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Synthesis of $LiCoO_2$ Particles with Uniform Size Distribution

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Abstract

$LiCoO_2$ cathode materials with uniform grain size were prepared using fine grained CO_3O_4 particles. The effects of the molar ratio of Li/Co and the sintering temperature on the microstructure (the grain size and its distribution) and the electric properties were studied. The AC impedance analysis indicated the presence of the secondary phases mainly at the grain boundary. The reversible Li^+-intercalation/deintercalation capacity was also examined, and the maximum value of 130 mAh g^{-1} was obtained using the optimum preparation conditions. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

Cathode materials containing a lithiated transition metal oxide have received intense research efforts, because of their use in high-energy density Li-ion secondary batteries. High voltage cathode materials have been synthesized mainly via the solid state reaction route.[1–3] The solid state synthesis is a simple and inexpensive method for ceramic powder production. Although different precursors are able to be chosen, the most popular precursors are Li_2CO_3 and $CoCO_3$.[1,4,5] It is considered that the $LiCoO_2$ formation in the air atmosphere is divided into two reactions.[4,5] The low-temperature reaction is related to the decomposition of $CoCO_3$ to Co_3O_4, and at the temperature higher than 700°C, the decomposition of Li_2CO_3 to Li_2O takes place and the reaction between Li_2O and the low-temperature product Co_3O_4 results in the $LiCoO_2$ formation. In the case of using Li-precursors with lower decomposition temperature, for example Li acetate,[6] it is possible to synthesize $LiCoO_2$ at a lower temperature. Additionally, the evaporation loss of Li ion is a serious problem especially in the preparation of $LiNiO_2$, therefore, many inorganic or organic Li-precursors have been utilized in order to reduce both the calcination temperature and the calcination time.[7,8] However, to the best of our knowledge, there is only a limited number of experimental studies on the effect of Co_3O_4 particles.

In this study, we utilized the hydrothermal-precipitated Co_3O_4 particles to synthesize $LiCoO_2$ ceramics with various conditions, such as, Li/Co molar ratio and sintering temperature. In addition, we clarified the relationships between the preparation conditions and some properties of $LiCoO_2$ sintered ceramics. We also briefly discuss the reversible Li^+-intercalation/deintercalation capacity from the view point of the ceramics microstructure.

2 Experimental

Reagent grade Li_2CO_3 was utilized as Li raw material. Fine grained Co_3O_4 particles, used as starting materials, were specially synthesized by aerial oxidation of an alkaline $Co(OH)_2$ suspension: a $CoSO_47H_2O$ aqueous solution was mixed with a NaOH aqueous solution under N_2 bubbling, then the obtained alkaline suspension was heated to 90°C and oxidized by air bubbling under controlled temperatures. It produced black precipitates, which were identified as Co_3O_4 spinel oxide. The precipitates were then filtrated, and washed with distilled water then dried at 120°C in air. From the transmission electron microscopic observation, the oxidative precipitated Co_3O_4 particles were well-isolated, fine (the average diameter of approximately 25 nm) and spherical in shape with narrow particle size distribution.

$LiCoO_2$ sintered ceramics were synthesized using the usual ceramics technique. The obtained Co_3O_4

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*To whom correspondence should be addressed. Fax: +81-82-503-0085; e-mail: Tatsuya_Nakamura@todakogyo.co.jp fine particles were thoroughly mixed with predetermined amounts of Li_2CO_3 (the molar ratio of Li/Co = 1·00, 1·01, 1·03 and 1·05) by dry milling. The well-mixed powders were pressed into disks and calcined in air at 700°C for 5 h. Then they were thoroughly ground again, pressed into disks, and sintered in air for 10 h at temperature ranging from 800 to 900°C.

For all products, the X-ray diffraction measurement was used to identify the precipitated phases. A scanning electron microscopy was utilized to investigate the microstructure of the sintered ceramics. The average grain size was evaluated by geometrical estimation. The AC electrical resistivity of the obtained ceramics were measured via two-probe technique using an impedance analyzer (Hewlett Packard, HP-4192A) in the frequency range of 10^2 to 10^7 Hz.

