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Microstructural development and electrochemical characteristics of lithium cobalt oxide powders prepared by the water-in-oil emulsion process

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Abstract

Lithium cobalt oxide ($LiCoO_2$) powders, utilized as cathode materials in lithium–ion secondary batteries, have been synthesized through the emulsion process. When the emulsion-derived precursors are calcined at elevated temperatures, the amounts of residual Co_3O_4 and organic species decrease and the crystallinity of $LiCoO_2$ gradually improves with a rise in the calcination temperature. After calcination at 800 °C for 1 h, monophasic $LiCoO_2$ powders with a $R\bar{3}m$ structure are successfully obtained. Compared to the traditional solid-state reaction, the emulsion process not only significantly curtails the reaction time to prepare $LiCoO_2$, but also reduces the particle size. In the electrochemical test, both the specific discharge/charge capacity and the coulomb efficiency of $LiCoO_2$ increase with a rise in the calcination temperature. Increasing the calcination temperature results in the formation of pure $LiCoO_2$ without residual reactants, and also enhances the crystallinity of $LiCoO_2$ as well as the ordering arrangement of lithium and cobalt cations in the layered structure, thereby facilitating the intercalation and deintercalation of lithium ions. As a result, the combination of the emulsion method with proper calcination processes is highly successful in producing $LiCoO_2$ powders having large specific capacity and good cyclic stability along with high coulomb efficiency. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Batteries; Cathodes; Emulsions; $LiCoO_2$; Powders-chemical preparation

1. Introduction

Recently, lithium–ion secondary batteries have attracted considerable attention due to the rapidly growing demands for portable electronic devices. Compared to nickel metal hydride batteries and nickel–cadmium batteries, lithium–ion secondary batteries possess the advantages of large specific capacity, no memory effects, as well as high working voltage, and therefore become the most promising secondary batteries.[1–4] In order to improve the characteristics of batteries, the search for good cathode materials is important. Lithium cobalt oxide ($LiCoO_2$) is the first cathode material utilized in the commercialized lithium-ion secondary batteries. $LiCoO_2$ exhibits higher energy density and more stable cyclability than $LiMn_2O_4$, and better thermal stability than $LiNiO_2$.[5–7] On account of these properties, $LiCoO_2$ is widely applied in various applications and is currently the most commonly used cathode material in lithium–ion secondary batteries.

Considerable efforts have been devoted to investigate the crystal structure and electrochemical properties of $LiCoO_2$,[8–11] ever since it was first synthesized by Johnson et al. in 1958.[12] In general, $LiCoO_2$ powders are prepared by the solid-state reaction using mixed oxides or carbonates as the reactants. However, intensive mixing of the reactants is necessary in this process, and due to insufficient reactivity of the reactants, heating at elevated temperatures for 10–20 h is required.[13,14] The prolonged heating inevitably results in the coarsening of the formed powders, and reduces the electrochemical activity of cathode materials due to the decreased surface area. In addition, it is difficult to maintain the stoichiometry of the obtained $LiCoO_2$ powders due to the loss of lithium species at high temperatures.

To improve the drawbacks of the solid-state reaction, various types of solution processes such as sol-gel process and evaporation method have been developed

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recently for synthesizing $LiCoO_2$ powders.[15–17] The above processes can improve the reactivity of the precursors and control the morphology of $LiCoO_2$ powders; however, the heating time required to prepare $LiCoO_2$ still needs to last for several hours. In our previous study, a new solution method i.e. a water-in-oil emulsion process has been developed for synthesizing $LiCoO_2$ powders.[18] In the emulsion process, an aqueous phase consisting of lithium and cobalt cations is dispersed in an oil phase. By adding appropriate surfactants and using emulsifying treatment, tiny micelles containing the cations are homogeneously distributed in the oil phase and the emulsion is formed. Because of the uniform distribution of the constituents and increased reactivity of the emulsion-derived precursors, merely heating the precursors up to 900 °C without further soaking and quenching in air results in the formation of pure $LiCoO_2$. The $LiCoO_2$ particles formed by the quenching process exhibit a discharge capacity of around 96 mAh/g. In order to further increase the discharge capacity, the effects of calcination on the electrochemical properties of emulsion-derived $LiCoO_2$ powders are investigated in this study. The influence of calcination on the development of the microstructure and crystal structure of the emulsion-derived $LiCoO_2$ powders is also investigated. The relation between the crystallinity and electrochemical behavior of $LiCoO_2$ powders is discussed.

