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Ultrafine lithium cobalt oxide powder derived from a water-in-oil emulsion process

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Ultrafine lithium cobalt oxide ($LiCoO_2$) powder with the $R\bar{3}m$ structure has been successfully prepared by a newly developed water-in-oil emulsion process. This emulsion process not only significantly shortens the reaction time for preparing $LiCoO_2$, but also decreases the particle size of $LiCoO_2$ to submicron order.

Lithium cobalt oxide ($LiCoO_2$) has been attracting worldwide interest for its application to lithium ion batteries because this material exhibits high specific capacity, low self-discharge, and excellent cycle life.[1–3] Intensive research has been focused on the crystal structure and electrochemical properties of $LiCoO_2$.[4–7] In most studies, $LiCoO_2$ is prepared by solid-state reaction. Owing to insufficient mixing and the low reactivity of the starting materials, calcination at 850–900 °C for 10–20 h is required to synthesize $LiCoO_2$.[8–10] The prolonged calcination at elevated temperatures causes the inevitable coarsening of the powder and the evaporation of lithium species, which significantly impair the product's electrochemical properties.[11] Several kinds of solution processes have been investigated for synthesizing $LiCoO_2$ powder, such as the sol–gel process[12,13] and the evaporation method.[14] These processes can effectively reduce the particle size of $LiCoO_2$ powder; however, calcination at high temperature for several hours is still required to produce $LiCoO_2$. Therefore, in order to shorten the reaction time and conserve energy, it is important to develop a new process which makes feasible the preparation of $LiCoO_2$ by a fast reaction from the view points of economy and practical applications.

In this study, a new water-in-oil emulsion process has been adopted to synthesize monophasic $LiCoO_2$ powder with submicron sized particles. The emulsion process has been found to be an effective approach to synthesize ultrafine ceramic powders and to increase the reactivity of the precursors.[15–20] The basic concept of the emulsion process is to disperse a solution containing the desired species in an immiscible liquid by adding surfactants and using an emulsifying treatment. Tiny liquid micelles can be well dispersed in the immiscible liquid and each acts as an independent micro-reactor. Owing to the homogeneous distribution and the decrease in the diffusion length of reactants in the micelles, a fast reaction between the reactants is expected to occur in the emulsion-derived precursors. In this study, monophasic $LiCoO_2$ powder is rapidly synthesized by heating the precursors at 900 °C and quenching them in air. The phase development and microstructural evolution of the heated specimens are analyzed. The electrochemical behavior of the obtained powder is also examined.

In the water-in-oil emulsion process, the aqueous phase was prepared by dissolving equimolar amounts of lithium acetate and cobalt acetate in de-ionized water. The concentrations of lithium and cobalt cations were both set to 0.5 M. Kerosene was used as the continuous oil phase. To stabilize the water-in-oil (w/o) emulsions, surfactant Span-80 (sorbitan monooleate) was added to the kerosene. The prepared aqueous phase and oil phase were mixed together with a water/oil volume ratio of 1 : 5, and the amount of Span-80 was fixed at 5% (vol/vol) of the total volume of the mixed solution. After continuous mixing by a mixer for 1 h, homogeneous emulsions were obtained. The prepared emulsion was then dropped into hot kerosene (around 130 °C) to obtain the dried material. The dried materials were calcined at 300 °C for 1 h to burn away the residual organic species. The obtained precursors were subjected to thermal analysis (DTA and TGA) to examine the reaction process and weight loss. The precursors were also heated at various temperatures at a ramp rate of 10 °C min^{-1} and then quenched in air. The compounds present in the heated specimens were identified *via* X-ray powder diffraction (XRD) and infrared spectrometry (IR). The microstructure and the particle size of the specimens were examined *via* scanning electron microscopy (SEM). The electrochemical behavior of the obtained $LiCoO_2$ was examined in a laboratory cell. Lithium foil was used as the anode, and 1 M $LiPF_6$ in ethylene carbonate (EC)–dimethyl carbonate (DMC) (1 : 1 by volume) was used as the electrolyte solution. Cells were charged and discharged at 0.097 mA cm^{-2} (1/3C rate) and 0.065 mA cm^{-2} (1/2C rate) within the potential range of 3–4.2 V.

