vehicle (HEV). Currently, graphite was widely used as anode material for commercial Li-ion batteries in cell phones, laptops, and cameras [1]. However, its performance has not been satisfactory for applications in power systems which require frequent high rate charge/discharge such as in EV or HEV [2, 3]. Owing to the low lithium intercalation voltage of approximately 0.1 V (versus. Li/Li$^+$), lithium metal is easily deposited on the surface of graphite anode forming dendritic lithium particularly during fast charge, resulting in safety issue [2, 4]. Spinel Li$_4$Ti$_5$O$_{12}$ has acquired much attention as alternative anode to graphite in Li-ion batteries, due to its excellent reversibility, zero-strain structure, and high lithium ion mobility in the Li$_4$Ti$_5$O$_{12}$ lattice [5~7]. Especially, the material has a high Li-insertion voltage operating at 1.55 V (versus. Li/Li$^+$), which could hinder dendritic lithium formation [1, 5]. However, the low electronic conductivity (10$^{-13}$ S cm$^{-1}$) of Li$_4$Ti$_5$O$_{12}$ has been the main obstacle limiting rate performance of the material [6].

To improve electronic conductivity and electrochemical performance of Li$_4$Ti$_5$O$_{12}$, extensive works have been taken to address the issue, and the common strategies are to reduce particle size [4, 5], coat conductive material on the surface of Li$_4$Ti$_5$O$_{12}$ [2, 6, 7], or dope with other metal ions [8, 9]. Reducing particle size can shorten lithium ion diffusion distance and enhance both the electrode capability of Li storage and kinetics; thus the rate capability and electrochemical performance of electrode material can be improved [10]. Various metal ions such as Ni$^{3+}$, Ca$^{3+}$, Ta$^{5+}$, V$^{5+}$, and Mg$^{2+}$ were employed in doping to substitute a small quantity of Li$^+$ or Ti$^{4+}$ to improve the electronic conductivity and rate capability [8, 11–13]. Coating conductive materials on the surface of Li$_4$Ti$_5$O$_{12}$ can improve surface conductivity and reduce contact resistance [2]. Conductive materials (carbon black, carbon nanotubes, grapheme, Ag, Cu, and Sn [6, 10, 14, 15]) have been reported to be used to modify the electric conductivity of Li$_4$Ti$_5$O$_{12}$.
Many kinds of carbon have been examined as coating source in synthesis of Li$_4$Ti$_5$O$_{12}$/C composite material with excellent electrochemical performance by conventional methods (e.g., solid state reaction and sol-gel methods) [3, 16, 17]. Starch is not only a good template in synthesis of various function materials with excellent electrochemical performance [18, 19] but also a good carbon source of coating to improve electric conductivity and reduce particle size [20]. Starch-sol-assisted rheological phase method has been developed to synthesize LiFePO$_4$/C composite [20]. However, to the best of our knowledge, synthesis of Li$_4$Ti$_5$O$_{12}$/C composite has not been reported previously by using this method. In this work, we have used inexpensive starch as carbon source and adopted rheological phase method to prepare high-capacity Li$_4$Ti$_5$O$_{12}$/C material. The composite was characterized by XRD, SEM, and TG techniques, and galvanostatic charge/discharge and EIS methods were used to examine electrochemical performance. The results show that carbon is cohesively coated on the surface of Li$_4$Ti$_5$O$_{12}$, and the composite has demonstrated high rate performance with good cycle stability when it was tested as anode in Li-ion batteries.

