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Preparation and electrochemical characterization of $LiCoO_2$ by the emulsion drying method

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Abstract

Fine powders of $LiCoO_2$ were successfully synthesized through an emulsion drying method. The oxide powders were characterized by thermogravimetric-differential thermal analyses, X-ray diffractometry, scanning electron microscopy, elemental analysis and electrochemical method including charge–discharge cycling. By post-annealing the powders obtained by the emulsion drying method in the temperature range 600 $\sim$ 900 °C, we obtained $LiCoO_2$ powder which has a layer structure ($R\bar{3}m$) and consists of fine particles with submicrometre order in diameter. The charge–discharge characteristics as a cathode for lithium ion battery depended on the post-annealing temperature. $LiCoO_2$ powder made by the emulsion drying method displays a good electrochemical performance, suggesting that this soft chemistry approach has the potential to synthesize a high quality electrode material.

1. Introduction

Recently, extensive attention has been devoted to novel types of rechargeable cathodic materials, such as $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$, for lithium secondary batteries. These materials are traditionally prepared by a conventional ceramic method, that is, firing solid reactants at high temperatures and grinding the product. $LiCoO_2$, of which the structure alternates $\{1\,1\,1\}$ layers with octahedral site occupied by Li and Co ions, was synthesized by firing at a high temperature of 900 °C with prolonged heat-treating time [1]. To simplify the powder preparation process and enhance the powder property, soft chemistry routes have been developed, such as the precipitation method [2, 3], the sol–gel method [4], the freeze drying method [5–7] and the organic complex method [8]. Using such a soft chemistry method, a solid phase is formed through a chemical reaction in a liquid phase (aqueous or organic medium) at moderate temperature. Hence, the soft chemistry route essentially gives a purer phase product because of homogeneous mixing in the initial liquid state [9]. For example, Chiang et al. [5] adopted a freeze drying method to prepare submicrometre sized electroactive $LiCoO_2$, and the subsequent calcination at a higher temperature improved the discharge characteristic and cyclability. Sheu et al. [10] investigated the influence of the $LiCoO_2$ particle size on the cathode performance of lithium-ion batteries, elucidating that a smaller particle size distribution has a better cycle stability and smaller *IR* drop than a larger one.

In previous work, we have successfully obtained single phase lithium transition metal oxides, such as $LiMn_2O_4$ [11] and $LiNiO_2$ [12] using the emulsion drying method. Moreover, their particle sizes are less than 1 μm irrespective of the calcination temperature. Here, we also employed the emulsion drying method to synthesize layered $LiCoO_2$ and described the powder properties including charge–discharge cycling performance.

2. Experimental details

$LiNO_3$ (Kanto, 99%), $Co(NO_3)_2.6H_2O$ (Kanto, 98%), Tween 85 (polyoxyethylene sorbitan trioleate) and Kerosene (Junsei) were used as the starting materials for the emulsion drying method. Details of the synthesis routes were previously described [11]. Figure 1 shows the flow chart of the synthesis procedure. An aqueous solution was prepared by dissolving $LiNO_3$ and $Co(NO_3)_2.6H_2O$ in distilled water at the molar ratio of Li:Co = 1:1, and stirred for 1 h. An emulsifying agent (Tween 85) was also mixed with Kerosene, and stirred vigorously for 1 h. The aqueous solution was dropped into the oil mixture at a rate of 4 or 5 droplets per second at 180 °C, and stirred at over 4000 rpm by an impeller, resulting in an emulsion at room temperature. As soon as the resultant emulsion was dropped into the

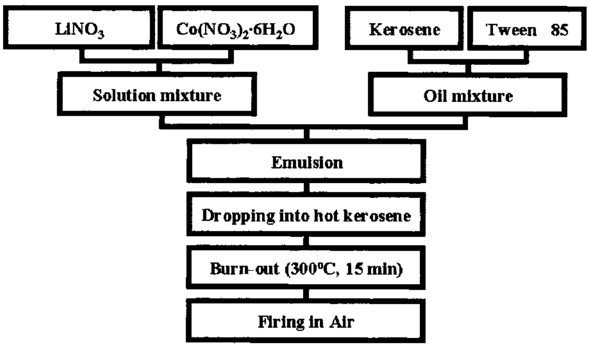

Fig. 1. Flow chart of synthesis procedure.

hot kerosene (180 °C) to dry the emulsion, water and Kerosene contained in the emulsion were evaporated and gathered in the spiral-type condenser. Finally the oxide powder precipitated on the bottom of the glass bottle. The obtained powder precursor was heat treated in a steel tray at around 300 °C for 15 min to remove the residual oil component.