The electrochemical Li^+-intercalation/deintercalation were evaluated by galvanostatically discharging and charging at the constant current density (0·5 mA cm^{-2}) using Li foil as the counter electrode and 1·0 M-$LiClO_4$/PC-DME organic electrolyte solution: the upper and lower limit of the discharging and charging voltage of 4·2 and 2·5 V, respectively. After the sintered disks were ground until the particle diameter attained less than 50 μm, the obtained $LiCoO_2$ powder was well-mixed with acetylene black and poly-tetra-fluoro-ethylene binder, then pressed into the pellet, which were used as the cathode electrode.

3 Results and Discussion

All the sintered products were identified as a single phase of layered rock-salt structure with the cation ordering from powder X-ray diffraction. The impurity phases such as Co_3O_4 and Li_2CO_3 were not detected in the X-ray diffraction pattern. The lattice parameters were independent on the preparation conditions, and remained almost constant of $a = 0{\cdot}2815$ mn and $c = 1{\cdot}4045$ nm in the hexagonal representation.

The microstructural variation of the sintered ceramics was examined with the SEM observation of the fractured surface of the sintered ceramics. The typical SEM photograph is shown in Fig. 1. It is found that the $LiCoO_2$ grains are isotropic in shape and have rounded edges, the grain size distribution is narrow and the grains are tightly packed. It is possible to obtain these uniform and dense microstructure using the well-isolated, fine and uniform Co_3O_4 particles, synthesized by the hydrothermal precipitation method. According to the SEM observation, it was also found that the average grain size increased with an increase in the Li/Co molar ratio and with an increase in the sintering temperature. The grain growth is accelerated with the presence of excess amount of Li-compound and with the temperature. However, since most of the excess Li-compound may be lost by the evaporation during the sintering process, the products are identified as a single $LiCoO_2$ phase.

Next, the AC resistivity was examined. Figure 2 shows the AC resistivity of $LiCoO_2$ sintered ceramics plotted in a complex plane. The complex resistivity trace is represented as a semi-circle.[9] AC

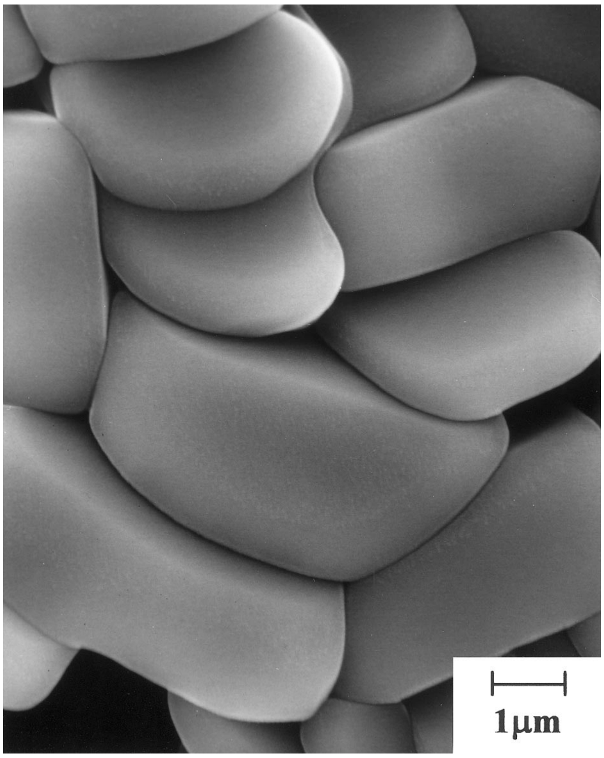

Fig. 1. Scanning electron microphotograph of fractured surface of $LiCoO_2$ sintered ceramic: Li/Co = 1·05 and sintering temperature of 800°C.

