Synthesis of LiCoO$_2$ via a facile hydrothermal-assisted route

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A hydrothermal-assisted route was applied to prepare LiCoO$_2$ particles. The starting material prepared by hydrothermal reaction was calcinated at different temperatures from 300 to 800°C in air and LiCoO$_2$ particles with various sizes were obtained. The morphology and size effects of LiCoO$_2$ particle were investigated by X-ray powder diffraction (XRD) and scanning electron microscope (SEM). LiCoO$_2$ prepared by this method was homogenous plate-like particles and the particle size could be easily controlled by calcination temperature.

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1. Introduction

Lithium-ion batteries have been studied for the past several decades because they exhibit the highest specific energy among the rechargeable batteries. Lithium transition metal oxides, such as LiCoO$_2$, LiNiO$_2$, LiMn$_2$O$_4$, LiMnO$_2$, and Li$_2$V$_2$O$_8$ are all high performance cathode materials for lithium-ion batteries. Among them, LiCoO$_2$ is one of the most promising for commercial application because of its favorable features such as high capacity, high specific energy, good power rates, low self-discharge, and excellent cycle life.

The traditional method for synthesizing LiCoO$_2$ is a solid-state reaction at high temperature, which may result in inhomogeneity, abnormal grain growth, and poor control of stoichiometry. In addition, the rate-limiting step is diffusion of atoms or ions through the reactant, the intermediate and the product. Unfortunately, the activation energy for diffusion often presents a barrier for the solid-state reaction. Many advanced chemical processes, such as the sol–gel process, electrostatic spray decomposition, reflux reaction, coprecipitation, water-in-oil emulsion method, electrostatic spray deposition, freeze-drying rotary evaporation, etc. have been developed to prepare highly active materials of high purity and crystallinity. However, synthesis of nanometer particles is generally difficult due to the tendency of particles to agglomerate. In addition, these methods require difficult condition or a large quantity of solvent and organic materials.

To the best of our knowledge, there are few reports concerning synthesis of LiCoO$_2$ via a hydrothermal-assisted route. In this study, a facile hydrothermal-assisted route using cobalt naphthenate was developed to synthesize LiCoO$_2$ with various calcination temperatures for the first time, in which plate-like LiCo(OH)$_2$ prepared by hydrothermal reaction was used to as precursor. Compared with the traditional solid-state reaction, this method has the desirable features of operation at lower calcination temperature and shorter time for calcination. This technique may offer a route to prepare LiCoO$_2$ particles with the size that ranges from nanometer to micrometer.

2. Experimental procedure

2.1 Preparation of plate-like $\beta$-Co(OH)$_2$

15 ml of 6% cobalt naphthenate ([R(CH$_2$)$_3$COO]$^-$Co$^{2+}$, where R is a cyclopetnyl or cyclohexyl group), DIC Co., Ltd.) in xylene solution was added to 15 ml of LiOH solution (15 mol dm$^{-3}$) where distilled water was used as solvent at room temperature. Then, the pink mixed solution was put in a 50 ml teflon-lined autoclave. The autoclave was sealed, and maintained at 160°C for 10 h, and then cooled to room temperature naturally. After centrifugation, the products were obtained and washed with distilled water and absolute ethanol two times, and finally dried in air at 60°C for 6 h.

2.2 Preparation of LiCoO$_2$

Plate-like cobalt hydroxide [$\beta$-Co(OH)$_2$] prepared by hydrothermal reaction was thoroughly mixed with LiNO$_3$ with the molar ratio of 1.0. Then, the mixture was calcinated in the same muffle furnace at different temperatures from 300 to 800°C for 6 h, and then cooled down outside the furnace to room temperature. Afterwards, the products were thoroughly washed with distilled water, and dried at 60°C for 6 h. Commercial cobalt hydroxide [$\beta$-Co(OH)$_2$] (Wako Pure Chemical Industries, Ltd.) was used for comparison.

2.3 Characterization

X-ray powder diffraction (XRD) was performed on a Rigaku X-ray diffractometer (RINT2000V Japan) with graphite-monochromatized Cu K$_\alpha$ radiation ($\lambda = 1.54056$ Å) using 30 mA and 40 kV. The diffraction pattern over the range of 10–70° in 2θ was recorded with a scanning speed of 3°/min. Scanning electron microscopy (SEM) images were taken with JEOL JEM-6500F field emission scanning electron microscope.

3. Results and discussion

Figure 1 shows X-ray powder diffraction (XRD) patterns of the products prepared by hydrothermal reaction calcinated at different temperatures. As shown in Fig. 1(a), all the peaks in the XRD pattern can be indexed to the hexagonal cell of $\beta$-Co(OH)$_2$, and are consistent with reported values (ICPDS 30-4443). When the temperature increased to 300°C, as shown in Fig. 1(b), pure

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CoO$_2$ phase is obtained. LiCoO$_2$ is formed at 500°C. Once the temperature increases, the crystallinity of LiCoO$_2$ is improved. The XRD pattern shows consistency with that reported in JCPDS No. 44-151,$^{21}$ and the diffraction peaks in the XRD pattern have been indexed to the hexagonal form. For example, in the Fig. 1(f), the calculated lattice parameters are $a = 2.8174(9)$ and $c = 14.055(5)$ Å, and these values can be compared with those [$a = 2.8161(5)$ and $c = 14.0536(5)$ Å] reported in the literature.$^{22}$ Therefore, it confirms that the obtained LiCoO$_2$ exhibits a $R-3m$ structure, and the pure phase of LiCoO$_2$ is successfully obtained via the hydrothermal-assisted process. In comparison with the conventional solid-state reaction,$^{23}$ it is found that the required temperature for preparing LiCoO$_2$ particles is significantly reduced from 700 to 500°C by the hydrothermal-assisted process. It is considered to result from the improved homogeneity of constituents and the enhanced reactivity of the hydrothermal-assisted precursors.

