Synthesis of LiCoO$_2$ from cobalt–organic acid complexes and its electrode behaviour in a lithium secondary battery

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Abstract

Well-crystallized, layered LiCoO$_2$ has been prepared by heating cobalt–organic acid complexes (such as malic acid and succinic acid) at 900 °C in air after preheating at 400 °C (2 h) and at 650 °C (6 h). LiCoO$_2$ obtained by this method shows a high (003) peak intensity and low (104) or (101) intensities in X-ray diffraction (XRD). The first discharge capacity of LiCoO$_2$ obtained from this method in ester-based electrolyte is 132 mA h g^{-1} on cycling between 4.3 and 3.7 V. The value is larger than that obtained by the conventional method. X-ray diffraction studies and open-circuit voltage curves show the presence of at least two types of reaction. A two-phase reaction occurs in the region of 0.71 < x < 1.0 in Li$_x$CoO$_2$. The lithiation proceeds as a homogeneous reaction together with expansion of the c-axis in the region of 0.47 < x < 0.71. The expansion of the c-axis against Δx change at $x = 0.56$ corresponds well with the voltage jump observed in the charge/discharge curves.

Introduction

Lithium secondary batteries have been studied as high energy power sources for applications ranging from automobile propulsion to semiconductor memory maintenance.

Four-volt cathode materials, such as LiCoO$_2$ [1], LiNiO$_2$ [2] and LiMn$_2$O$_4$ [3], were prepared over ten years ago. The materials did not, however, attract strong attention from battery researchers until Nagaura [4, 5] proposed the use of a Li–carbon intercalation compound as an anode material for a safer Li secondary battery. After this proposal, some research on LiCoO$_2$ was carried out [6–8], but there have been no studies of the crystal structure during charge or discharge.

In this paper, a new preparation method for LiCoO$_2$ has been investigated, and the electrochemical properties of the material have been investigated. Comparison with the Li insertion behaviour of conventionally prepared LiCoO$_2$ has been carried out. Further, the crystal structure of Li$_x$CoO$_2$ has been studied in detail.

Experimental

Conventional synthesis of LiCoO$_2$

Mixtures of Li$_2$CO$_3$ with Co$_3$O$_4$ or CoCO$_3$ were heated at 900 °C for 20 h in air.

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Synthesis of LiCoO₂ by organic acid method

A solution containing equimolar amount of $Co(NO_3)_2$, LiOH and one of the organic acids (oxalic, succinic, malic or tartaric acids) was adjusted to pH 4 to 8 with aqueous ammonia. The mixture was evaporated at a temperature of 60 to 150 °C under reduced pressure. This treatment caused solidification of a viscous red solution (in the case of oxalic acid, the cobalt complex precipitated). The resulting sample was ground to a powder and heated at 400 °C, to drive off the organic compounds. The final $LiCoO_2$ was obtained by heating the prepared pellet (pressed at 400 kg cm^{-2}) at 900 °C for 20 h after preheating (650 °C for 6 h) the powdered sample.

Powder X-ray diffraction (XRD) analyses were carried out using an automated Rigaku diffractometer with Fe Kα radiation. The peak intensities and angles were corrected using graphite as an internal standard.

Testing in lithium secondary battery

The cycling character of the cathode materials was evaluated in laboratory cells [9] as follows:

Li/1 M LiPF$_6$ in PC:DEC (1:4 in volume ratio)/LiCoO$_2$, TAB2

where PC = propylene carbonate, DEC = diethyl carbonate, and TAB2 = teflonized-acetylene black.

The cathode comprised 50 mg of $LiCoO_2$ mixed with 15 mg of semihydrophilic TAB2 [10]. The mixture was pressed onto a stainless steel screen at 800 kg cm^{-2}. Cells were cycled in the voltage range 3.7 to 4.3 V with a current density of 0.4 mA cm^{-2}.

