Influence of the Carbon Source on the Surface and Electrochemical Characteristics of Lithium Excess Li$_{4.3}$Ti$_5$O$_{12}$ Carbon Composite

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ABSTRACT

We have investigated the preparation and electrochemical characteristics of a lithium excess Li$_{4.3}$Ti$_5$O$_{12}$ carbon composite (Li$_{4.3}$Ti$_5$O$_{12}$/C) with different carbon sources (polyacryl acid, polyvinyl alcohol, and carboxy methyl cellulose sodium). We have prepared the lithium excess Li$_{4.3}$Ti$_5$O$_{12}$/C by a spray-drying method followed by calcining at 800°C in a nitrogen atmosphere. The TEM observations indicated that the surface of the Li$_{4.3}$Ti$_5$O$_{12}$/C particle was clearly covered with an amorphous carbon layer. The Li$_{4.3}$Ti$_5$O$_{12}$/C materials employing polyvinyl alcohol as the carbon source showed the best rate performance with the highest discharge capacity of 117 mAh (g-Li$_{4.3}$Ti$_5$O$_{12}$/C)$^{-1}$ at the 10C rate.

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Keywords: Lithium-Ion Battery, Li$_{4.3}$Ti$_5$O$_{12}$, Spray-Drying, Carbon Source

1. Introduction

The spinel-type Li$_4$Ti$_5$O$_{12}$ (LTO) has been widely investigated as an alternative material to graphite which is conventionally used as a negative electrode material for lithium-ion batteries (LiBs). Compared to graphite (0.085 V vs. Li/Li$^+$), LTO shows a higher operating potential (1.55 V vs. Li/Li$^+$). At this operating potential, lithium metal cannot be deposited. Additionally, LTO does not need a solid electrolyte interface film with a low thermal stability to exhibit a stable charge-discharge performance. Furthermore, the LTO volume change is very low during the charge-discharge cycling, thus LTO shows an excellent cycling performance. As described above, LTO is a much safer electrode material compared to graphite (0.085 V vs. Li/Li$^+$), but LTO has the advantage of safety. To overcome the disadvantage, the synthesis of the LTO materials by sol-gel, spray reaction of the starting materials, etc., have been reported. In order to improve the electrochemical characteristics of LTO, we have prepared the lithium excess carbon composite LTO material (Li$_{4.3}$Ti$_5$O$_{12}$/C) using various carbon sources by a spray-drying method. Furthermore, the electrochemical characteristics of the LTO including charge-discharge cycling tests were examined as the negative electrode material for the LiBs.

2. Experimental

The lithium excess Li$_{4.3}$Ti$_5$O$_{12}$ was prepared by a spray-drying method in a way similar to that previously reported. Li$_2$CO$_3$ (Kanto Chemical Co., 99.0%, 4.3 × 10$^{-2}$ mol) and titanium tetrabutoxide (Ti(OSCH(CH$_3$)$_3$)$_4$, Kanto Chemical Co., 97.0%, 1.0 × 10$^{-1}$ mol) dissolved in ethanol (Wako Pure Chemical Industries, 99.5%, 20 ml) were added to the aqueous solutions consisting of (COOH)$_2$·2H$_2$O (Wako Pure Chemical Industries, 99.5%, 2.0 × 10$^{-1}$ mol) in distilled water (400 ml). The solutions were stirred at 80°C for 3 h, and then spray-dried using a spray dryer (Tokyo Rikakikai Co., Ltd., SD-1000) to obtain the Li$_{4.3}$Ti$_5$O$_{12}$ precursor. For the synthesis of the Li$_{4.3}$Ti$_5$O$_{12}$/C materials, the carbon sources, such as carboxy methyl cellulose sodium (CMC-Na, 10 wt%, 2.40 g), poly acryl acid (PAA, Wako Pure Chemical Industries, Ltd.; average molecular weight, 5,000, 10 wt%, 2.04 g), and polyvinyl alcohol (PVA, Kanto Chemical Co., polymerization abt 2000, 10 wt%, 2.04 g) were added to the aqueous solutions consisting of Li$_2$CO$_3$, Ti(OSCH(CH$_3$)$_3$)$_4$, and (COOH)$_2$·2H$_2$O. The solutions were stirred at room temperature for 3 h, and then spray-dried using a spray dryer to obtain the Li$_{4.3}$Ti$_5$O$_{12}$/C precursors. The Li$_{4.3}$Ti$_5$O$_{12}$/C precursor and the Li$_{4.3}$Ti$_5$O$_{12}$/C precursors were calcined at 800°C for 12 h in air and in a nitrogen atmosphere, respectively. The powder X-ray diffraction (Rigaku Co., Rint 2200, XRD) measurements were performed to identify the synthesized materials. The surface of the samples was examined by transmission electron microscopy (Hitachi, Ltd., H-800, TEM with the accelerating voltage at 200 kV). The specific surface areas of the samples were measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption (BEL Japan, Inc., BEL SORP MINI). The residual
and Li4.3Ti5O12 materials. The prepared Li4.3Ti5O12 XRD patterns of the Li4.3Ti5O12 materials were broadened by the addition of the carbon sources. The diffraction peaks of the Li4.3Ti5O12 materials were calcined at 800°C in (a) air or (b)–(d) nitrogen atmosphere for 12 h.