2. Experimental

In the preparation of the aqueous phase, lithium and cobalt acetates were mixed in distilled water in a 1:1 molar ratio. The concentration of all of the cations in the aqueous phase was set to be 1.0 M. Kerosene was used as the oil phase. The prepared aqueous phase was mixed with the oil phase in a water/oil volume ratio of 1:5. To stabilize the water-in-oil emulsion, sorbitan mono-oleate (5 vol.%) was used as the surfactant and was added into the mixed solution. The mixed solution was continuously agitated by a magnetic stirrer for 1 h at a rotation rate of 600 rpm. After thorough mixing, the obtained emulsion solution was dropped into hot kerosene (around 130 °C) to evaporate water from the aqueous phase, and then gel-like products were obtained. Further drying the gel at 300 °C for 1 h resulted in the production of $LiCoO_2$ precursors. The precursors were then calcined at various temperatures ranging from 500 to 800 °C for 1 h for synthesizing $LiCoO_2$.

The specimens calcined at elevated temperatures were characterized using X-ray powder diffraction (XRD) (MAC M03XHF) with CuK_α radiation (wave length = 1.54056 Å) to identify the formed compounds. The microstructure of the obtained powders was examined using transmission electron microscopy (TEM) (Hitachi model H7/100). The average particle size of the calcined powders was analyzed using a particle size analyzer (Coulter LS 230). The electrochemical properties of the obtained $LiCoO_2$ powders was examined in two-electrode cells. The electrochemical cell contained a $LiCoO_2$-based composite as the cathode, Li foil as the anode, and an electrolyte solution of $LiPF_6$ in ethylene carbonate (EC)–dimethyl carbonate (DMC) (1:1 by volume). The assembled cells were charged and discharged at 1/5 C-rate within the potential range of 3 to 4.2 V.

3. Results and discussion

3.1. Emulsion synthesis of $LiCoO_2$ powders

Fig. 1 illustrates the XRD patterns of the precursor powders calcined at various temperatures for 1 h. From the XRD patterns, it is found that $LiCoO_2$ starts to form at as low as 500 °C. In addition to the diffraction peaks of $LiCoO_2$, the figure also shows that there exists some residual reactant Co_3O_4 at this temperature. With an increase in calcination temperature, the crystallinity of $LiCoO_2$ monotonously increases along with a decrease in the amount of Co_3O_4. In addition, the ratio of the intensity of the (003) diffraction peak to that of (104) diffraction peak also increases with calcination temperature. This ratio increases from 0.82 to 1.45 when the temperature rises from 500 to 800 °C. In general, the ratio of $I_{(003)}/I_{(104)}$ is decreased when partial cobalt cations are misplaced in the octahedral sites of the

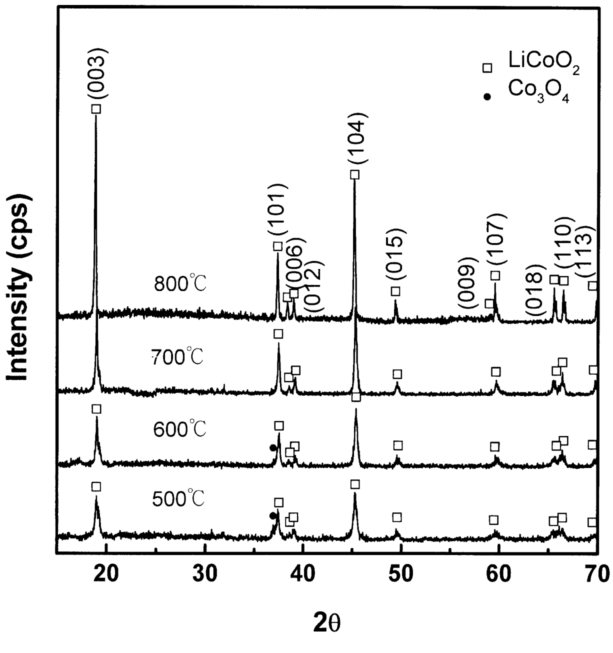

Fig. 1. X-ray diffraction patterns of the emulsion-derived $LiCoO_2$ powders calcined at various temperatures.