The DTA and TGA results for the emulsion-derived precursors of $LiCoO_2$ are illustrated in Fig. 1. In the TGA curve, several stages of weight loss are observed. The first weight loss stage occurs from 60 to 120 °C, and an associated endothermic peak appears at around 100 °C in the DTA trace. This weight loss results from the evaporation of absorbed water from the surface of the precursors. The second weight loss

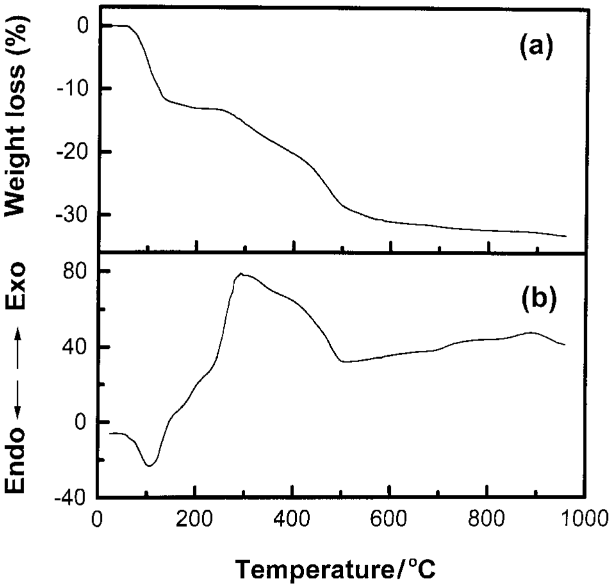

Fig. 1 TGA and DTA curves of the $LiCoO_2$ precursors prepared by the water-in-oil emulsion process.

occurs from 240 to 420 °C, and is attributed to the combustion of residual organic species, which also causes a large exothermic reaction in the DTA. Above 430 °C, the last stage of weight loss is found, and a broad endothermic peak is observed at around 500 °C in the DTA. Based on the analysis of XRD and IR (described later), the last stage of weight loss is ascribed to the formation of $LiCoO_2$.

In order to analyze the reaction processes of the precursors of $LiCoO_2$, when the specimens were heated to the desired temperature, they were rapidly quenched in air and then examined by XRD. The soaking time at the desired temperature was around 1 s. The obtained XRD patterns are shown in Fig. 2. After heating at 500 °C, a small amount of $LiCoO_2$ begins to form, and unreacted Li_2CO_3 and Co_3O_4 also exist. With increasing heating temperature, the $LiCoO_2$ content monotonously increases, associated with a corresponding reduction in the content of residual reactants. After heating to 900 °C, a highly crystalline monophasic $LiCoO_2$ powder is obtained. The XRD pattern shows good consistency with that reported in JCPDS file no. 44-151,[21] and the diffraction peaks in the XRD pattern have been indexed to the hexagonal form (high-temperature polymorph), thereby confirming that the obtained $LiCoO_2$ exhibits the $R\bar{3}m$ structure.

