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# Synthesis of $LiCoO_2$ powders from precursors prepared by precipitation process

Do Youn Kim, Jung In La and Cheong Song Choi†

*Department of Chemical Engineering, Sogang University, Seoul 121-742, Korea*

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**Abstract** $LiCoO_2$ powders were synthesized at various temperatures using lithium hydroxide and cobalt hydroxide as precursors prepared by precipitation process and freeze-drying. In this study, the $LiCoO_2$ samples were synthesized via a solid state reaction with various LiOH concentration between 10 % and 30 % excess. And $LiCoO_2$ powders were calcined at 600~800°C in a short time. Measurements of XRD and SEM were performed to characterize the properties of the prepared materials. The effect of amount of Li ions on the structural change in powder has been examined using the XRD analysis. For the not added excess of LiOH, CoOOH phase presented in the XRD pattern of $LiCoO_2$ due to loss of Li ions during firing. The morphology and particle size of the powders were examined using SEM. The obtained powders are high temperature-$LiCoO_2$(HT-$LiCoO_2$) and homogeneous with the range of grain size in the order of hundreds of nanometers. The effects of variation of LiOH concentration on the structural change in powder were investigated using the Rietveld analysis. As an analysis result, c/a is constant by 4.99 on all occasions. Finally, the structure of HT-$LiCoO_2$ was simulated by the commercial software Creius$^2$ (Molecular Simulations, Inc.) from the results of Rietveld analysis.

**Key words** Lithium ion battery, Intercalation, $LiCoO_2$, Rietveld analysis, layered structure, Synthesis

## 1. Introduction

The increasing demand for portable and cordless electronic appliances such as mobile phone, camcorder and laptop computer is driving the development of compact batteries. Lithium-ion batteries in particular have attracted much attention because of the following attributes: high output voltage, high specific energy, long cycle-life and no memory effect [1].

Lithium transition metal oxides such as $LiCoO_2$, $LiNiO_2$, $LiMnO_2$, $LiMn_2O_4$ and $LiV_3O_8$ are all high performance cathode materials for lithium-ion batteries [2]. Criteria for cathode material selection include: (i) electrochemical compatibility with the electrolyte solution over the required charge/discharge potential range; (ii) facile electrode kinetics; (iii) a high degree of reversibility, and (iv) air stability in the fully lithiated state.

At present, $LiCoO_2$ is widely used in commercial lithium-ion batteries. The traditional method for synthesizing $LiCoO_2$ is a solid-state reaction at high temperature and in a long time [3]. In this paper, a novel technique is introduced for the preparation of cathode materials for lithium-ion batteries. Precipitation process is used to produce the precursor which is calcined to give superfine $LiCoO_2$ powders.

†Corresponding author
Tel: +82-2-705-8481
Fax: +82-2-3273-0317
E-mail: cschoi@ccs.sogang.ac.kr

## 2. Experimental

$Co(OH)_2$ was precipitated by adding a 0.1 M solution of $Co(NO)_3 \cdot 6H_2O$ (ALDRICH, 98 %) in deionized water to a stirred aqueous solution of $LiOH \cdot H_2O$ (SIGMA, 99 %) in deionized water, continuously monitored and titrated by a solution of $LiOH \cdot H_2O$ to maintain the pH at 11, near the minimum solubility point $Co(OH)_2$ [4]. A critical step was the removal of nitrate ions from the suspension by a rinsing procedure, which otherwise reform low-melting nitrate compounds upon drying. On subsequent calcining, melting of these salts can cause compositional segregation [5]. The supernatant liquid from the precipitation was first decanted, and the $Co(OH)_2$ ultrasonically dispersed in a buffer solution of $LiOH \cdot H_2O$ in water at pH 11. The precipitate was settled by centrifugation and the supernatant again decanted. For complete rinsing, this cycle of dispersion in buffer solution, settling by centrifugation, and decanting was conducted a total of five times [5].

To obtain the uniformly discrete $Co(OH)_2$ powders, the rinsed precipitate was freeze-dried by a freeze dryer (EYELA, FD-81). After $LiOH \cdot H_2O$ particles were dehydrated by a freeze dryer, the dried particles were ground by a mortar. The mixture of $Co(OH)_2$ and LiOH was

calcined in a programmable muffle furnace with various LiOH concentrations, ranging from 10 % to 30 % excess at 800°C for 4 hr and at various temperatures between 600 and 800°C for 4 hr.