The open-circuit voltage was obtained after the cell was allowed to stand for 23 h. In this case, a conventional electrolyte [9] was used to avoid a decrease in potential. A three-electrode cell was used. The counter and reference electrodes were lithium.

Results and discussion

Figure 1 shows the cyclic behaviour of $LiCoO_2$, obtained by the new method (at pH 4) using succinic acid and by the conventional method, in Li secondary batteries.
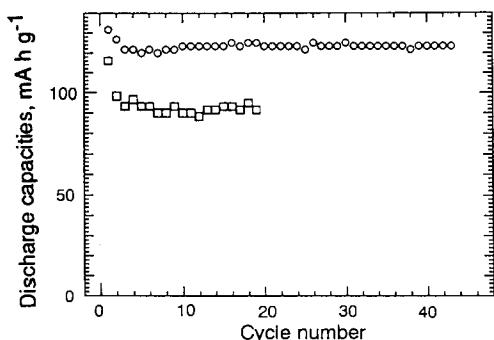

Fig. 1. Discharge capacities of $LiCoO_2$ obtained by: (○) cobalt complexes and (□) conventional method ($Li_2CO_3 + CoCO_3$).

The charge and discharge capacities coincide after 3 cycles in both cases. The discharge capacity of the LiCoO$_2$ prepared by the new and conventional methods are 120 to 125 and 90 to 95 mA h g^{-1}, respectively. This result shows that LiCoO$_2$ obtained by heating the cobalt–succinic acid complex delivers excellent cycling performance.

Figure 2 presents typical XRD patterns for LiCoO$_2$ obtained by the new, at pH 4, (patterns (a) to (d)) and the conventional methods (patterns (e) and (j)). High values of I$_{003}$ are obtained when using succinic or oxalic acid as complexing agents. It is observed that the intensities of the peaks (101), (104), etc, are very low in the case of a high (003) intensity of the samples.

Relative peak intensities of the (003) line of LiCoO$_2$ are given in the Table 1. The intensities increase when the cobalt complexes are formed at lower pH in the case of succinic and oxalic acids, while the intensity is decreased with decrease in pH when using malic acid. LiCoO$_2$ obtained with succinic acid exhibits the highest (003) line intensity among the samples.
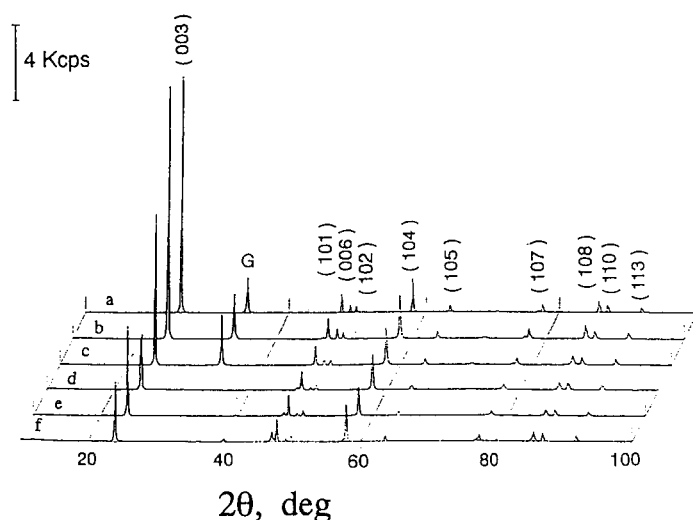

Fig. 2. Typical XRD patterns for LiCoO$_2$ obtained by heating cobalt–organic acid complexes prepared at pH 4.0 with LiOH: (a) succinic acid; (b) oxalic acid; (c) malic acid; (d) tartaric acid, and by heating mixtures of cobalt compound and Li$_2$CO$_3$: (e) Li$_2$CO$_3$+CoCO$_3$; (f) Li$_2$CO$_3$+Co$_3$O$_4$. Miller indices are based on a hexagonal unit cell; graphite peaks are denoted by G.