When assembling the cell, the Li4.3Ti5O12 electrode as the working electrode and a lithium metal foil as the counter electrode, 1.0 mol dm−3 LiPF6 in ethylene carbonate and dimethyl carbonate (30:70 in volume) as the electrolyte, and Celgard 2325 as the separator were used. All cells were cycled in an argon atmosphere.

3. Results and Discussion

Figure 1 shows the XRD patterns of the prepared Li4.3Ti5O12/C materials prepared by the spray-drying method with various carbon sources. (a) no carbon source, (b) CMC-Na, (c) PVA, and (d) PAA. The samples were calcined at 800°C in (a) air or (b)–(d) nitrogen atmosphere for 12 h.

Table 1. Synthesis conditions, a-lattice parameters, residual carbon contents, and BET surface area of the Li4.3Ti5O12/C materials with various carbon sources.

<table>
<thead>
<tr>
<th>No.</th>
<th>Carbon sources</th>
<th>Calcination conditions</th>
<th>a-lattice parameter (nm)</th>
<th>Residual carbon content (wt%)</th>
<th>BET surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>No carbon</td>
<td>800</td>
<td>0.8358(7)</td>
<td>0.00</td>
<td>1.06</td>
</tr>
<tr>
<td>b</td>
<td>CMC-Na</td>
<td>800</td>
<td>0.8359(5)</td>
<td>3.54</td>
<td>3.54</td>
</tr>
<tr>
<td>c</td>
<td>PVA</td>
<td>800</td>
<td>0.8361(9)</td>
<td>6.51</td>
<td>33.74</td>
</tr>
<tr>
<td>d</td>
<td>PAA</td>
<td>800</td>
<td>0.8358(9)</td>
<td>3.98</td>
<td>3.47</td>
</tr>
</tbody>
</table>

The electrochemical measurements were performed using an R2032 coin-type half-cell. The Li4.3Ti5O12/C materials or Li4.3Ti5O12 material were mixed with acetylene black and a polyvinylidene difluoride binder in the weight ratio of 88:6:6. When assembling the cell, the Li4.3Ti5O12/C electrodes or Li4.3Ti5O12 electrode as the working electrode and a lithium metal foil as the counter electrode, 1.0 mol dm⁻³ LiPF6 in ethylene carbonate and dimethyl carbonate (30:70 in volume) as the electrolyte, and Celgard 2325 as the separator were used. All cells were cycled in an argon-filled glove box (Miwa Mfg. Co., Ltd., DBO-1NKP-1U-2). The assembled cells were cycled between 1.2 and 3.0 V at the current densities of 17.5 mA (g-Li4.3Ti5O12/C) at 25°C.