2. Experimental

2.1. Preparation of Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$/C. The starting raw materials, TiO$_2$-anatase (Aldrich), LiOH (Aldrich), and starch, were analytical grade and used without further purification. Firstly, the soluble starch (3.0 g starch/0.02 mol Li$_4$Ti$_5$O$_{12}$) was mixed with appropriate amount of deionized water; the resultant mixture was heated initially at 110°C until the solution became transparent under stirring in oil bath. Then the starch sol was mixed with stoichiometric amount of LiOH and TiO$_2$ (molar ratio of Ti:Li = 4.2:5) under vigorous agitation to obtain a solid-liquid rheological body, which appears to be a mushy slurry. Finally, the mushy slurry was transferred to tubular furnace and heated at the rate of 5°C min$^{-1}$ to 850°C and sintered at 850°C for 4 h in N$_2$ atmosphere and then cooled to room temperature to obtain a grey Li$_4$Ti$_5$O$_{12}$/C powder. For comparison, pure Li$_4$Ti$_5$O$_{12}$ without carbon coating was synthesized by solid state method, which was prepared by mixing TiO$_2$-anatase and LiOH (mole ratio of Li:Ti = 4.2:5); the mixture was heated at 850°C for 4 h in air to obtain well-crystallized white powder Li$_4$Ti$_5$O$_{12}$.

2.2. Electrode Fabrication. The electrochemical characterization was carried out by galvanostatic charge and discharge using a two-electrode type of 2025 coin cell. The working electrode was prepared with 84 wt.% active material Li$_4$Ti$_5$O$_{12}$ or Li$_4$Ti$_5$O$_{12}$/C, 10 wt.% super-P-Li carbon black, and 3 wt.% CMC (carboxymethyl cellulose sodium), and 3 wt.% SBR (styrene butadiene rubber) dissolved into deionized water to form mixed slurry. The slurries were dispersed in a planetary mixer and then spread uniformly on an aluminum foil by using doctor blade. Finally, the laminates were dried under vacuum at 100°C for 24 h before electrochemical evaluation. Electrode disks were punched out of the laminates for the half-cell. The cells were assembled based on the configuration of Li/electrolyte/Li$_4$Ti$_5$O$_{12}$/C (or Li$_4$Ti$_5$O$_{12}$) with a liquid electrolyte (1.3 M LiPF$_6$ in a mixture (1:3 by mass) of ethylene carbonate and dimethyl carbonate), metallic Li foil was used as the counter electrode in 2-electrode cell, and Celgard 2320 was used as the separator; the coin cells were assembled in a glove box (Braun, [O$_2$] < 1 ppm, [H$_2$O] < 1 ppm) filled with pure argon.

2.3. Characterization. The samples of Li$_4$Ti$_5$O$_{12}$/C and Li$_4$Ti$_5$O$_{12}$ were characterized by X-ray diffraction (XRD) with D/Max-III A instrument using Cu Ka ($\lambda = 1.54056$ Å) as radiation source at a scanning rate 2° min$^{-1}$ for 20 in the range of 10°–80° to identify the structure and phase. The morphologies of the samples were investigated by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, JEOL JEM-2010). Thermogravimetric and differential thermal analyses (TG/TGA) were performed on a TG/TGA instrument (Pyris Diamond) using a heating rate of 5°C/min.

The charge/discharge behavior and rate capacity of the cell were tested at various current densities in the range 1.0–2.0 V using land battery test station at room temperature. The AC impedance spectrum was employed at a constant potential of 1.55 V against Li metal electrode, the voltage amplitude of the AC signal was 5 mV, and the frequencies were scanned from 100 kHz to 100 mHz by using an electrochemical workstation IM6ex (Zahner).

3. Results and Discussion

3.1. Physicochemical Characterization. Figure 1 presents the XRD pattern of the two samples. Figure 1(a) is for the pure Li$_4$Ti$_5$O$_{12}$ prepared by solid-state method, and Figure 1(b) is for the Li$_4$Ti$_5$O$_{12}$/C composite synthesized by starch-sol-assisted rheological phase method. According to JCPDS file...
Figure 2: SEM images of pure Li$_4$Ti$_5$O$_{12}$ (a) and Li$_4$Ti$_5$O$_{12}$/C composite (b). HRTEM image and the inset (c) clearly show the carbon coating on the Li$_4$Ti$_5$O$_{12}$ crystallites.

no. 49-0207, all the main peaks are investigated, which correspond to Li$_4$Ti$_5$O$_{12}$ without other impurity phases. The pattern could be indexed to spinel structure with Fd3m space group. The lattice parameter of “a” for Li$_4$Ti$_5$O$_{12}$/C composite is 8.359 Å, which is close to the reported value of the literature [21]. No carbon diffraction peak is observed in Figure 1(b) since the carbon generated from starch is in low content, and it is amorphous, which suggests that the addition of starch in the precursor does not influence the formation of spinel Li$_4$Ti$_5$O$_{12}$ crystal during heat treatment in the N$_2$ atmosphere. It was found through Scherrer equation that the average crystallite size was about 400–600 nm.