To observe the thermal behaviour of the as-prepared powder, thermogravimetric (TG, MAC Science, Japan) – differential thermal measurements (DTA, MAC Science, Japan) were performed at the rate of 10 °C min^{-1} in the temperature range from room temperature to 1000 °C in air. The obtained powder samples were heat treated at a rate of 5 °C min^{-1} at given temperatures for 24 h in air, then cooled to room temperature in the furnace (ETR-13K, Isuzu, Japan). The calcined powders were ground in an agate mortar, and then the fine powders were analysed using an automated X-ray diffractometer (RINT2000, Rigaku, Japan, CuK$_\alpha$ radiation). To observe the particle size and shape of the firing powders, scanning electron microscopy (SEM, Jeol, Japan) was employed. To detect the residual carbon ingredient, wavelength dispersive spectrometric measurement (WDS, Jeol, Japan) was carried out.

A two-electrode type experimental cell was used to evaluate the electrochemical properties of the samples. To fabricate a composite cathode, polvinylidene fluoride (PVDF, Kureha) dissolved in *N*-methyl pyrrolidone (NMP, Kanto), which was used to enhance the adhesive strength, a conducting agent (graphite, Nakalai) and the LiCoO$_2$ samples were mixed together. The weight ratio of the resultant composition of PVDF, graphite and the sample was 3:7:90. This mixture was pasted onto nickel exmet, and then dried at 100 °C in air to remove the NMP ingredient. After drying, the electrode was pressed and vacuum dried at 100 °C for one day. The cathode characteristics were tested using lithium metal as the anode. The electrolyte used was a 1 M LiClO$_4$ solution in ethylene carbonate – dimethyl carbonate (1:1 in volume). Cell assembly was carried out in a glove box filled with high purity Ar gas. A constant current such as 0.1 mA cm^{-2} was applied across the working electrode to investigate the cathode performance in the voltage range between 4.3 and 3.4 V at 25 °C.

3. Results and discussion

In the emulsion drying method, the preparation of the emulsion may produce oily particles in water or water particles in oil. Though an emulsion is easily separated into water and oil phases, addition of emulsifying agent prevents this separation, stabilizing the emulsion. Figure 2 shows schematic drawings of the two types of emulsion stabilized by the emulsifying agent, that is, oil-in-water (O/W) and water-in-oil (W/O). The emulsion type is determined by the ratio of the two types, the kind of emulsifying agent, reaction temperature etc. To prepare the fine powders of LiCoO$_2$, we selected the W/O type, because it was expected that the powder size depends on aqueous phase particles (Figure 2(b)).

Figure 3 shows the TG–DTA curves of the as-prepared black powder obtained by drying the emulsion at 300 °C for 15 min. The measurements were performed at a rate of 10 °C min^{-1} in air using a Pt crucible. The weight loss and a broad exothermic peak were observed in the temperature range from 300 to 450 °C. These are mainly attributed to the evaporation

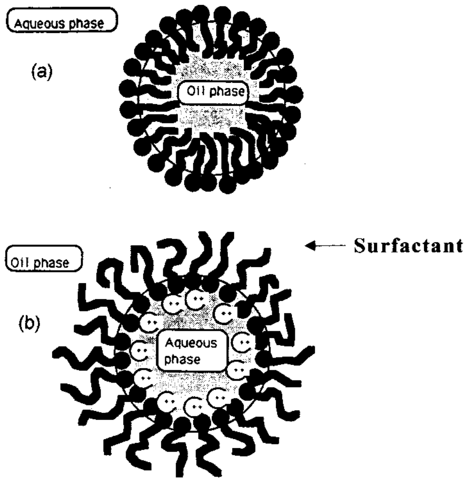

Fig. 2. Orientation and packing of surfactant molecules at emulsion interfaces: (a) formation of a monomolecular film at the O/W interface for the stabilization of O/W type emulsion and (b) stabilization W/O emulsion by the oriented adsorption of divalent soap salts.

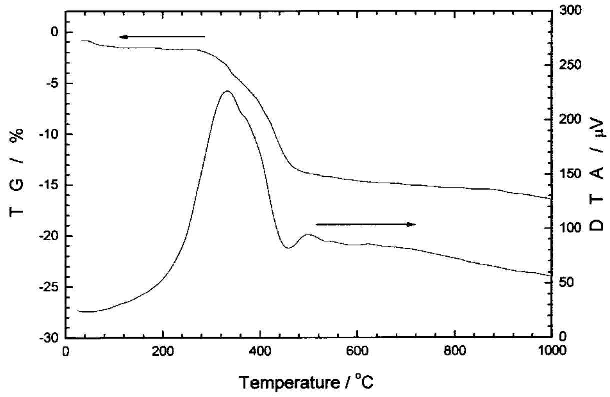

Fig. 3. TG–DTA curves of as-prepared powder obtained by the emulsion drying method.

of the residual water and the combustion of organic compounds such as Kerosene and Tween 85.