The IR spectra of the quenched samples are illustrated in Fig. 3. The characteristic peak of $LiCoO_2$ begins to appear at 600 cm^{-1} after heating at 500 °C, which is consistent with the XRD results. With increasing heating temperature, the characteristic peak of $LiCoO_2$ gradually develops, and the peaks at 870, 1450 and 1520 cm^{-1}, originating from the carbonate group of Li_2CO_3, are found to decrease. In the IR spectrum of the sample heated to 900 °C, only the characteristic peak of $LiCoO_2$ is observed,[22] and the peaks associated with residual carbonate groups all disappear. From the XRD and IR analyses, the monophasic $LiCoO_2$ powder is confirmed to be successfully synthesized after heating to 900 °C. In the conventional solid-state reaction, heating at 900 °C for 20 h is required to prepare $LiCoO_2$ powder.[8] In the sol–gel process, prolonged heating for 10 h at elevated temperatures is also necessary.[12] However, in this newly developed emulsion process, heating the specimens to a mere 900 °C and quenching them in air results in the formation of pure $LiCoO_2$. It is obvious that the emulsion process significantly curtails the reaction time for synthesizing $LiCoO_2$, which is attributed to the improved homogeneity of the constituents and the enhanced reactivity of the obtained precursors.

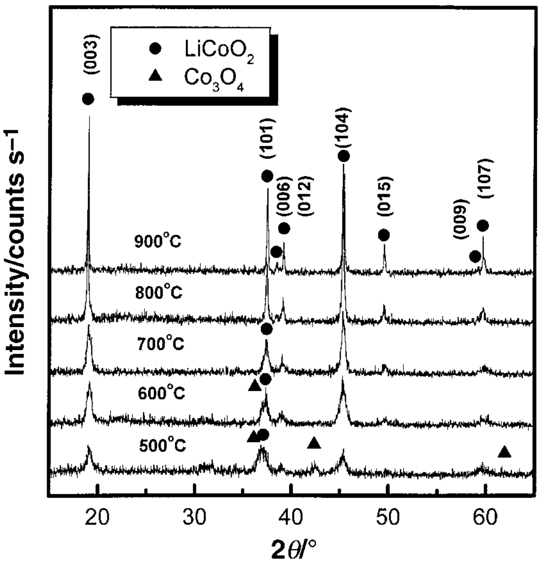

Fig. 2 X-Ray diffraction patterns of the emulsion-derived $LiCoO_2$ precursors quenched at various temperatures.

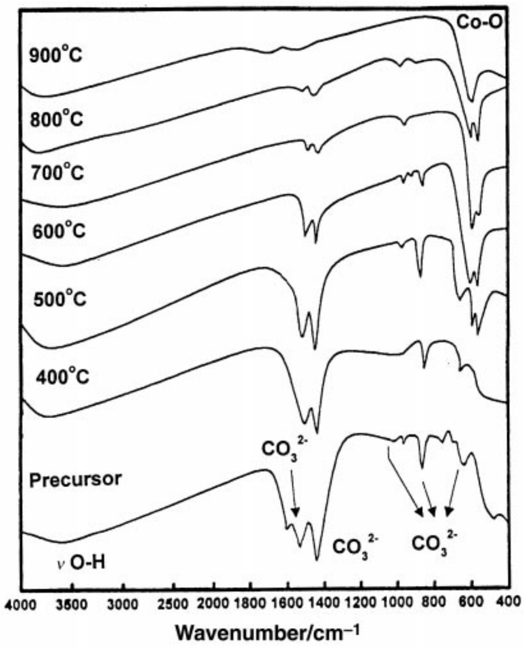

Fig. 3 Infrared spectra of the emulsion-derived $LiCoO_2$ precursors quenched at various temperatures.

The microstructure of $LiCoO_2$ powder prepared by the emulsion process after heating at 900 °C is shown in Fig. 4. This powder exhibits a homogeneous morphology in a dispersed state. The particle size of this powder is within a narrow size distribution in the range of 0.2–0.4 µm, whereas that of the commercial $LiCoO_2$ powder prepared by Aldrich Co. using a solid-state reaction route (lot no. 11813HR) is found to be 1–4 µm with a wide size distribution. Apparently, this emulsion process significantly reduces the particle size of $LiCoO_2$ powder, and also facilitates the formation of $LiCoO_2$ powder with a uniform morphology.