TABLE 1

Effects of preparation pH of cobalt complexes on relative intensities of (003) peak of LiCoO$_2$[a]

pH	4.0	6.0	8.0
Succinic acid	2.78	1.06	1.00
Oxalic acid	2.31	2.05	1.57
Malic acid	1.27	1.07	1.83

[a]The peak intensities are normalized by graphite (002) peak. The LiCoO$_2$ obtained from cobalt–succinic acid complex at pH 8.0 is selected as a standard.
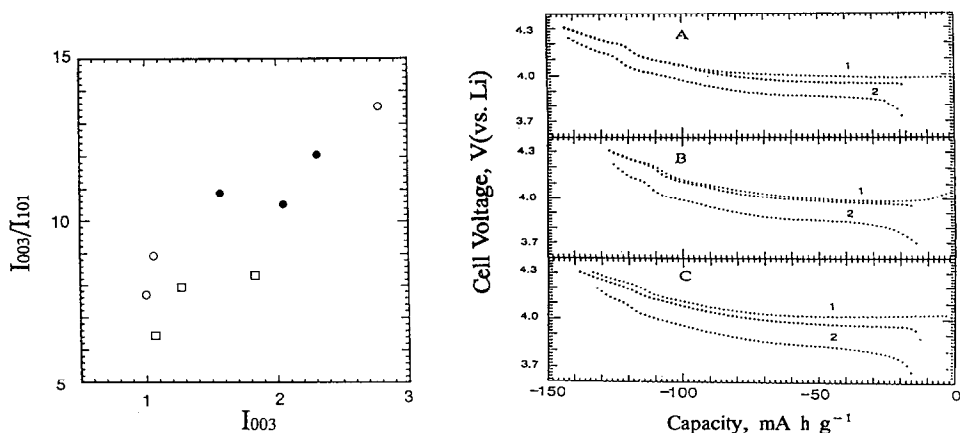
Fig. 3. Relation between I_{003}/I_{101} and relative intensities of (003) peak (I_{003}): (○) succinic acid; (●) oxalic acid, and (□) malic acid.

Fig. 4. Charge/discharge behaviour of $LiCoO_2$ obtained using (A) succinic acid at pH 4.0 and (B) the conventional method $Li_2CO_3 + Co_3O_4$, and (C) $Li_2CO_3 + CoCO_3$. Cycling between 4.3 and 3.7 V (vs. Li) at 0.4 mA cm^2. Negative sign in the capacity indicates charging, numbers denote charge/discharge cycles.

The relation between the corrected (003) line intensity and I_{003}/I_{101} is presented in Fig. 3. A linear relationship between the (003) line intensities and I_{003}/I_{101} is observed. In the $LiMO_2$ phase (M:V, Cr, Co, Fe and Ni), alternate layers of Li and M cations occupy the octahedral sites of a compact cubic close packing of oxide anions [11]. When an M atom occupies part of the octahedral sites of the Li layer, the (003) line intensity would decrease. A strong intensity of the (003) line means that $LiCoO_2$ has a well-developed layered structure.

Figure 4 gives the charge/discharge behaviour on the first cycle and the second charge process for a $LiCoO_2$/Li coin cell using $LiCoO_2$ obtained from a succinic acid solution (curve A) and by the conventional solid state reaction (curves B, C). The shapes of the three curves resemble each other and that reported in ref. 8. Lithium is deintercalated from $LiCoO_2$ during the first charge. The capacities for the first charge process for three $LiCoO_2$ samples are about 9 to 13% (i.e., 12–18 mA h g^{-1}) larger than those of the subsequent discharge process.

Discharge curves would probably show the existence of three electrode reactions during cycling from 4.3 to 3.7 V. The first reaction (region 1) occurs at a discharge voltage between 4.3 to 4.05 V, and the corresponding capacity, expressed as the Δx value of Li_xCoO_2, for sample A was $\Delta x = 0.099$ (27 mA h g^{-1}). The voltage ranges of the second (region 2) and third (region 3) reactions are 4.05 to 3.87 V and 3.87 to 3.7 V, respectively. The capacities of both reactions are about $\Delta x = 0.18$ (50 mA h g^{-1}). The voltage decrease in region 3 is much less than that in either region 1 or 2.