For comparison, Figure 2(a) shows the SEM image of pure Li$_4$Ti$_5$O$_{12}$ synthesized by solid-state method. The Li$_4$Ti$_5$O$_{12}$ crystallites have smooth sphere-like shape morphology, large blocks of particles at about 700 nm–1 μm in size. Figure 2(b) presents SEM image of the Li$_4$Ti$_5$O$_{12}$/C composite. It is seen that the carbon uniformly covers the surface of Li$_4$Ti$_5$O$_{12}$ and links together forming a carbon network. The particles of Li$_4$Ti$_5$O$_{12}$/C have a relatively less extent of agglomeration, and the average particle size is about 500 nm, which is consistent with the result from XRD calculation. Figure 2(c) shows the high-resolution TEM image of the Li$_4$Ti$_5$O$_{12}$/C composite; it is clearly seen that the Li$_4$Ti$_5$O$_{12}$ has sphere-like shape and the particle size ranges from 400 nm to 600 nm, consistent with the SEM observation in Figure 2(b). The inset HRTEM also shows a 5 nm thick carbon film coated on the surface of Li$_4$Ti$_5$O$_{12}$ crystallites. Due to the adhesive nature of starch sol, the carbon binds cohesively on the surface of reactants during calcination process, and the heating process further results in decomposition of the starch into a carbonaceous deposit on the surface of Li$_4$Ti$_5$O$_{12}$. The carbonization of starch precursor effectively restrains the growth of Li$_4$Ti$_5$O$_{12}$ crystallites into larger size.

In order to investigate the content of carbon in the composite Li$_4$Ti$_5$O$_{12}$/C, TG/DTA was carried out with 15°C min$^{-1}$ heating rate from 30°C to 1000°C in air. The profile of TG/DTA is given in Figure 3. A broad exothermic peak appears at about 580°C, which is owing to the combustion of the starch into carbonaceous species on the surface of Li$_4$Ti$_5$O$_{12}$, and the TG indicates that the content of carbon in the composite Li$_4$Ti$_5$O$_{12}$/C is about 5%. The weight loss after 700°C is due to the loss of lithium during the high temperature process [22, 23].
3.2. Electrochemical Characterization. The electrochemical performance of Li$_4$Ti$_5$O$_{12}$/C and Li$_4$Ti$_5$O$_{12}$ electrodes was examined in coin cells with metallic lithium as counter electrode. The cycle behavior of the cell was investigated in the range of 1.0~2.0 V. The initial charge-discharge curves of Li$_4$Ti$_5$O$_{12}$ (a) and Li$_4$Ti$_5$O$_{12}$/C (b) at various charge/discharge rates are compared as shown in Figure 4. At the current density of 0.2C, the initial discharge capacity of Li$_4$Ti$_5$O$_{12}$/C is 171.5 mAh g$^{-1}$, which is very close to its theoretical capacity (175 mAh g$^{-1}$), and at a 20C high rate, the capacity is 110 mAh g$^{-1}$. Furthermore, the profile shows very flat discharge/discharge plateau at around 1.55 V (versus. Li/Li$^+$). However, the initial specific capacity of pure Li$_4$Ti$_5$O$_{12}$ is only about 160 mAh g$^{-1}$ at 0.2C and 34.5 mAh g$^{-1}$ at 20C, the cell voltage is lower, and the polarization increases with the increasing of charge/discharge rate, as it is shown that the plateau voltage difference between charge and discharge is 60 mV at 0.5C and 440 mV at 20C. With carbon-coated Li$_4$Ti$_5$O$_{12}$/C, the polarization was obviously smaller as it is seen that the voltage gap between charge and discharge plateau is narrower as shown in Figure 4(b), and the plateau appears more flat especially at high rates. This improved high-rate discharge ability of Li$_4$Ti$_5$O$_{12}$/C which may be attributed to the facts that (1) the carbon generated from starch was coated uniformly on the surface of Li$_4$Ti$_5$O$_{12}$ resulting in enhanced electrical conductivity and (2) the starch limited the growth of Li$_4$Ti$_5$O$_{12}$ crystallite size during calcination process, which benefits Li$^+$ diffusion with shortened distance in Li$_4$Ti$_5$O$_{12}$.

