

Syntheses of LiCoO_2 for cathode materials of secondary batteries from reflux reactions at 130–200 °C

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Abstract

Low temperature syntheses of LiCoO_2 cathode materials for Li-secondary battery applications were studied in aqueous solutions by hydrothermal and reflux reactions. By controlling the oxidation potential of the reaction environments, we could synthesize phase pure LiCoO_2 directly from Co(OH)_2 at as low as 130 °C, contrary to the reported hydrothermal reactions at 200–220 °C starting with CoOOH . Having high pH over 15 and an O_2 flow induced the oxidation reaction of the divalent cobalt in Co(OH)_2 . The products so obtained have well-crystallized high temperature form of LiCoO_2 with the layered structure as proved by powder X-ray diffraction (XRD) and the Raman spectroscopy data. The particles have a uniform size distribution around 100 nm with well-developed crystallite morphology. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Battery; Synthesis; Reflux; Lithium cobalt oxide; High temperature form

1. Introduction

Lithiated transition metal oxides, such as LiCoO_2 , LiMnO_2 (orthorhombic), LiMnO_2 (layered), and LiMn_2O_4 , have been studied widely as cathode materials in lithium-secondary batteries because of their high operating voltage and energy density, large capacity, and long cycle life [1–5]. Despite the highest cost among the candidate materials, LiCoO_2 is produced and used most widely for its good thermal and structural stability during electrochemical operations.

Commercial LiCoO_2 is synthesized by solid state reactions at high temperatures of 800–1000 °C, usually requiring a pre-treatment step at lower temperatures. Many researchers have attempted to find new synthetic methods at lower temperatures in order to reduce the production cost. For example, sol–gel method [6–12], co-precipitation method [13–15], hydrothermal synthesis [16,17], and ion exchange reactions [18,19] between Li^+ and H^+ of CoOOH have been reported. Generally, the low temperature synthesis result in fine powdery samples, which can be an additional useful feature for battery materials as long as the crystallinity is not affected by the small particle sizes. However, although these approaches have achieved the synthesis of LiCoO_2 at

significantly low temperatures as low as 100 °C [18,19], they do not appear to be greatly advantageous over the conventional solid state methods in terms of the cost because of the expensive reagents and/or the difficult synthesis conditions. Some of these techniques do not appear appropriate for a large-scale production. Moreover, many of the low temperature synthesis methods, besides the hydrothermal technique, employ post-heat treatment at 300–900 °C and result in the so-called low temperature phase of LiCoO_2 (LT- LiCoO_2) with poorer electrochemical performance than the layered-type high temperature (HT) phase [6–15]. On the basis of these observations, the hydrothermal method appears to be the best alternative to the traditional solid state reactions. However, most of the hydrothermal reactions in the literature started from the preparation of CoOOH precursor from Co^{2+} -containing compounds prior to the hydrothermal treatment, complicating the process [17–19], with one exception in which the oxidation of CoCl_2 and formation of LiCoO_2 were performed in a one step reaction by using NaClO_3 oxidizing agent [16].

Because the oxidation state of metal ions in an aqueous solution can be controlled by adjusting oxidation potential and pH along with many other variables [20,21], we have performed systematic studies on the low temperature reactions of Co(OH)_2 in an aqueous system at as low as 130 °C by hydrothermal and reflux reactions. These two methods are different in that reactions are run under a high pressure in

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the former method while reflux reactions are run under an ambient pressure. Because the solutions can be continuously stirred throughout the reactions and the reaction atmosphere can be easily controlled during reactions, the reflux technique appears more advantageous over the hydrothermal method for a large-scale production. There is a paper that reports very briefly that LiCoO_2 can be obtained from boiling water [22]. However, none of the details for the reaction conditions or the characterization of the material so-obtained are available in the paper, let alone the chemistry of the system.

In this paper, we report the details of the reaction conditions in the hydrothermal and reflux methods, and their consequences in terms of the phase purity, crystallinity, and particle sizes are described. The electrochemical charging and discharging characteristics of a representative sample from a reflux reaction is also presented.

