Structure and electrochemical properties of LiCoO₂ synthesized by microwave heating

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Abstract: Microwave synthesis method was applied to the fast preparation of LiCoO₂. The structure of the synthesized oxides was analyzed by using X-ray diffraction. Only single-phase LiCoO₂ was obtained. Electrochemical behaviors of LiCoO₂ were investigated by charge-discharge cycling properties in the voltage range of 3.00 - 4.35 V (vs Li). The results show that the prepared LiCoO₂ powders calcinated at 900 °C for 120 min exhibit an initial charge and discharge capacity of 168 and 162 mA • h • g⁻¹ at 0.1C current rate, respectively, as compared to 159 and 154 mA • h • g⁻¹ of LiCoO₂ synthesized by conventional means. In addition, more than 95% of the capacity is retained even after 10 cycles. But with the increase of calcinating time, its electrochemical properties deteriorate. Compared with the conventional method, the microwave heating method is simple, fast, and with high energy efficiency.

Key words: microwave synthesis method; Li-ion battery; cathode material; LiCoO₂

1 INTRODUCTION

Since Sony corporation produced the first Li-ion battery in 1990[1], there has been an increasing interest in the development of this kind of power source. As one kind of cathode material, which plays a critical role in a Li-ion battery, LiCoO₂ with some marked advantages, such as high energy density, high discharge voltage, good cycling performance, is produced commercially and used widely in various electronic devices.

In order to get LiCoO₂ material which has good performances in electrochemistry, researchers have tried different ways to synthesize it, such as high temperature solid state synthesis, sol-gel, co-precipitation methods[2-4]. Currently, LiCoO₂ has often been synthesized by conventional route of high temperature solid state synthesis method in factories. This route has some disadvantages such as long reaction time and high energy consuming. In view of these reasons, as well as the continuous need for time-saving, energy-efficient techniques, in the recent few years, microwave synthesis method has been paid attention to by researchers for the advantages in heating and sintering of ceramics and its great flexibility for thermal treatment which influences the microstructure of the materials[5-9]. As for the sintering process, it leads to a product of metastable phase, which is an ensemble that consists of a great number of crystals and pores as well as many grain boundaries[10].

The temperature of microwave reactions is lower than that of conventional methods. The rapidity of the reactions offers excellent condition for retention of metastable phases[11].

Microwaves are electromagnetic radiations, whose frequencies lie in the range from 0.3 GHz to 300 GHz, wavelength range from 1 mm to 1 m. Unlike other preparation methods, microwave radiation is characterized by high volume energy. Its conversion in thermal energy leads to a rapid heating of the whole mass of solid body. Also it is possible to reduce thermal stresses, and the grain size of product[12]. So microwave heating is generally quiet, fast, simple and with high energy efficiency.

The purpose of this paper is to synthesize LiCoO₂ by microwave synthesis method and compare the structure and electrochemical properties of LiCoO₂ prepared by microwave heating method with those of LiCoO₂ prepared by high temperature solid state synthesis method.

2 EXPERIMENTAL

2.1 Synthesis and characterization of LiCoO₂

Li₂CO₃ and Co₃O₄ were used as the raw materials. The powders with a mole ratio of n(Li) : n(Co) = 1.05 : 1.00, were mixed uniformly by ball milling. The mixture was divided into
three parts: (a) calcinated by conventional method at 900 °C; (b) and (c), heated by microwave applied in two different regimes, at 900 °C for 120 min and 900°C for 180 min respectively and conducted in air with a multimode microwave oven (2.45 GHz, 980 W). The crystal structures of the samples were determined by X-ray diffraction (XRD). The morphologies of samples were observed using scanning electron microscopy (SEM).

2.2 Electrochemical measurements

The cathode consisted of 80% (mass fraction) cathode material, 10% carbon black and 10% polytetrafluoroethylene (PTFE). The anode was pure-lithium foil. The electrolyte was 1 mol L⁻¹ LiPF₆ in ethylene/diethyl carbonate (EC/DEC) solution with V(EC)/V(DEC)=1:1. The separator was a Celgard 2400 microporous polyethylene membrane. The charge-discharge experiment was carried out in the range of 3.00 - 4.35 V and at 0.1C current rate. The cells were assembled in a glove-box filled with argon. The charge-discharge curve was obtained by using battery testing system.

3 RESULTS AND DISCUSSION

3.1 Analysis of XRD patterns

Fig. 1 shows the XRD patterns of the samples. Compared with the pattern of sample (a), the crystal structures of samples (b) and (c) belong to layered hexagonal system. The impurity-phase peaks cannot be observed, so pure-phase solid is obtained, which indicates that LiCoO₂ can be synthesized fast by microwave energy. As to XRD patterns of samples (b) and (c), it can be found that the peak intensity increases with increasing calcinating time, as can be seen from the value of I₀₀₃ and I₁₀₄. And the tiny differences in the positions of the main peaks can be detected from the data as follows. (003) peak appears at 2θ = 18.937°, 18.936°, respectively; (104) peak appears at 2θ = 45.259°, 45.255°, respectively. Table 1 lists the relative intensity of main XRD pattern peaks and lattice parameters of the samples. The parameters were calculated by the least square method.

In the XRD patterns, (003) peak indicates the property of layer structure of LiCoO₂, (104) peak indicates the property of the basic units of Co—O—Co which forms this kind layer compound, and the intensity ratio of (003) peak to (104) peak indicates the perfection of crystallization. The larger the value of the intensity ratio, the better the crystallization. Moreover, the distance between two CoO₂ layers is indicated by the value of c/a, the larger the value of c/a, the more flexible to deintercalation-intercalation of Li⁺. From Table 1, it can be concluded that with increasing calcinating time, the crystallization of sample (c) is not as perfect as that of sample (b), which can be explained by the decrease of the value of I₀₀₃/I₁₀₄. At the same time, due to the decrease of the value of c/a, it can be predicted that the deintercalation-intercalation of Li⁺ may become more difficult. As a result, the charge-discharge capacity will be affected. From Table 1, it can also be found that the crystallization of samples (b) and (c) is not as perfect as that of sample (a), which may be related to the characters of microwave energy.

![XRD patterns of samples](image)

Table 1 Relative intensity of main XRD pattern peaks and lattice parameters of samples (a), (b) and (c)

<table>
<thead>
<tr>
<th>Sample</th>
<th>I₀₀₃/CPs</th>
<th>I₁₀₄/CPs</th>
<th>I₀₀₃/I₁₀₄</th>
</tr>
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<tbody>
<tr>
<td>(a)</td>
<td>3 085</td>
<td>1 908</td>
<td>1.616</td>
</tr>
<tr>
<td>(b)</td>
<td>2 374</td>
<td>1 546</td>
<td>1.535</td>
</tr>
<tr>
<td>(c)</td>
<td>2 418</td>
<td>1 579</td>
<td>1.531</td>
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</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>a/nm</th>
<th>c/nm</th>
<th>c/a</th>
</tr>
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<tbody>
<tr>
<td>(a)</td>
<td>0.280</td>
<td>1.402</td>
<td>4.991</td>
</tr>
<tr>
<td>(b)</td>
<td>0.282</td>
<td>1.407</td>
<td>4.992</td>
</tr>
<tr>
<td>(c)</td>
<td>0.281</td>
<td>1.406</td>
<td>4.991</td>
</tr>
</tbody>
</table>

3.2 Morphologies of samples

Fig. 2 shows the SEM micrographs of LiCoO₂ powders. It can be seen that the size of particles of