The specific capacity and cyclability of $LiCoO_2$ powder obtained by quenching at 900 °C at current densities of 0.097 and 0.065 mA cm^{-2} are shown in Fig. 5(a) and (b), respec-

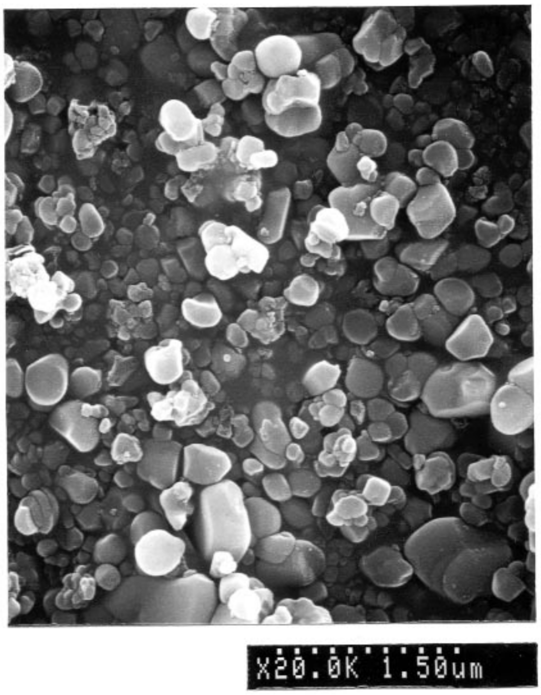

Fig. 4 Scanning electron micrographs of $LiCoO_2$ powder prepared by quenching at 900 °C.

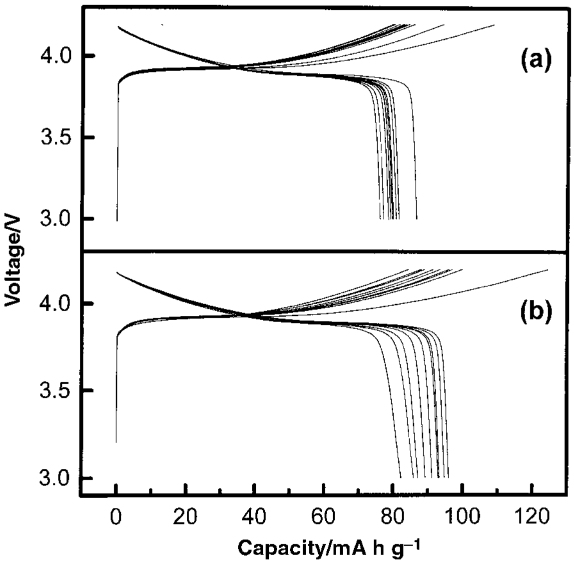

Fig. 5 Cycled charge and discharge characteristics of 900 °C quenched $LiCoO_2$ at a current density of (a) 0.097 mA cm^{-2} and (b) 0.065 mA cm^{-2} within the potential range between 3 and 4.2 V.

tively. In both (a) and (b), a plateau at 3.9 V during both the charge and discharge cycles is clearly observed, which is characteristic of the layer-structured $LiCoO_2$.[23] At a current density of 0.097 mA cm^{-2} (1/2C rate), the charge and discharge capacities are 108.5 and 86.6 mA h g^{-1} respectively, in the first cycle (Fig. 5(a)). At a decreased current density of 0.065 mA cm^{-2} (1/3C rate), the first discharge capacity increases to 96 mA h g^{-1}, implying that the variation in the current density changes the kinetics of lithium ion in the intercalation/deintercalation reactions. Although the discharge capacity is moderate, it is sufficient to be applied to lithium ion batteries. At both current densities, the discharge capacity slightly decreases after ten charge and discharge cycles. In conclusion, it is demonstrated that the emulsion process is an effective method for the synthesis of $LiCoO_2$ cathode powder for the use in lithium ion batteries. This process significantly reduces the reaction time for synthesizing $LiCoO_2$, and results in the formation of submicron particles with good electrochemical characteristics.

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Communication a908240i