To investigate the crystallization process during heat treatment, the as-prepared powder was calcined at given temperatures. Figure 4 shows the X-ray diffraction patterns of the samples heat treated in the range from 300 to 900 °C. All the diffraction peaks could be indexed by assuming the structure to be a hexagonal lattice of the α-$NaFeO_2$ ($R\bar{3}m$) type [13]. Crystallization of the as-prepared powder occurred at the relatively low temperature of 300 °C. The intensity of the diffraction peaks due to the $LiCoO_2$ phase increased with increasing calcination temperature, although there were very small traces of the Co_3O_4 as observed around $2\theta = 31.3°$.

As described previously [11], a crystalline $LiMn_2O_4$ phase was prepared by a solid state reaction through more complicated steps at a higher temperature (600 °C $\sim$ 800 °C) than the emulsion drying synthesis. As seen from the single exothermic peak (Figure 3), a simple reaction occurred smoothly at a lower temperature of 200 °C $\sim$ 500 °C because of the homogeneous mixing of cations in the emulsion state. As previously reported by Garcia [14], the $LiCoO_2$ powder was prepared by heating at the low temperature of 300 °C for several days, and high resolution transmission electron microscopic measurement confirmed cubic symmetry of the low temperature phase. For the sample prepared by the present method, however, peak splitting clearly appeared between the (1 0 8) and (1 1 0) peaks (Figure 4), revealing the formation of the layer structure [14, 15]. This is attributable to the homogeneous mixing of Li and Co cations in the emulsion state.

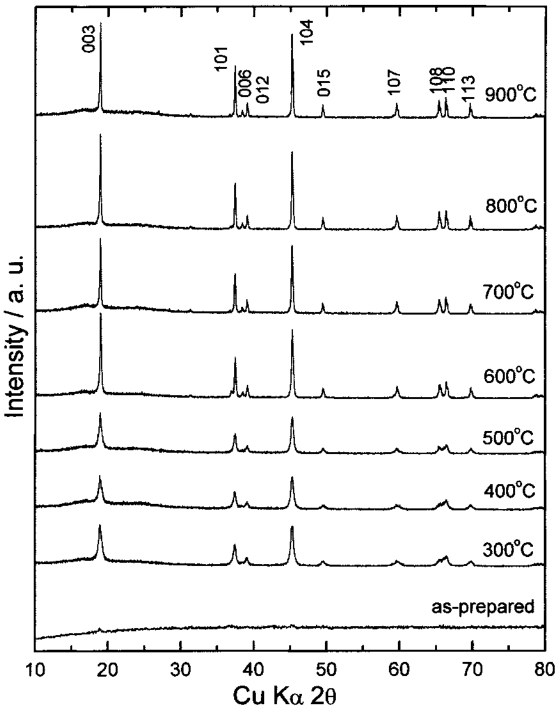

Fig. 4. XRD patterns of sample calcined at various temperatures for 24 h.

The variation in the lattice parameters of the *a*- and *c*-axes were determined as a function of calcination temperature. As presented in Figure 5, it is notable that a steep increase in the lattice parameters, especially in the *c*-axis, is observed up to 600 °C. This shows that the growth of the crystalline phase takes place in a relatively low temperature range below 600 °C, leading to the highly crystalline form with a highly ordered structure above 600 °C. As can be seen in Figure 4, clear peak splitting between the (1 0 8) and (1 1 0) planes, and the gradual decrease in the full width at half maximum of each peak with increasing temperature support this fact. Over 600 °C, there are only slight changes in the *a*-axis and *c*-axis with increasing calcination temperature. The lattice constants of the sample calcined at 900 °C ($a = 2.815$ Å, $c = 14.056$ Å) agree well with results of other research groups [5, 14].

To observe the particle size and shapes of the samples, SEM observations were carried out. Figure 6(a) and (b) illustrate the microstructure of $LiCoO_2$ powder which was calcined at 900 °C for 24 h in air. From Figure 6(a), agglomerates consisting of small particles are several micrometres in size. From the higher magnification picture of Figure 6(b), the oxide particles are seen to be well crystallized with a clear hexagonal shape which is a single crystal, and the particle diameter was less than 1 μm. In previous work [11], for samples calcined at lower temperature, much smaller particle size was observed and, it was found that crystal growth of the calcined powders depended strongly on the calcination temperature. Based on the SEM observation, the amorphous as-prepared powder (XRD pattern in Figure 4) is considerably reactive, resulting in highly crystalline $LiCoO_2$ on heat treatment.