Sample A shows wider range of region 1 than samples B and C that are prepared by the solid-state reaction. The second charge curve for sample A closely approaches the discharge curves, which demonstrates the lower polarization of sample A.

The total capacity in both region 1 and region 2 for sample A is higher than the counterparts for samples B and C. The discharge curve in region 1 for A is flatter than that for either B or C. This is the cause of the higher capacity of sample A.

Figure 5 shows the open-circuit voltage curves for sample A. The potential decrease in region 1 is relatively smaller than that of the closed-circuit voltage curve, so polarization is significant in this region. In region 2, the potential decreases gradually with increase in x value in Li_xCoO_2. This means that the electrode reaction occurs in a single phase. The potential in region 3 is roughly constant. This indicates that a two-phase reaction occurs in region 3.

For the purpose of confirming the single-phase reaction in region 2 and the two-phase reaction in region 3, XRD studies have been carried out at various charge depths. As shown in Fig. 6 (c: $x = 0.85$, 40 mA h g^{-1} charge depth), three separated
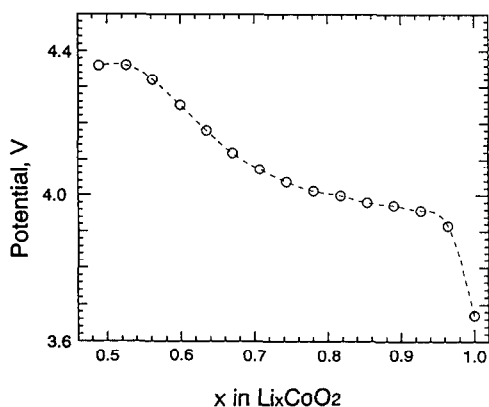

Fig. 5. Open-circuit voltage vs. Li$^+$/Li electrode as a function of x in Li_xCoO_2.
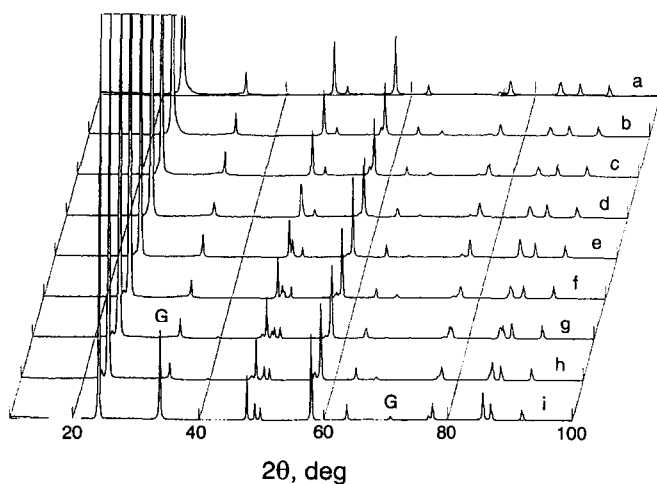

Fig. 6. XRD patterns for $LiCoO_2$ obtained by heating cobalt complex at various charge depths as a function of x in Li_xCoO_2: (a) $x = 0.42$; (b) $x = 0.49$; (c) $x = 0.56$; (d) $x = 0.64$; (e) $x = 0.71$; (f) $x = 0.78$; (g) $x = 0.85$; (h) $x = 0.93$ and (i) $x = 1.00$. G indicates the peaks due to graphite.