The synthetic conditions, a-lattice parameters, residual carbon amounts, and BET surface areas of the prepared Li4.3Ti5O12/C materials underwent no changes with the addition of the carbon sources, whereas the residual carbon amounts and BET surface areas of the prepared Li4.3Ti5O12/C materials depended on the carbon sources. In particular, the Li4.3Ti5O12/C material employing PAA as the carbon source had the highest BET surface area. This would be due to covering of the surface of the Li4.3Ti5O12/C material with a smooth amorphous carbon layer. However, there are some possibilities that the amorphous carbon layer made from PAA has a porous structure. The further study concerning the residual carbons is necessary.

Figure 2 shows the TEM images of the prepared Li4.3Ti5O12/C materials with various carbon sources. (a) no carbon source, (b) CMC-Na, (c) PVA, and (d) PAA. The samples were calcined at 800°C in (a) air or (b)–(d) nitrogen atmosphere for 12 h.

The Li4.3Ti5O12 materials consisted of spherical particles with diameters of about 1 μm. The Li4.3Ti5O12/C materials employing PVA and PAA as the carbon source had a smaller particle size compared to the Li4.3Ti5O12/C material. The amorphous component in the Li4.3Ti5O12/C materials clearly existed on the surface of the particles. The morphology of the amorphous component depended on the carbon sources. It should be noted that the Li4.3Ti5O12/C material employing PVA as the carbon source was covered with a smooth amorphous layer, whereas the Li4.3Ti5O12/C material employing PAA as the carbon source was covered with a rough amorphous layer. Thus, the particle growth and sintering of the Li4.3Ti5O12/C material would be effectively suppressed by covering the surface of the Li4.3Ti5O12/C material with a smooth amorphous layer.

The synthetic conditions, a-lattice parameters, residual carbon amounts, and BET surface areas of the prepared Li4.3Ti5O12/C and Li4.3Ti5O12 materials are summarized in Table 1. The a-lattice parameters and crystal structures of the prepared Li4.3Ti5O12/C materials underwent no changes with the addition of the carbon sources, whereas the residual carbon amounts and BET surface areas of the prepared Li4.3Ti5O12/C materials depended on the carbon sources. In particular, the Li4.3Ti5O12/C material employing PAA as the carbon source had the highest BET surface area. This would be due to covering of the surface of the Li4.3Ti5O12/C material with a smooth amorphous carbon layer. However, there are some possibilities that the amorphous carbon layer made from PAA has a porous structure. The further study concerning the residual carbons is necessary.

Figure 3 shows the initial charge-discharge curves of the prepared Li4.3Ti5O12/C and Li4.3Ti5O12 materials at various current densities between 0.1C~10C. The Li4.3Ti5O12/C materials employ-
Figure 3. First charge-discharge curves of the Li4.3Ti5O12/C materials with various carbon sources at different current densities; voltage range: 1.2–3.0 V; current density: 0.1C–10C (1C = 175 mA (g-Li4.3Ti5O12/C)⁻¹). (a) no carbon source, (b) CMC-Na, (c) PVA, and (d) PAA.

We have prepared the lithium excess Li4.3Ti5O12/C material using various carbon sources by a spray-drying method. The Li4.3Ti5O12/C materials employing PVA and PAA as the carbon source did not contain any impurity phases, whereas the Li4.3Ti5O12/C material using CMC-Na as the carbon source contained an impurity phase, such as Na0.23TiO2. The morphology of the amorphous component in the Li4.3Ti5O12/C materials depended on the carbon sources. The Li4.3Ti5O12/C materials employing PVA as the carbon source showed the best rate performance with the highest discharge capacity of 117 mAh (g-Li4.3Ti5O12/C)⁻¹ at the 10C rate. The improvement in the suppression of the particle growth and the increase in the BET surface area were effectively caused by the formation of the smooth amorphous carbon layer on the Li4.3Ti5O12/C materials employing PVA as the carbon source, resulting in this enhanced electrode performance. Thus, it was revealed that the electrode performance of the Li4.3Ti5O12/C material would be effectively enhanced by covering the Li4.3Ti5O12/C material surface with a smooth amorphous carbon layer.

Acknowledgment

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References