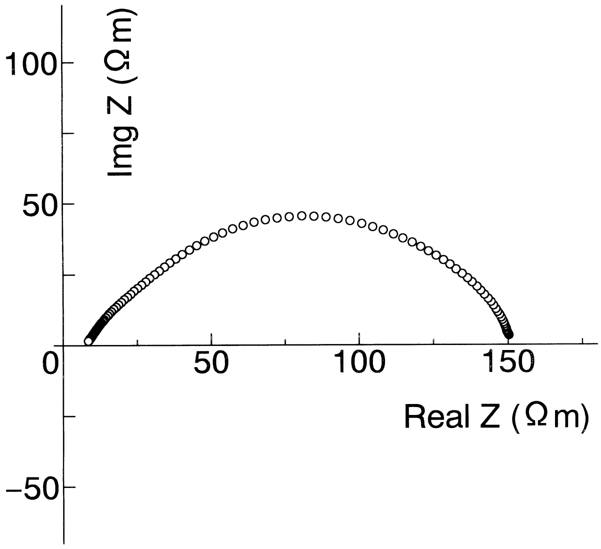

Fig. 2. The complex resistivity trace in a complex plane for $LiCoO_2$ sintered ceramic: Li/Co = 1·05 and sintering temperature of 850°C.

resistivity can be described as an equivalent circuit with grain resistivity R_g, grain boundary resistivity R_{gb} and inter-grain capacitance C_g.

$$Z = R_g + 1/[R_{gb}{}^{-1} + (j\omega C_g)^{1-\alpha}] \qquad (1)$$

Here, α is attributed to the distribution of the relaxation time, the origin of which is unknown. From the numerical fitting to this equivalent circuit, we obtained individually these parameter values. They depended on the Li/Co molar ratio rather than the sintering temperature.

Figure 3(a) shows the grain resistivity variation versus the Li/Co molar ratio. The grain resistivity is decreased with an increase in Li/Co molar ratio, and reaches almost constant at Li/Co > 1·03. Considering that $LiCoO_2$ has higher electrical conductivity than Co_3O_4, it is likely that higher grain resistivity at lower Li/Co molar ratio is related to the presence of unreacted Co_3O_4, the amount of which is below the detection limit of the X-ray diffraction analysis. Since evaporation loss of Li^+ during the sintering process causes the unreacted Co_3O_4, a small excess amount of Li^+ is required for the complete formation of $LiCoO_2$. The grain boundary resistivity variation with the Li/Co molar ratio is shown in Fig. 3(b). The grain boundary resistivity slightly decreases with an increase in the Li/Co molar ratio to 1·03, takes a minimum around Li/Co = 1·03, then significantly increases with the Li/Co molar ratio. At larger Li/Co molar ratio, higher grain boundary resistivity is thought to be attributed to the presence of high-resistive excess Li_2CO_3 phase at the grain boundary, the amount of which was also below the detection limit of the X-ray diffraction analysis. These resistivities variations versus the Li/Co molar ratio indicates the presence of the secondary phases,