lithium layers in $LiCoO_2$.[18] The above results imply that the disorder of lithium and cobalt cations in the crystal structure of $LiCoO_2$ is suppressed at elevated temperatures. After heating at 700 °C, all Co_3O_4 disappears, and monophasic $LiCoO_2$ with a well-crystallized structure is formed. All diffraction peaks found at this temperature are identical to that recorded in JCPDS No. 44-0145,[19] revealing that the formed compound exhibits a pure hexagonal structure with a $R\bar{3}m$ space group. The above results demonstrate that $LiCoO_2$ with high crystallinity is successfully synthesized at 700 °C after calcination for 1 h. The heating time in the emulsion process is much shorter than that in the solid-state method and other solution processes.[13–15,17] Compared to the previous emulsion process which uses quenching to prepare pure $LiCoO_2$,[18] it is found that the calcination treatment can significantly lower the heating temperature from 900 to 700 °C.

The relationship between the crystallite size of $LiCoO_2$ and the calcination temperature is shown in Fig. 2(a). The crystallite size of the obtained specimens was calculated using Scherrer formula, which can be expressed as follows:[20]

$$D = 0.9 \cdot \lambda / (B \cdot \cos\ \theta_B)$$

where λ is the wavelength of X-ray, B (radians) the full width at the half of the maximum of (003) peak, θ_B the diffraction angle of the (003) peak. The crystallite size of the powders increases from 37.8 to 167.0 nm as the calcination temperature rises from 500 to 800 °C. Fig. 2(b) illustrates the average particle sizes D_{50} as the function of calcination temperature. The particle sizes also increase with temperature, and as this figure reveals, the D_{50} for the powders obtained at 500 °C is 1.23 μm and it increases to 1.46 μm after calcination at 800 °C.

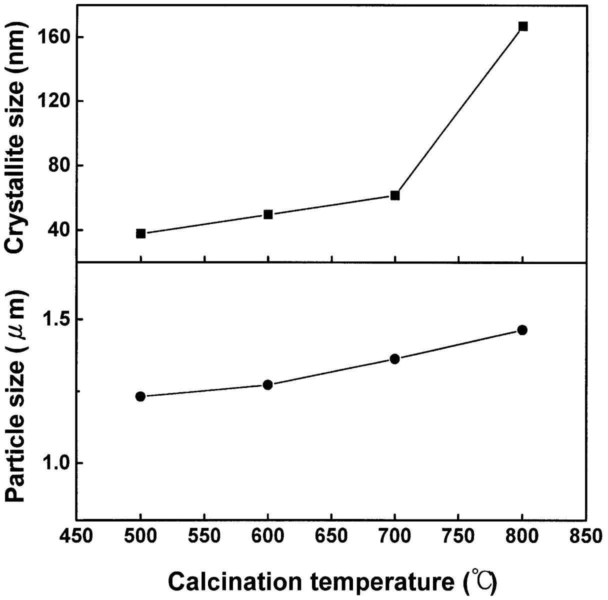

Fig. 2. (a) Crystallite size and (b) average particle size of the emulsion-derived $LiCoO_2$ powders calcined at various temperatures.

3.2. Microstructural development of $LiCoO_2$ powders during calcination

The TEM micrographs of the powders calcined between 500 and 800 °C for 1 h are shown in Fig. 3. From Fig. 3(a), it is observed that the particles are surrounded by some fiber-like materials at 500 °C. Since the fiber-like materials become distorted under the illumination of the electron beam, these fiber-like materials are considered to be the unreacted organic species. These organic species probably originate from the residual surfactants used in the emulsion process. After heating at 600 °C, the plate-like particles are formed, and the fiber-like materials gradually disappear. At 700 °C, angular-shaped $LiCoO_2$ powders become further developed. When the calcination temperature is raised up to 800 °C, the particle size of $LiCoO_2$ powders is enlarged to 0.5–1.5 μm and the electron beam can hardly transmit through the specimens.

Comparing with $LiCoO_2$ powders obtained by the solid-state process (Aldrich Co.) which have sizes around 1–4 μm, the powders synthesized by the emulsion process exhibit smaller particle size and less agglomeration state. This implies that $LiCoO_2$ powders with large surface area can be synthesized by the emulsion process, and the intercalation/deintercalation of lithium ions during charging and discharging process can therefore be facilitated.