To investigate the rate capability, the Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$/C have been cycled at various rates from 0.2C to 20C, and the results are presented in Figure 5. The charge and discharge cycles were taken for 5 cycles at each rate. As shown in Figure 5(a), the specific discharge capacity is gradually decreased with increased rates. However, the degree of capacity decay of Li$_4$Ti$_5$O$_{12}$/C sample is in less extent in comparison with the pure Li$_4$Ti$_5$O$_{12}$. At 20C the capacity remains 75% of that at 0.2C for Li$_4$Ti$_5$O$_{12}$/C, but for pure Li$_4$Ti$_5$O$_{12}$ the capacity is about 24% between 20C and 0.2C rates. Figure 5(b) shows the cycle performance of the Li$_4$Ti$_5$O$_{12}$/C electrode at 1C and 20C. The initial specific discharge capacity of Li$_4$Ti$_5$O$_{12}$/C is 168.6 mAh g$^{-1}$ at 1C, and it retains 87% after 500 cycles. At 20C cycle rate, the sample exhibits an initial discharge capacity of 110 mAh g$^{-1}$ in Figure 5(b), and there is no apparent capacity fading in the 1st~1000th cycles at 20C, indicating excellent rate performance of the material. After 2000 cycles, the capacity remains 73% of initial value. Compared to the literature data, the performance of the Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$/C composites synthesized by starch-sol-assisted rheological phase method in this work is superior to those reported in [4, 6, 24–28]. This cycle performance can be ascribed to the fact that the Li$_4$Ti$_5$O$_{12}$ itself has a low volume expansion structure, and the cohesive carbon coating that resulted from the starch sol rheological phase method increased electrical conductivity in Li$_4$Ti$_5$O$_{12}$/C.

EIS technique has been considered as an effective way to identify diffusion phenomena in electronic and ionic conductors. To study conductivities of the Li$_4$Ti$_5$O$_{12}$/C and Li$_4$Ti$_5$O$_{12}$, EIS measurements were carried out at 1.55 V at...
room temperature. The Nyquist plots of Li$_4$Ti$_5$O$_{12}$/C and Li$_4$Ti$_5$O$_{12}$ electrodes as well as the fitting results using an equivalent circuit are given in Figure 6. Both Nyquist plots are composed of a depressed semicircle in high frequency and a straight line in low frequency region in Figure 6(a). The solution resistance $R_s$ of the cell from $Z'$ axis interception at high frequency includes both electrolyte and electrode contact resistance. The charge transfer resistance $R_{ct}$ is determined by the semicircle in the middle frequency range, which is mainly related to the electrochemical reaction at the electrolyte/electrode interface. The straight line in low frequency range is attributed to the Warburg impedance $Z_w$, which is due to the solid-state diffusion of Li$^+$ ions into the bulk of active material. It can be seen from Figure 6(a) that the Li$_4$Ti$_5$O$_{12}$/C electrode displayed a much lower impedance than that of pure Li$_4$Ti$_5$O$_{12}$ which is similarly observed in [16, 29].