2. Experimental

2.1. Synthesis

In a typical reaction, 1.0 g (0.011 mol) of Co(OH)_2 and 0.5 g (0.012 mol) of $\text{LiOH}\cdot\text{H}_2\text{O}$ were dissolved/suspended into 20 ml of a 12 M KOH solution. The composition of the solution so prepared is approximately $\text{Co(OH)}_2\text{:LiOH}\cdot\text{H}_2\text{O}\text{:KOH:H}_2\text{O} = 1\text{:}1.1\text{:}20\text{:}100$. In some reactions, the amounts of the reagents were scaled up by factors of 3, 4, or 6, but the relative ratio was kept constant. This solution was placed in a Teflon-lined autoclave of 25 ml volume or a polypropylene bottle of 250 or 500 ml volume for hydrothermal reactions. The reactions were carried out at 130–200 °C for 48 h under an autogeneous pressure. For reflux reactions, the solution was placed in a round-bottomed flask made of Teflon with a water cooled condenser placed on top of it. The reflux reactions were carried out at 130–200 °C for 6–48 h under

a flow of O_2 or in air. Note that these reaction temperatures are in fact the temperatures of the oil bath in which the flask was immersed; the real reaction temperatures for these reactions may well be lower than the ones indicated. The solutions were cooled to room temperature after the reactions, and the products were filtered off, washed repeatedly with distilled water, and dried at 120 °C in an oven. The synthesis results for various reaction conditions are summarized in Table 1.

2.2. Characterization

The products were identified by X-ray powder diffractometry (MAC Science, 18XMF) using monochromatized $\text{Cu K}\alpha$ radiation. Rietveld profile refinement on a sample from the 200 °C reflux reaction (rxn 7 in Table 1) was performed by using the Fullprof software [23]. For comparison sake, a commercial LiCoO_2 sample (Nippon Chemical Co., Japan) from a solid state reaction was also analyzed by the Rietveld method. Infrared spectra of samples dispersed on KBr pellets were recorded on a Nicolet 205 FT-IR spectrometer. Scanning electron microscope (SEM) images were obtained by a JSM-6330F field emission scanning electron microscope. Raman spectra were obtained using a Jobin-Yvon U1000 Raman spectrometer. The samples were excited by a 514 nm line of an argon ion laser at 100 mW with 1/5 filter for 300 s.

Electrochemical analysis was performed by obtaining charge–discharge cycle curves from a coin-type cell of lithium battery [24]. The powders were mixed with PVDF binder and activated carbon, and casted into a tape cut into a circular shape of 1.6 cm diameter. The anode of the cell was metallic lithium and the electrolyte was LiPF_6 dissolved in EC/DMC (1:1) [25]. The charge–discharge cycles were carried out in a constant current mode with voltages from 2.8 to 4.3 V and performed stepwise at rates C/10 for four cycles, at C/5 for nine cycles and then 1C for a total of 100 cycles.

Table 1
Reaction conditions and products of the hydrothermal and reflux syntheses of LiCoO_2

| rxn no. | Composition (mol) | | | rxn temperature (°C) | rxn time (h) | Condition | Product ^a |
|---------|-------------------|--------------------------------------|------------------|----------------------|--------------|---|---|
| | Co(OH)_2 | $\text{LiOH}\cdot\text{H}_2\text{O}$ | KOH ^b | | | | |
| 1 | 0.011 | 0.012 | 20 | 130 | 48 | H ^c , pp bottle ^d | LiCoO_2 (100) |
| 2 | 0.011 | 0.012 | 20 | 150 | 48 | H, autoclave ^c | LiCoO_2 (75), Co_3O_4 (15), Co(OH)_2 (10) |
| 3 | 0.011 | 0.012 | 20 | 200 | 48 | H, autoclave | LiCoO_2 (80), Co_3O_4 (15), Co(OH)_2 (5) |
| 4 | 0.066 | 0.072 | 120 | 130 | 48 | R ^c , O_2 | LiCoO_2 (100) |
| 5 | 0.044 | 0.048 | 80 | 130 | 48 | R, air | LiCoO_2 (95), Co_3O_4 (5) |
| 6 | 0.066 | 0.072 | 120 | 180 | 48 | R, O_2 | LiCoO_2 (100) |
| 7 | 0.066 | 0.072 | 120 | 200 | 48 | R, O_2 | LiCoO_2 (100) |
| 8 | 0.066 | 0.072 | 120 | 130 | 6 | R, O_2 | LiCoO_2 (35), Co_3O_4 (50), Co(OH)_2 (15) |
| 9 | 0.066 | 0.072 | 120 | 130 | 12 | R, O_2 | LiCoO_2 (60), Co_3O_4 (30), Co(OH)_2 (10) |

^a Estimated from the relative peak intensities in the powder X-ray diffraction pattern.

^b Volume of a 12 M KOH solution.

^c H: hydrothermal reaction, R: reflux reaction.

^d pp bottle: polypropylene bottle of volume 500 ml.

^e Teflon-lined autoclave with 25 ml of volume.