3.3. Electrochemical analysis of emulsion-derived $LiCoO_2$ powders

The charge–discharge curves of $LiCoO_2$ powders calcined at various temperatures are shown in Fig. 4. All the specimens clearly display a plateau at around 3.9 V during charging and discharging processes, which represents the typical characteristics of $LiCoO_2$.[21] With a rise in the calcination temperature, both the specific charge capacity and the specific discharge capacity of $LiCoO_2$ progressively increase. When the temperature is raised from 500 to 800 °C, the specific charge capacity increases from 96.1 to 135.2 mAh/g, and the specific discharge capacity increases from 59.5 to 125.6 mAh/g, respectively. The coulomb efficiency of $LiCoO_2$ in the first cycle as a function of calcination temperature is plotted in Fig. 5. This efficiency is defined as the value of the discharge capacity divided by the charge capacity. The coulomb efficiency of $LiCoO_2$ powders strongly depends on the calcination temperature. When the calcination temperature rises from 500 to 800 °C, the coulomb efficiency of $LiCoO_2$ increases from 61.9 to 92.1%.

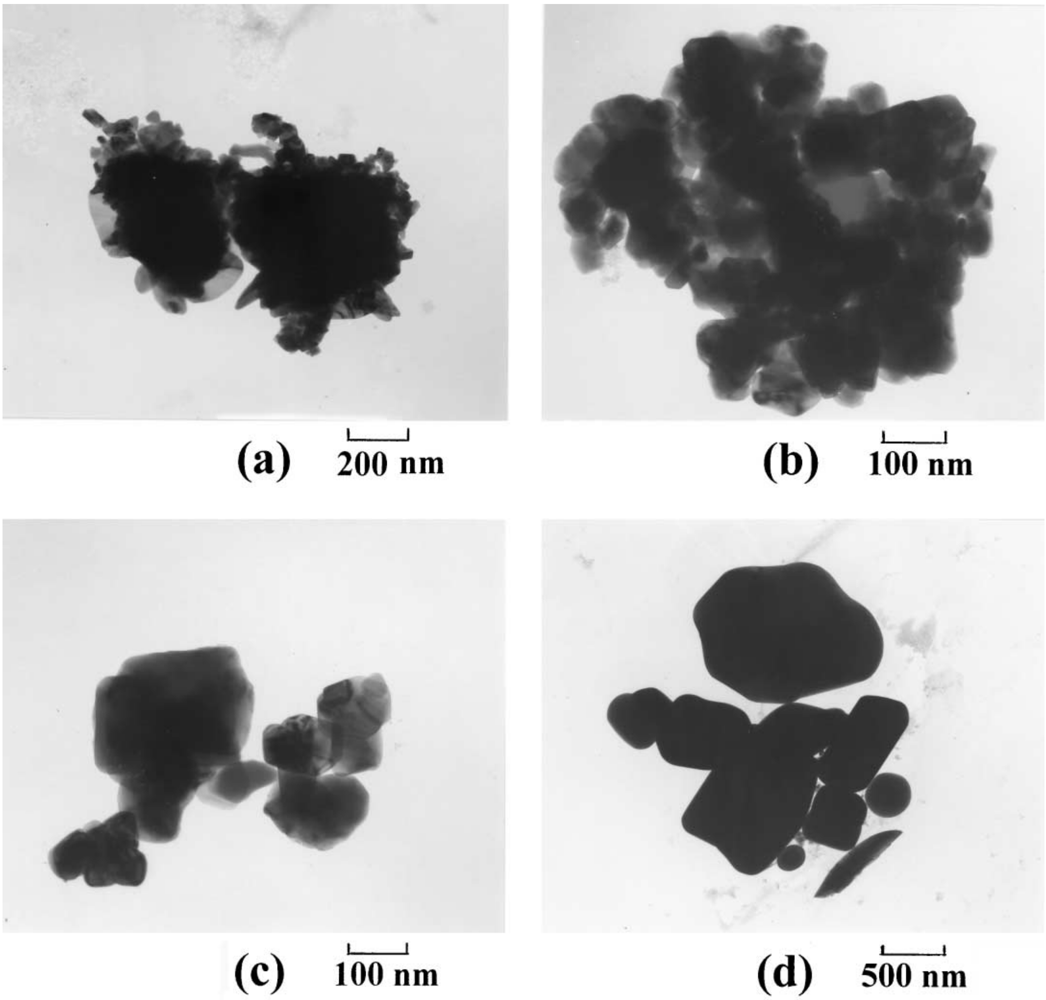

Fig. 3. Transmission electron micrographs of the emulsion-derived $LiCoO_2$ powders calcined at (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 800 °C.