The equivalent circuit model is depicted in Figure 6(b), where the $R_s$ and $R_{ct}$ are solution resistance and charge transfer resistance, respectively. CPE is the constant phase-angle element, involving double layer capacitance of the electrolyte-electrode interface. $R_f$ is the surface polarization resistance, and the $C_f$ is the surface capacitance. The equivalent circuit model is well suited to the fitting of experiment data, and the simulation results of the EIS data for the Li$_4$Ti$_5$O$_{12}$/C and Li$_4$Ti$_5$O$_{12}$ electrodes are given in Table 1. It can be seen that the $R_s$ and $R_{ct}$ are much smaller for the Li$_4$Ti$_5$O$_{12}$/C electrode ($R_s = 1.92 \Omega$, $R_{ct} = 24 \Omega$) than for the pure Li$_4$Ti$_5$O$_{12}$ ($R_s = 3.33 \Omega$, $R_{ct} = 107 \Omega$). This result indicates that the carbon coating has enabled easier charge transfer at electrode/electrolyte interface, and the overall battery internal resistance is also decreased. The electrode polarization resistance of Li$_4$Ti$_5$O$_{12}$/C ($R_p = 0.184 \Omega$) is much smaller than that of Li$_4$Ti$_5$O$_{12}$ ($R_p = 1.08 \Omega$), which implies that the carbon reduced the polarization. The results are also consistent with the charge/discharge curves shown in Figure 4. The two values of $Z_w$ are almost identical; this is reasonable since the Li$^+$ diffusion rate in Li$_4$Ti$_5$O$_{12}$ crystal lattice should be independent of carbon coating. The in situ starch sol coating in the synthesis of Li$_4$Ti$_5$O$_{12}$ significantly enhances the conductivity of Li$_4$Ti$_5$O$_{12}$ material. The adhesive conductive carbon coating facilitates electronic conductive paths in the Li$_4$Ti$_5$O$_{12}$ particle surroundings, that is considered a key factor in improving the discharge capacity, rate capability, and cycle life of the Li$_4$Ti$_5$O$_{12}$/C material.

4. Conclusions

With the starch precursor as carbon source, the carbon was cohesively coated on the surface of Li$_4$Ti$_5$O$_{12}$ crystallites in the Li$_4$Ti$_5$O$_{12}$/C composite by using starch-sol-assisted rheological phase method. This synthesis approach is relatively simple and effective to obtain the high electronic conductive material. The electrochemical characterization indicates that the Li$_4$Ti$_5$O$_{12}$/C exhibits high rate capability and long cycle life compared to pure Li$_4$Ti$_5$O$_{12}$ from solid-state method. The Li$_4$Ti$_5$O$_{12}$/C anode shows specific capacity of 168.6 mAh g$^{-1}$ at 1C and 110 mAh g$^{-1}$ at 20C, and the discharge capacity retains 73% after 2000 cycles at 20C cycle rate. The excellent rate capability and cycling performance of Li$_4$Ti$_5$O$_{12}$/C are mainly attributed to the cohesive carbon coating that enhances conductivity and to the intrinsic structural stability of Li$_4$Ti$_5$O$_{12}$ that allows reversible Li$^+$ intercalation in charge-discharge process.

Acknowledgments

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Table 1: EIS simulation parameters of Li4Ti5O12 and Li4Ti5O12/C from the equivalent circuit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rs (Ω cm²)</th>
<th>Rct (Ω cm²)</th>
<th>CPE (S cm⁻²)</th>
<th>W (S¹ cm⁻²)</th>
<th>Rf (Ω cm²)</th>
<th>Cf (S cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li4Ti5O12</td>
<td>3.33</td>
<td>107</td>
<td>2.5 × 10⁻⁴</td>
<td>2.55 × 10⁻⁴</td>
<td>1.08</td>
<td>8.66 × 10⁻⁶</td>
</tr>
<tr>
<td>Li4Ti5O12/C</td>
<td>1.92</td>
<td>24</td>
<td>2.45 × 10⁻⁴</td>
<td>2.2 × 10⁻⁴</td>
<td>0.184</td>
<td>2.72 × 10⁻⁶</td>
</tr>
</tbody>
</table>

Figure 6: EIS Nyquist plots of the Li4Ti5O12 and Li4Ti5O12/C electrode (a) and the corresponding equivalent circuit model that is used to fit the experimental data (b).

References