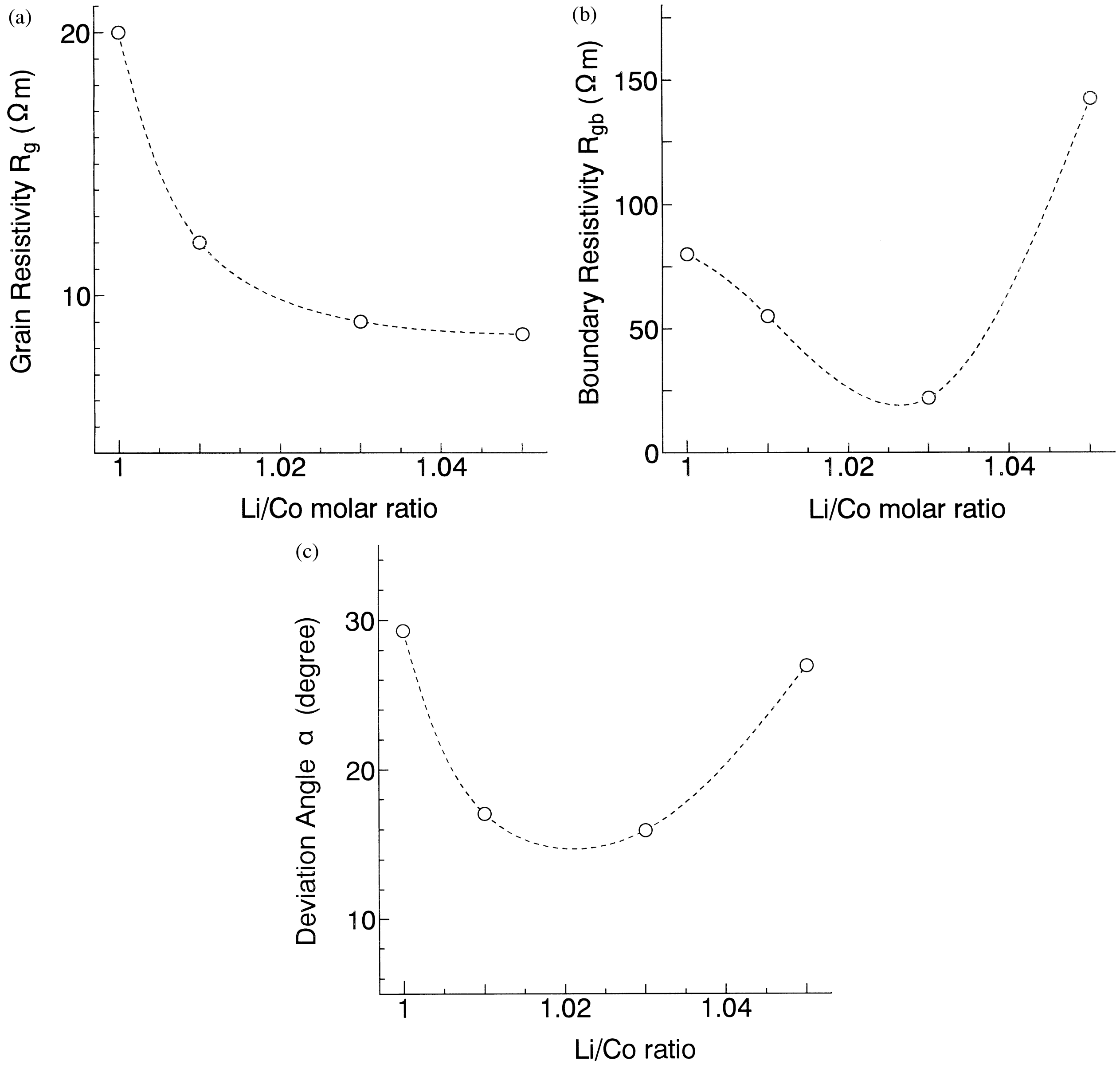

Fig. 3. The variations of (a) grain resistivity, (b) grain boundary resistivity and (c) deviation angle versus Li/Co molar ratio.

which could not be detected with the X-ray diffraction analysis. It is found that there exists an optimum Li/Co molar ratio and that it is approximately Li/Co = 1·03. It was also confirmed from the experimental results on the galvanostatically charging and discharging performance. And the variation of the α value versus the Li/Co molar ratio is also shown in Fig. 3(c). The α value also has a minimum around Li/Co = 1·03. It means that the distribution of the relaxation time takes a minimum at the above optimum Li/Co molar ratio.

Using the above $LiCoO_2$ particles, we measured the Li-ion secondary battery cell performance via a galvanostatically charging and discharging technique. The reversible capacity had a maximum value of 130 mAh g^{-1} at the Li/Co molar ratio of 1·03, irrespective of the sintering temperature ranging from 800 to 900°C. It is explained that this variation of the reversible capacity is not attributed to the particle size of $LiCoO_2$ but to the presence of the secondary phases.

4 Conclusions

We prepared $LiCoO_2$ ceramics using hydrothermal-precipitated Co_3O_4 particles as the starting materials. The $LiCoO_2$ grain size depended on both the Li/Co molar ratio and the sintering temperature. The AC impedance analysis clarified the relationships between the preparation conditions and the microstructure, especially for the presence of the secondary phases. And it was certain that the presence of the secondary phases degraded the reversible Li^+-intercalation/deintercalation capacity. We obtained the optimum synthesis conditions for $LiCoO_2$ cathode particles and the maximum reversible Li^+-intercalation/deintercalation capacity of approximately 130 m Ah g^{-1} was attained.

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