The coulomb efficiency of $LiCoO_2$ as a function of calcination temperature as well as cycle number is illustrated in Fig. 6. In the first cycle the coulomb efficiency for all specimens is less than unity; however, it increases gradually with the cycle number and reaches a saturated value after cycling several times, implying that the electrochemical system has achieved a state of equilibrium. It is found that during the entire cycling process, the coulomb efficiency of $LiCoO_2$ at the same cycle number increases with calcination temperature. In addition, the powders calcined at high temperature are found to reach an equilibrium state faster than those calcined at low temperature. The coulomb efficiency of $LiCoO_2$ powders calcined at 500 °C reaches a stable value after eight cycles; on the other hand, that for 800 °C-calcined $LiCoO_2$ powders reaches a stable state from as early as the second cycle.

Fig. 7 shows the specific discharge capacity of $LiCoO_2$ powders as the function of cycle number. It is found that, at the same cycle, increasing the calcination temperature significantly raises the discharge capacity of $LiCoO_2$ powders. The charge and discharge characteristics of the 800 °C-calcined powders at the first, fifth and tenth cycles are illustrated in Fig. 8. After 10 cycles, the discharge capacity still preserves 97.4% of its initial value, demonstrating the good cyclability of the obtained powders. Comparing the electrochemical properties of $LiCoO_2$ powders obtained by quenching the emulsion-derived precursors,[18] it is found that the calcination treatment not only increases the discharge capacity considerably, but also decreases the fading percentage significantly. It is considered that although quenching the emulsion-derived precursors at elevated temperatures can produce $LiCoO_2$ powders, the formation of $LiCoO_2$ powders with a more rigid structure needs more time for the complete diffusion of constituent cations.

In general, both the particle size and crystal structure of the cathode materials effect the electrochemical properties. When the calcination temperature rises, the increase in the particle size lengthens the diffusion distance of lithium ions, which is detrimental to the intercalation and deintercalation of lithium ions in the host structure. On the other hand, the intensity of diffraction

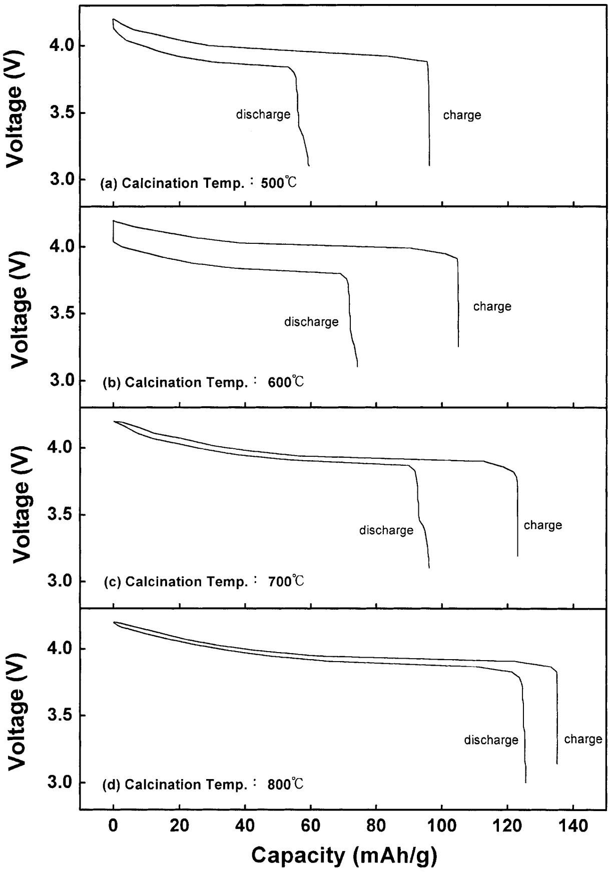

Fig. 4. Charge and discharge curves of the emulsion-derived $LiCoO_2$ powders obtained at different calcination temperatures.