Figure 2 shows scanning electron microscopy (SEM) images of the products prepared by hydrothermal reaction calcinated at different temperatures. SEM images [Fig. 2(a)] indicate that precursors prepared by hydrothermal reaction consist of a large quantity of hexagonal plate-like $\beta$-Co(OH)$_2$ with good uniformity. These $\beta$-Co(OH)$_2$ had a mean length of about 500 nm, the corners and edges of the plate-like $\beta$-Co(OH)$_2$ are clearly observed. The average thickness and edge size of these hexagonal $\beta$-Co(OH)$_2$ are about 50 and 200 nm, respectively. Figure 2(b) shows the Co$_3$O$_4$ particles have plate-like shape with a mean length of about 1 μm. For the LiCoO$_2$ prepared at 500°C, as shown in Fig. 2(c), nanometer plate-like particles with the size of 100 nm are obtained. When the temperature increased to 600°C, the size of the plate-like LiCoO$_2$ particles increased to 600 nm [Fig. 2(d)]. Figure 2(e) shows plate-like particles with the size of 2 μm are obtained in 700°C. The size of plate-like particles is abruptly increased up to 10 μm as the temperature exceeded 800°C [Fig. 2(f)]. Therefore, LiCoO$_2$ particles with the size that ranges from nanometer to micrometer can be prepared only by adjusting calcination temperature.

At low temperature (300°C), $\beta$-Co(OH)$_2$ was oxidized by the oxygen in the air and transformed into Co$_3$O$_4$. When the temperature increased to 400–500°C, plate-like LiCoO$_2$ nanoparticles could be obtained by reacting with LiNO$_3$ [Fig. 2(c)]. A crystal growth process at high temperature (600–800°C), growth kinetics were favored and thus the particles grew in the shape of plate-like with a broader particle size distribution at higher temperatures, as shown in Figs. 2(d)–2(f). At lower temperature (300°C), the particles kept the same plate-like shape as the precursor $\beta$-Co(OH)$_2$ with a narrower particle size distribution, as shown in Fig. 2(b).
For comparison, commercial $\beta$-Co(OH)$_2$ was used as precursor, instead of hydrothermal-precipitated $\beta$-Co(OH)$_2$. The full width at half maximum (FWHM) of the peaks was obviously increased in the Fig. 3(a) compared to Fig. 1(a), which is the result of reduced crystallinity. Therefore, commercial $\beta$-Co(OH)$_2$ was lower crystallized than $\beta$-Co(OH)$_2$ prepared by hydrothermal reaction. Figure 3 shows X-ray powder diffraction (XRD) patterns of the commercial $\beta$-Co(OH)$_2$ calcined at different temperatures. Similar results can be obtained when compared to the results of Fig. 1.

Figure 4 shows scanning electron microscopy (SEM) images of the commercial $\beta$-Co(OH)$_2$ calcined at different temperatures. Figure 4(a) indicates that commercial $\beta$-Co(OH)$_2$ precursors consist of nanoparticles with the size of 80 nm. Although they have similar morphologies, the crystallinities are poorer than those of hexagonal plate-like $\beta$-Co(OH)$_2$ precursors with a mean length of 500 nm prepared by hydrothermal reaction, as shown in Fig. 1. Figure 4(b) shows the $\text{LiCoO}_2$ nanowires with a mean length of about 100 nm. However, the $\text{LiCoO}_2$ prepared from commercial $\beta$-Co(OH)$_2$ is not plate-like morphology and less uniform in Figs. 4(c)–4(f) compared to results of Figs. 2(c)–2(f). The particle size increased from nanometer to micrometer with the calcination temperature.

Consequently, uniform fine particles prepared by hydrothermal reaction can produce particles with homogeneous morphology and size even by the solid-state reaction.

4. Conclusions

In this paper, a facile hydrothermal-assisted route was adopted to prepare nanometer and micrometer LiCoO$_2$ for lithium-ion batteries. Plate-like LiCoO$_2$ particles were easily obtained with homogeneity and narrow particle size distribution using plate-like $\beta$-Co(OH)$_2$ prepared by hydrothermal reaction as reaction precursor. While, in the case of commercial $\beta$-Co(OH)$_2$ precursors, only LiCoO$_2$ particles which have not plate-like morphology were obtained. The particle size of the LiCoO$_2$ particles increases with the increasing preparation temperature. The dependence of electrochemical performance of LiCoO$_2$ on the particle size is under investigation.

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