In the 2θ range from 15° to 18° (Figure 4) small hills, which seemed to indicate an amorphous structure were detected. Therefore, it was considered possible that carbon-containing organics might be contained in the product because the powder samples were prepared

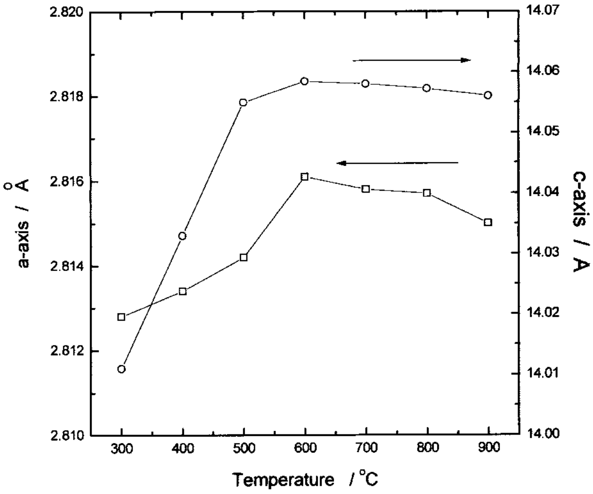

Fig. 5. Variation in lattice parameter with firing temperature; open square and open circle correspond to *a*- and *c*-axes, respectively.

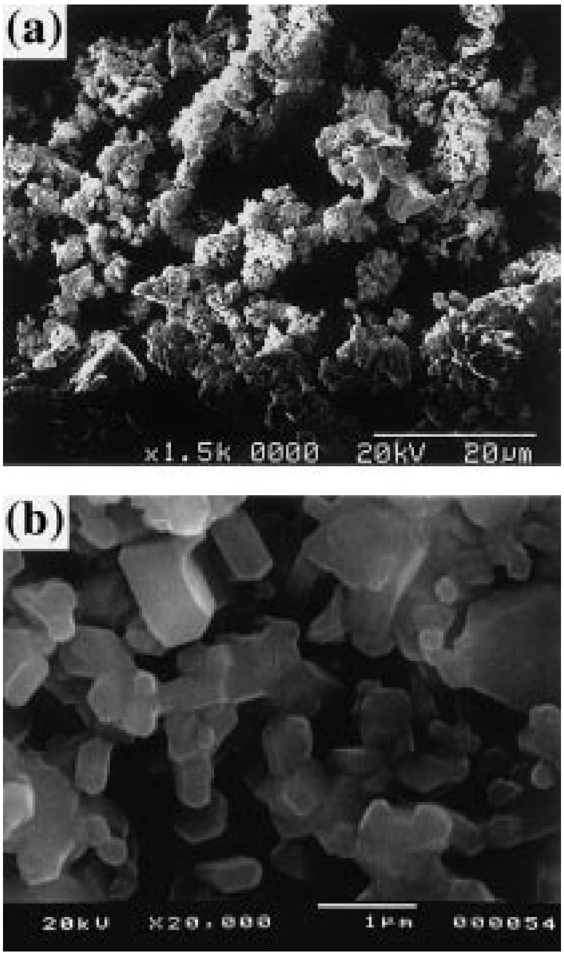

Fig. 6. SEM images of the sample calcined at 900 °C for 24 h in air; (a) low and (b) high magnification.

from an emulsion consisting of some organic compounds. Therefore, an elemental analysis was performed with a WDS for the samples calcined at 300 °C and 900 °C for 24 h in air. There was no trace of carbon, and only the Co and O signals were observed. Thus, the hill like amorphous sign in the XRD pattern (Figure 4) may be due to the sample holder which consisted of an organic polymer.