peaks as well as the ratio of diffraction peak intensity of (003) peak to that of (104) peak increases with increasing calcination temperature (see Fig. 1). These results indicate that the crystallinity of $LiCoO_2$ powders is enhanced, and the disorder of lithium and cobalt cations in the crystal structure is suppressed at elevated temperatures; as a result, a more ideal layered structure will be generated and the intercalation and deintercalation of lithium ions will be facilitated. Besides, the elimination of the impure Co_3O_4 phase and residual organic species also contribute to the improved electrochemical performance of the obtained materials. According to the above results, the positive effects of the improved crystal structure of $LiCoO_2$ and the formation of pure compound on the electrochemical properties observed as a result of the rising of the calcination temperature are appreciably greater than the negative effects of the coarsening of the particle size. As shown in Fig. 4 and Fig. 7, the rise in the charge and discharge capacities of $LiCoO_2$ with increasing temperature is ascribed to the diminished amounts of residual Co_3O_4 and organic species, as well as the improved crystallinity of $LiCoO_2$.

The high calcination temperature also results in the formation of an ideal layered structure, which provides a rigid skeleton for lithium cations to be extracted and intercalated in the host structure and improves the reversibility of lithium ions during the cycling processes, thereby increasing the coulomb efficiency (as shown in Fig. 5), and reducing the required cycle number for the cathode materials to reach a steady state (as shown in Fig. 6). Consequently, the calcination treatment on the emulsion-derived precursors is found to be crucial for controlling the electrochemical properties of $LiCoO_2$ powders. The use of the emulsion method combined with appropriate calcination processes is proved to

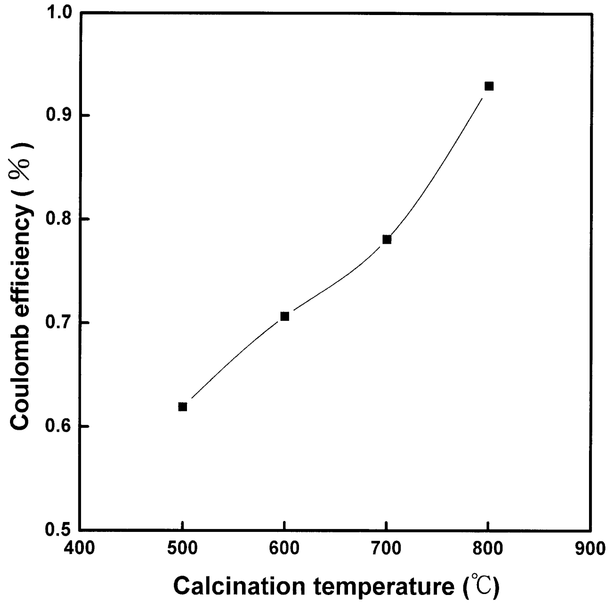

Fig. 5. Coulomb efficiency for the first cycle of the emulsion-derived $LiCoO_2$ as the function of calcination temperature.

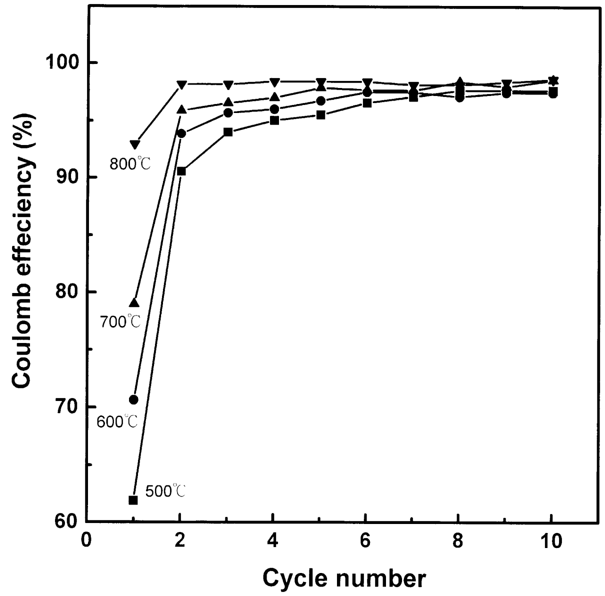

Fig. 6. Coulomb efficiency vs. cycle number for the emulsion-derived $LiCoO_2$ powders calcined at various temperatures.