Powder X-ray diffraction (XRD, Rigaku, D/MAX-A) with $CuK_\alpha$ radiation was used to identify the crystalline phase of the material calcined at various conditions such as described above. Particle morphologies of the material were examined by scanning electron microscopy (SEM, Hitachi, S-3500N). The structure was investigated by X-ray diffraction data using the Rietan program with a pseudo-Voigt function. The structure of HT-$LiCoO_2$ was simulated by the commercial software Creius[2].

## 3. Results and Discussion

Figure 1 shows XRD patterns characterized by step mode for $LiCoO_2$ calcined with various LiOH concentrations at 800°C for 4 hr. For the Li : Co = 1 : 1 system [Fig. 1(a)], CoOOH peak as well as the HT-$LiCoO_2$ phase is observed. But the HT-$LiCoO_2$ phase is only observed for the other systems added more lithium between 10 % and 30 % [Fig. 1(b)~(d)]. The reason is that the slight excess of lithium was included to compensate for loss of lithium during firing because of volatility. Table 1 shows the calculated lattice parameters.

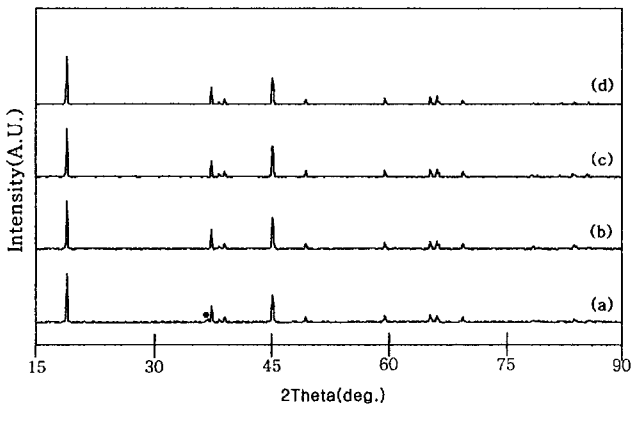


Fig. 1. XRD patterns of $LiCoO_2$ prepared from precursor mixtures which are include excess of lithium (a) no excess, (b) 10 % excess, (c) 20 % excess, (d) 30 % excess (●: CoOOH).

Table 1
Rietveld analysis of $LiCoO_2$ powders

| Amount of Li excess | a = b | c | c/a |
|---|---|---|---|
| 10 % | 2.81698 | 14.05446 | 4.99 |
| 20 % | 2.81157 | 14.03700 | 4.99 |
| 30 % | 2.81115 | 14.03325 | 4.99 |

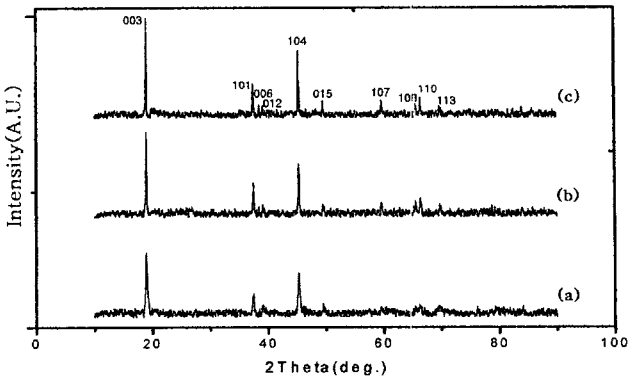


Fig. 2. XRD patterns of $LiCoO_2$ calcined at different temperatures (a) 600°C, (b) 700°C, (c) 800°C (Li 10 % excess).

The lattice parameters (a, b, c) decrease with increasing amount of LiOH. The c/a is constant by 4.99 on all occasions, which implies a cation ordering in our samples. This value is in good agreement with the value reported by others [6, 7].

Figure 2 shows XRD patterns characterized by continuous mode for $LiCoO_2$ calcined at various temperatures for 4 hr. All samples appear HT-$LiCoO_2$ in XRD patterns. The (006) and (012) peaks and (108) and (110) peaks are well-separated in the patterns of HT-$LiCoO_2$ samples. It is well-known that the presence of the well-ordered HT-$LiCoO_2$ is evidenced by splitting of the (006)/(012) peaks and (108)/(110) peaks [6]. This can be compared with the samples calcined at temperatures of T > 900°C and times of > 24 hr to obtain single-phase material in conventional processing with carbonate precursors.