TABLE 2

Observed ($x = 0.85$) and calculated 2θ value for $LiCoO_2$ (1) and its product $Li_{0.71}CoO_2$ (2) in region 3

2θ observed	I/I_0	Miller indecis	2θ (1) calculated[a]	2θ (2) calculated[b]
23.72	100	003	23.72	23.59
47.44	10	101	47.49	47.57
48.30	2	006		48.25
48.72	3	006	48.54	
49.60	3	102	49.64	49.69
57.64	18	104	57.66	57.62
63.28	2	105	63.23	63.13
75.80	1	009	76.13	75.63
76.76	3	107		76.75
77.16	3	107	76.99	
84.94	3	108		84.94
85.42	4	108	85.16	
86.82	4	110	86.83	87.02
91.66	4	113	91.67	91.81

[a]$a_0 = 2.819$ Å, $c_0 = 14.14$ Å.
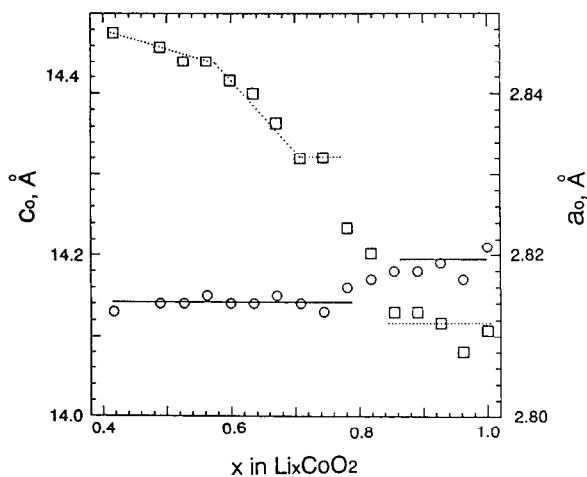[b]$a_0 = 2.814$ Å, $c_0 = 14.22$ Å.

Fig. 7. Hexagonal lattice parameters calculated at various charge depths as a function of x in Li_xCoO_2: (O) a-axis and (□) c-axis.

peaks (namely, (006), (107), (108)) can be clearly observed. New peaks due to delithiated product diffract at lower angles than the corresponding peaks of $LiCoO_2$. The peaks of $LiCoO_2$ are completely displaced by those of the product at $x = 0.71$. The hexagonal cell parameters of $LiCoO_2$ and the delithiated product calculated using the (003), (101), (104) and (110) lines are $a_0 = 2.819$ Å and $c_0 = 14.14$ Å and $a_0 = 2.814$ Å and $c_0 = 14.22$ Å, respectively. This demonstrates that two phases are present in region 3. Hence, both the XRD and open-circuit voltage data support the occurrence of a two-

phase reaction in region 3. The 2θ values calculated by the cell parameters of the two crystalline materials and observed at $x = 0.81$ are summarized in Table 2. The 2θ values of the observed peaks agree well (to within $0.2°$) with those of the calculated values. For the delithiation in region 3, the a axis shrinks 0.2% and the c axis expands 0.6%. The increase in unit-cell volume is only 0.2%, so this reaction might proceed reversibly.

The peaks shift continuously to lower angles on further charging. Nevertheless, the (110) peak shows constant 2θ values at a charge depth between $x = 0.71$ and 0.42. These results indicate that only the c-axis of the delithiated product produced in region 3 elongates with further delithiation in regions 1 and 2. The XRD study suggests that the electrochemical reaction is a single-phase reaction in regions 1 and 2.

The hexagonal lattice parameters are calculated at various charge depths to examine the electrode reaction in more detail in regions 1 and 2. The resulting calculated values of a_0 and c_0 are shown in Fig. 7. The expansion of the c-axis versus degree of delithiation (slope) in region 1 is roughly one-third that in region 2. With the delithiation, the c-axis expands more easily in region 2 than in region 1.

Conclusions

A well-developed layered structure of $LiCoO_2$ is obtained using an organic acid method. $LiCoO_2$ obtained by the new method shows lower polarization and higher capacity than that obtained by the conventional method. The cycling behaviour of the new material is also excellent. The electrode reactions of $LiCoO_2$ are composed of a two-phase reaction (region 3) and a single-phase reaction (regions 1 and 2).

Acknowledgement

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