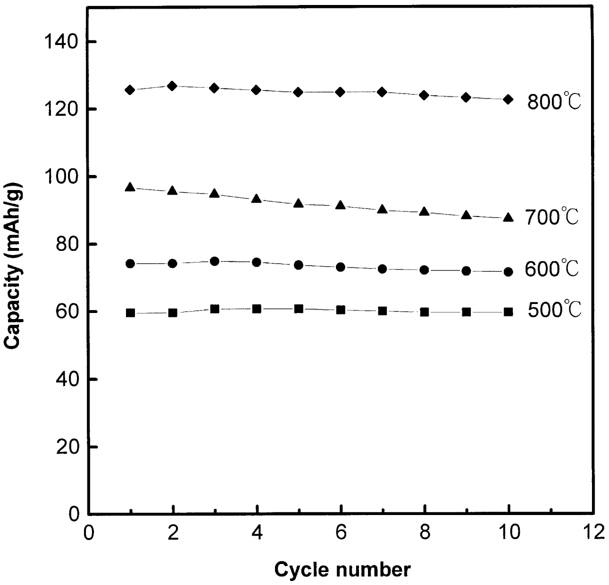

Fig. 7. Discharge capacity vs. cycle number for the emulsion-derived $LiCoO_2$ powders calcined at various temperatures.

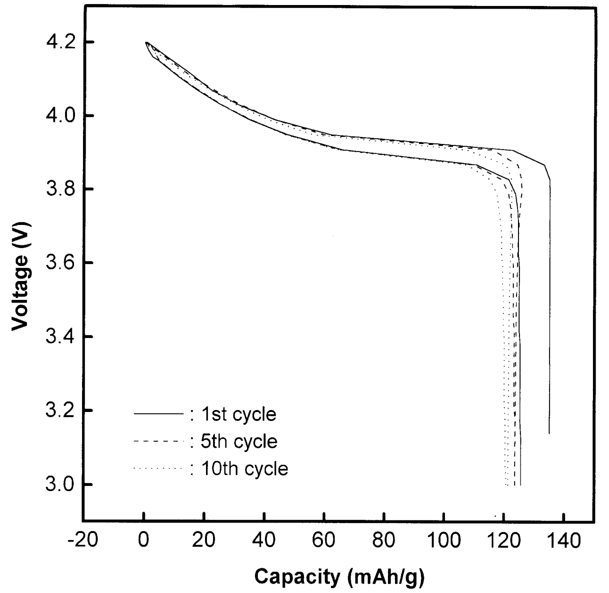

Fig. 8. Charge and discharge curves in the 1st, 5th and 10th cycles of the emulsion-derived $LiCoO_2$ powders calcined at 800 °C.

produce $LiCoO_2$ powders with large specific capacity and good cyclic stability along with high coulomb efficiency successfully.

4. Conclusion

Lithium cobalt oxide ($LiCoO_2$) powders have been synthesized using the water-in-oil emulsion process. After calcining the emulsion-derived precursors at 500 °C, $LiCoO_2$ is produced along with some residual Co_3O_4. With an increase in the calcination temperature, the crystallinity of $LiCoO_2$ is enhanced in conjunction with a decrease in the amounts of Co_3O_4 and organic species. After calcination at 800 °C for 1 h, $LiCoO_2$ with a highly crystallized structure is formed without the existence of second phases. In comparison with the solid-state reaction, the emulsion process significantly shortens the required reaction time for synthesizing $LiCoO_2$, and also reduces the particle size of $LiCoO_2$. In the electrochemical test, it is found that the specific discharge/charge capacity as well as the coulomb efficiency substantially increase with an increase in the calcination temperature. It is considered that increasing the calcination temperature expedites the formation of monophasic $LiCoO_2$ without residual reactants, and improves the crystallinity of $LiCoO_2$ as well as the ordering arrangement of lithium and cobalt cations in the layered structure, thereby facilitating the intercalation and deintercalation of lithium ions. Consequently, with the use of the emulsion method and proper calcination processes, $LiCoO_2$ powders with large specific capacity and good cyclic stability along with high coulomb efficiency are successfully produced. This emulsion process can be utilized for preparing other potential cathode materials used for lithium-ion secondary batteries.

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