SEM microphotographs of the powders calcined at various temperatures for 4 hr are shown in Fig. 3. As the calcination temperature increased, the size of the grains increases systematically and the shape of the grains changes to hexagonal plate. The presence of loosely agglomerated particles with a submicron particle size was observed from the powders calcined at 600 and 700°C. When the precursor powders were calcined at 800°C, the average particle size of the powders was abruptly increased up to 2~3 μm and the mosaic submicrostructure largely disappears via the diffusion of atoms away from the grain boundary between adjacent particles.

The $LiCoO_2$ sample was characterized by Rietveld refinement of powder X-ray diffraction data. The refinement results are presented in Table 2. The $LiCoO_2$ X-ray diffraction pattern simulated by Rietan [8] is shown in Fig. 4. In the Fig. 4, the solid line is calculated patterns and points superimposed on it are observed intensities.

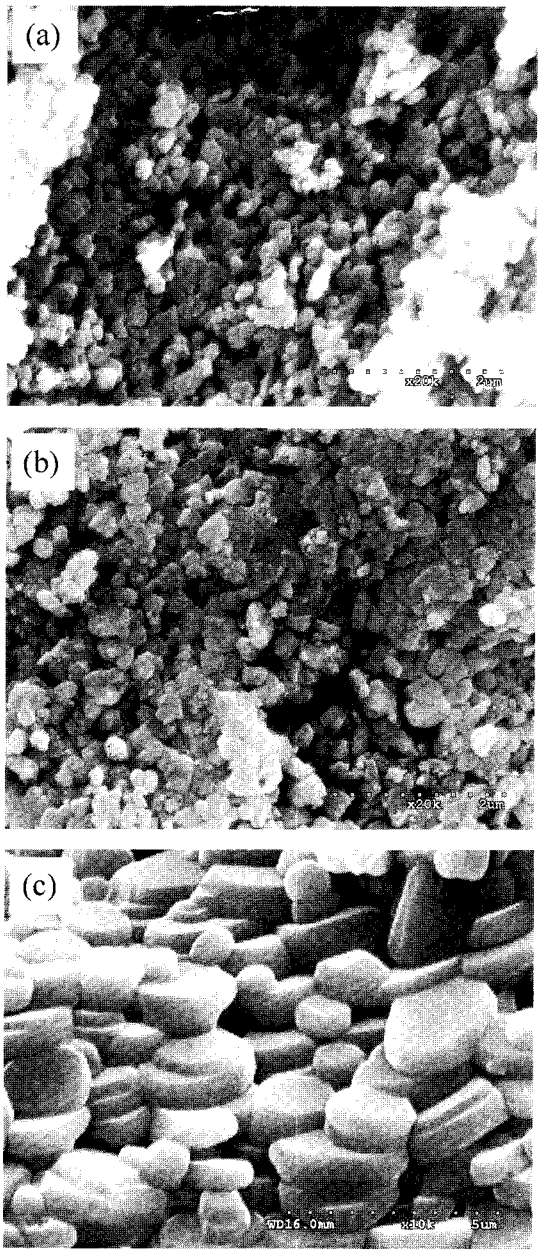


Fig. 3. Scanning electron micrographs of the powders calcined at (a) 600°C, (b) 700°C, (c) 800°C.

Table 2
Rietveld refinement of synthesized $LiCoO_2$ X-ray diffraction spectra space group R-3m, a = b = 2.81698, c = 14.05446

| Atom | Site | x | y | z | B (Å$^2$) | Occupancy |
|---|---|---|---|---|---|---|
| Li | 3a | 0 | 0 | 0 | 0.533 | 1.0 |
| Co | 3b | 0 | 0 | 0.5 | −0.135 | 1.0 |
| O | 6c | 0 | 0 | 0.2417 | 0.007 | 1.0 |

$R_{wp} = 0.47$, $R_e = 0.32$, $S = 1.4635$

where, $R_{wp}^2 = \frac{\Sigma W[Y_{obs} - Y_{calc}]^2}{\Sigma W[Y_{obs}]^2}$; $R_e^2 = \frac{N - P + C}{\Sigma W[Y_{obs}]^2}$, $S = \frac{R_{wp}}{R_e}$

and $Y_{obs}$ = observation at time of flight, $t_{obs}$; W = weights and N − P + C = number of observations − number of variables + number of constraints.

