Synthesis and electrochemical performances of LiCoO$_2$ recycled from the incisors bound of Li-ion batteries

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Abstract
A new LiCoO$_2$ recovery technology for Li-ion batteries was studied in this paper. LiCoO$_2$ was peeled from the Al foil with dimethyl acetamide (DMAC), and then polyvinylidene fluoride (PVDF) and carbon powders in the active material were eliminated by high temperature calcining. Subsequently, Li$_2$CO$_3$, LiOH·H$_2$O and LiAc·2H$_2$O were added into the recycled powders to adjust the Li/Co molar ratio to 1.00. The new LiCoO$_2$ was obtained by calcining the mixture at 850°C for 12 h in air. The structure and morphology of the recycled powders and resulting samples were studied by XRD and SEM techniques, respectively. The layered structure of LiCoO$_2$ synthesized by adding Li$_2$CO$_3$ is the best, and it is found to have the best characteristics as a cathode material in terms of charge-discharge capacity and cycling performance. The first discharge capacity is 160 mAh·g$^{-1}$ between 3.0-4.3 V. The discharge capacity after cycling for 50 times is still 145.2 mAh·g$^{-1}$.

Keywords: LiCoO$_2$; Li-ion batteries; discharge performance; cycling performance

1. Introduction

Since Sony Energytec unveiled the first commercial Li-ion cell, the Li-ion battery has become the most attractive energy source for portable electronic products, such as mobile phones and notebook computers. Layered LiCoO$_2$ is the most widely used positive electrode material in commercial lithium secondary batteries due to the ease of preparation, high electronic conductivity, good rate capability, and excellent cycling performance. The market for Li-ion batteries has expanded rapidly because of the increase in demand for mobile electronics. It is reported that the total sales of the cells have reached more than 10 billion dollars in 2006 [1]. A large amount of cobalt is needed to meet the market demand. Therefore, LiMn$_2$O$_4$ [2-3], LiFePO$_4$ [4-5], and Li(NiCoMn)O$_2$ [6-7] with low or no content of Co have attracted more and more attention because of their low price and abundant resources, and many researchers have paid attention to the recycling of Li-ion battery (LIB) [8-12].

In Ref. [8], it has been reported that cobalt ions extracted from waste LiCoO$_2$ by a nitric acid leaching solution were transformed into cobalt hydroxide on a titanium electrode, and cobalt oxide was then obtained via a dehydration procedure. Zhang et al. [9] reported the recycling of the valuable metals such as cobalt and lithium from the spent Li-ion secondary batteries. Micheal [10] recycled valuable metals from the cell using AEA technology. They just recycle valuable metals from the waste batteries. However, Churl et al. [11] and Contestaile et al. [12] not only recycled the valuable metals but also prepared new LiCoO$_2$ using the recycled valuable metals.

In this paper, a new technology for the recycling and synthesis of LiCoO$_2$ from the incisors bound of a Li-ion battery was studied. The impurities in the cathode, PVDF, and carbon powders were eliminated by calcining at high temperature. A certain amount of Li$_2$CO$_3$, LiOH·H$_2$O, and LiAc·2H$_2$O were added in the recycled powders to adjust the Li/Co molar ratio to 1.00. The structure, morphology and electrochemical behaviors of recycle-synthesized LiCoO$_2$ were studied.

2. Experimental

First, a certain amount of incisors bound was marinated in DMAC, and the aluminum foil was picked out after 3 h. The solution was filtrated after 2 h deposition. Then it was heated at 120°C in air for 12 h. The dry powders were heated at 450°C in air for 2 h, 600°C for 5 h, and then washed with hot water. The structure and morphological property of the recycled powders were characterized with
Li J.H. et al., Synthesis and electrochemical performances of LiCoO₂ recycled from the incisors bound of Li-ion batteries 329

XRD and SEM. The content of Co was analyzed by titrating, and the content of element Li was analyzed by atomic absorption spectrometry.

A certain amount of Li₂CO₃, LiOH·H₂O, and LiAc·2H₂O was added in the recycled powders to adjust the Li/Co molar ratio to 1.00. The final LiCoO₂ was synthesized by calcining at 850°C for 12 h in air, and cooled to room temperature in a tube-furnace.

The powder X-ray diffraction (XRD) (Rint-2000, Rigaku) measurement using Cu Kα radiation was employed to identify the crystalline phase of the synthesized materials. The particle size and morphological property of the LiCoO₂ powders were measured by a scanning electron microscope (SEM) (JSM-5600LV, JEOL) with an accelerating voltage of 20 kV.

The electrochemical characterizations were performed using a CR2025 coin cell. For cathode fabrication, the prepared powders were mixed with 10 wt.% of carbon black and 10 wt.% of polyvinylidene fluoride in n-methyl pyrrolidinone until the blended slurry was obtained. The blended slurries were pasted onto an aluminum current collector, and the electrode was dried at 100°C for 12 h in vacuum. The test cell consisted of the cathode and lithium foil anode coated by a porous polypropylene film, Cellgard 2300 as the separator and the solution consisting of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC) containing 1 mol/L LiPF₆ (EC:EMC:DMC = 1:1:1 in volume) as the electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box. Capacity measurements and cycling tests of the coin-type cells were carried out between 3.0 and 4.3 V at 0.2C rate at 25°C.

3. Results and discussion

Fig. 1 shows the surface morphologies of recycled LiCoO₂ powders. Some small particles with a diameter of 1 μm are observed in Fig. 1. The particles are smashed during the recycling process such as at high temperature calcining and washing stages.

The X-ray diffraction pattern of recycled LiCoO₂ powders is shown in Fig. 2. The diffraction peaks of Co₃O₄ at 31.3° and 36.8° are observed in Fig. 2. The recycled powders were washed and filtrated by hot water to analyze the reaction and validate the reaction results. White deposition appeared after adding CaCl₂ solution into the hot filtrate. The white deposition should be CaF₂. It is reasonably concluded that PVDF gives out HF when it is heated, and the HF reacts with LiCoO₂ to produce Co₃O₄.

Fig. 1. SEM images of the recycled powders ((b) is the further magnification of (a)).

Fig. 2. XRD pattern of the recycled LiCoO₂ powders.

The contents of elements in the recycled powders were analyzed. The results are listed in Table 1. It shows that the contents of C and F are little, and the molar ratio of Li/Co is 0.914, which is not consistent with that of normal LiCoO₂.

<table>
<thead>
<tr>
<th>Element</th>
<th>wt.%</th>
</tr>
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<tbody>
<tr>
<td>Li</td>
<td>6.760</td>
</tr>
<tr>
<td>Co</td>
<td>62.880</td>
</tr>
<tr>
<td>C</td>
<td>0.018</td>
</tr>
<tr>
<td>F</td>
<td>0.021</td>
</tr>
</tbody>
</table>

Table 1. Contents of elements in the recycled LiCoO₂

The SEM images of the LiCoO₂ synthesized by adding different lithium salts are shown in Fig. 3. Compared with Fig. 1, the small particles disappear and the particle size increases. This is because the small particle reunites when the lithium salt melts at high temperature. Also, the powder