Figure 7 shows the initial charge and discharge curves as a function of specific capacity for the samples fired at various temperatures for 24 h. The charge–discharge cycling tests were performed in the range 3.4 to 4.3 V. Although the charge curves for the samples are similar, the discharge capacity significantly increased with increasing calcination temperature. The discharge capacities for the products at 300, 400, 600, 700, 800 and 900 °C were 35, 70, 100, 110, 150 and 156 mA hg^{-1}, based on the weight of active materials, respectively. Even though the layer $LiCoO_2$ materials were prepared from the lower temperature ($\geqslant$300 °C) in air without subsequent heat treatment [1, 13], the difference in charge and discharge capacity was varied considerably with calcination temperature. As shown in Figure 5, large difference in the lattice parameter between the low temperature and high temperature samples were observed. The lower values of the *a*- and *c*-axes at low temperature may be due to disordering of Li^+ and Co^{3+} in the $LiCoO_2$. Therefore, it is possible that this disordering leads to a lower discharge capacity for the low temperature samples. Manthiram et al. [16] have suggest that a firing temperature much higher than 800 °C is essentially required to obtain good electrochemical properties of samples prepared by the solution method. In the case of the product prepared by the emulsion drying method, the samples fired at 800 °C $\sim$ 900 °C also exhibited higher discharge capacities of 150 $\sim$ 156 mA hg^{-1}, corresponding to an amount of intercalated lithium of about Li/Co = 0.52 $\sim$ 0.57.

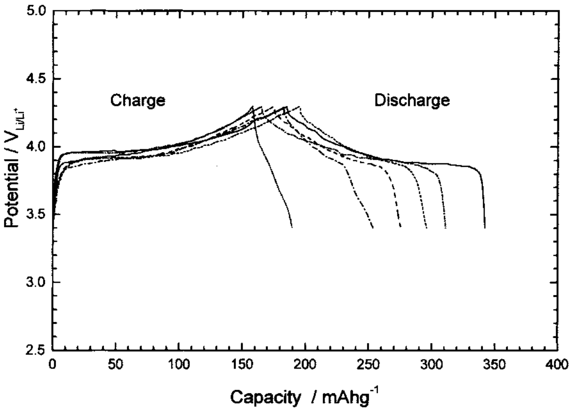

Fig. 7. Initial charge and discharge profiles of the cathodes fabricated from $LiCoO_2$ heat treated at various temperatures. Key: (······) 300 °C, (–·–·) 400 °C, (----) 600 °C, (– – –) 700 °C, (-··-··) 800 °C and (——) 900 °C.

Figure 8 shows the cyclability of samples calcined at various temperatures. All samples showed capacity loss up to the 5th cycle. After the 5th cycle the cells displayed stable cycling behavior, apart from the 300 °C sample. The high temperature samples (800 °C and 900 °C) demonstrated a better cyclability than the lower temperature ones. It is thought that their superior crystallinity and the presence of single-crystallized particles with a hexagonal submicrometre order, as mentioned above, contribute to the good electrochemical characteristics.

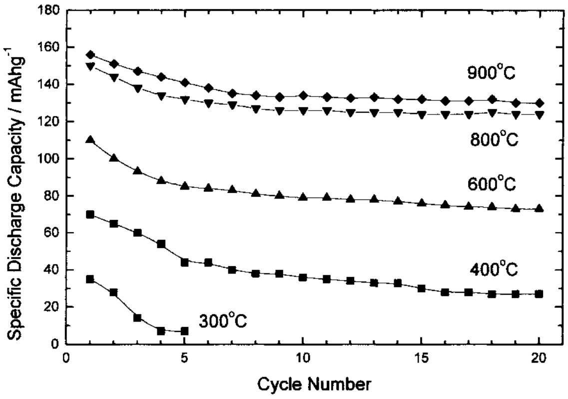

Fig. 8. Specific discharge capacity versus cycle number for several powders cycled between 3.4 V and 4.3 V. Prolonged charge–discharge experiment was carried out at room temperature. In the all cases a constant current was applied across the cathode, 0.1 mA cm^{-1}.

The material prepared by the emulsion drying method has the following advantages: much smaller particle size ($\leqslant 1\ \mu$m), homogeneous powder, single crystal-like form, and cost benefit mass production. It is also expected that this powder preparation method will enable a new approach to the synthesis of various electrode materials for Li-ion secondary batteries.

4. Conclusion

$LiCoO_2$ powder was synthesized by the emulsion drying method for rechargeable lithium-ion batteries cathode material. The layer structure was formed around 300 °C due to the homogeneous mixing of Li^+ and Co^{3+} cations in the emulsion state, thus reflecting a simpler reaction than the solid state one. The discharge capacities of the low temperature and high temperature samples, which have the layer structure ($R\bar{3}m$), were strikingly different due to the differences in the crystallinity and the disordering in the atomic arrangement. Furthermore, the calcined powder was very fine and the particle size was less than 1 μm in diameter. The discharge capacity of the samples heat treated at various temperatures increased with increasing heat-treatment temperature; 800 °C (150 mA hg^{-1}) and 900 °C (156 mA hg^{-1}).

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