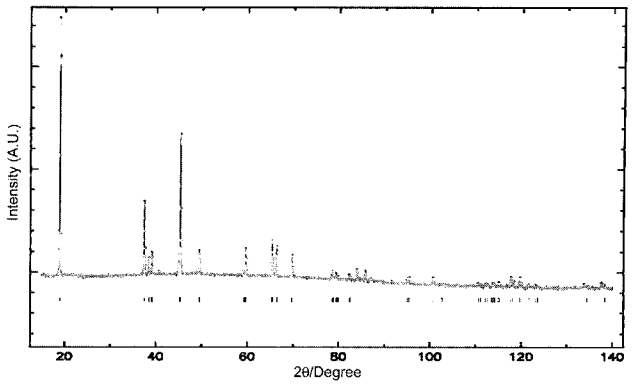


Fig. 4. Observed and calculated X-ray diffraction profiles for $LiCoO_2$ : (●) observed; (—) calculated; lower trace, difference plot; bar, reflections.

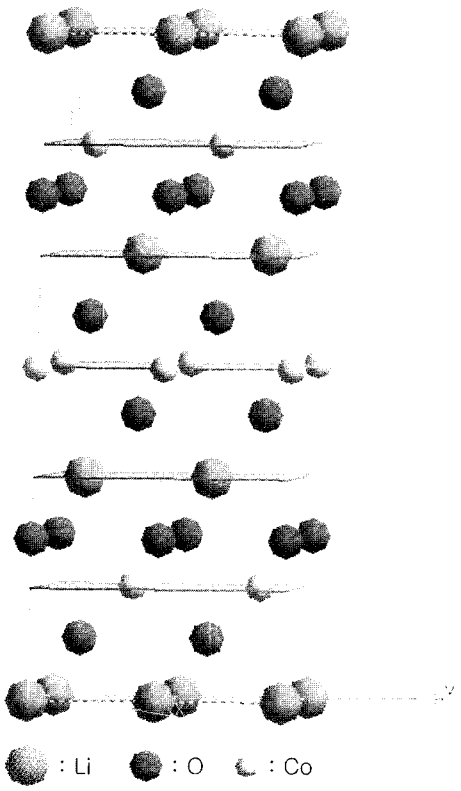


Fig. 5. Structure of well-ordered HT- $LiCoO_2$.

The differences between the observed and calculated diffraction patterns are shown by the solid line at the bottom. Tick marks below the profile indicate the positions of all allowed peaks. Figure 5 shows the structure of well-order HT-$LiCoO_2$ simulated by using Cerius$^2$ module from Table 2.

CoOOH (space group R-3m, $a_0 = 0.2855$ nm, $c_0 = 1.3156$ nm) is conceptually a likely intermediate in the transformation, being the product of $Co(OH)_2$ decomposition and being isostructural with $LiCoO_2$. The decomposition and intercalation steps can be written as the sepa-

rate reactions

$$2Co(OH)_2 + 1/2O_2(g) \rightarrow 2CoOOH + H_2O \quad (1)$$

$$CoOOH + LiOH{\cdot}H_2O \rightarrow LiCoO_2 + 2H_2O(g) \quad (2)$$

The hydrothermal synthesis of Amatucci *et al.* [9] used reaction (2). In the present experiments, both reactions occur in sequence. The absence of a clearly distinguishable CoOOH intermediate indicates that (2) occurs rapidly and is not the rate-limiting step for the overall transformation.

## 4. Conclusion

$LiCoO_2$ powders were synthesized by a solid-state reaction incorporating precipitation and freeze-drying of hydroxides precursors. Firing of simple physical mixture of hydroxides results in synthesis of well-ordered HT-$LiCoO_2$ at reduced temperatures and times compared to conventional solid-state reactions. XRD results showed the optimum condition which can synthesize a single-phase HT-$LiCoO_2$. From the SEM results, the size of $LiCoO_2$ particles depended on the calcination temperature. The Rietveld refinement and simulation results showed that $LiCoO_2$ powder has a layered rock-salt structure which is based on a close-packed network of oxygen atoms with $Li^+$ and $Co^{3+}$ ions ordering on alternating (006) planes.

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