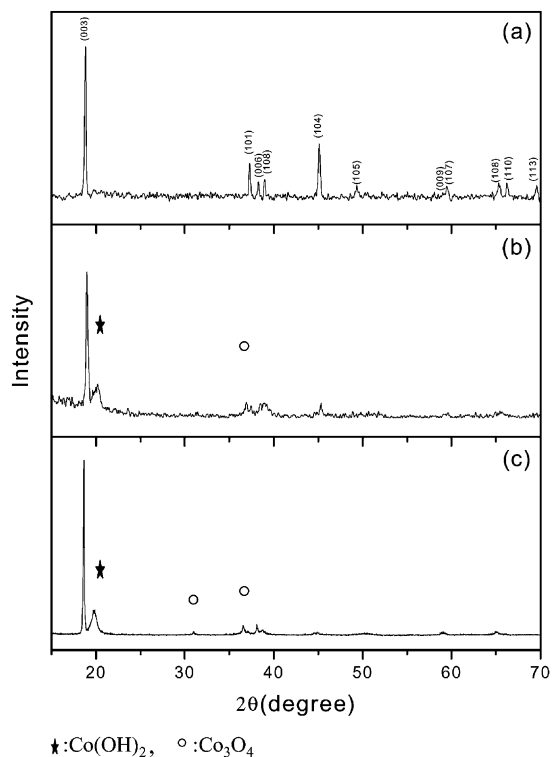


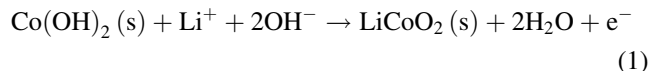
Fig. 1. X-ray powder patterns of LiCoO_2 samples from hydrothermal reactions between Co(OH)_2 and LiOH for 48 h at (a) 130 °C, (b) 150 °C, and (c) 200 °C.

3. Results and discussion

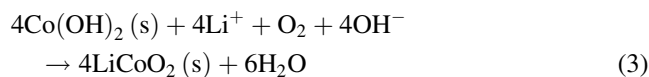
During our attempts to reduce the reaction temperature of the hydrothermal synthesis, we have found that LiCoO_2 can be synthesized at temperatures as low as 130 °C (rxns 1–3 in Table 1). The X-ray diffraction (XRD) patterns of these samples are shown in Fig. 1. There are some important observations to be noted from these reactions. First, these reactions demonstrate that the LiCoO_2 compound can be synthesized from Co(OH)_2 with Co^{2+} instead of Co^{3+} -containing species in most of the hydrothermal literature [17–19]. In fact, we found that the similar results were obtained when other types of Co^{2+} compounds such as $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ or $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ were used as the starting materials. The choice of Co(OH)_2 in the present study is because it does not produce any by-products such as Cl^- or NH_4^+ , a desirable feature for applications. Second, the reaction temperature is considerably lower than those of 200–220 °C in the literature. Because the reaction during the hydrothermal synthesis involves a Co^{3+} -containing intermediate (below), the successful low temperature synthesis of LiCoO_2 does not appear to be related with the nature of the starting material. Rather, this implies that the thermodynamic equilibrium under the given condition is favorable for the formation of LiCoO_2 at as low as 130 °C. Notice that we have not tried any lower temperature than 130 °C in the present study. Therefore, it is very likely that the 130 °C is not the lowest limit for the LiCoO_2 formation.

The hydrolysis reaction of $[\text{Co}(\text{NH}_3)_6]^{3+}$ in a 3 M LiOH solution at room temperature, reportedly, yields a mixture of LiCoO_2 and HCoO_2 [26], supporting this projection. Third, the products from the higher temperature reactions at 150 and 200 °C (rxns 2 and 3) contain small amounts of Co(OH)_2 and/or Co_3O_4 impurities, while the 130 °C product is a single phased LiCoO_2 . Besides the different reaction temperature, the 130 °C reaction was run in a polypropylene bottle with a larger volume (500 ml) than that of the autoclave (25 ml) for the higher temperature reactions. The presence of Co^{2+} -containing impurities Co(OH)_2 and Co_3O_4 in the products of higher temperature reactions suggests that the oxidation potentials of these reactions are not high enough to convert all the divalent cobalt of starting Co(OH)_2 into the trivalent state of LiCoO_2 . Therefore, we can explain the synthesis of pure LiCoO_2 phase from the 130 °C hydrothermal reaction is because of the larger amount of O_2 available to oxidize Co^{2+} in the free volume of the 500 ml polypropylene container than that in the 25 ml autoclaves used in the higher temperature reactions. Reactions under the same condition as rxn 1 but in a 250 ml bottle or in a 500 ml bottle with the amounts of reagents triplicated resulted in samples contaminated by small amounts of impurities, supporting our explanation of the oxidation by O_2 in the free volume.

Above observations can be explained by considering the following half reactions:



Combining these equations gives the overall reaction:



The amount of O_2 available in the free volume ($\sim 480 = 500$ (bottle) – 20 (solution) ml) for the rxn 1 was estimated to be 0.0042 mol, slightly more than required to oxidize all of Co^{2+} in the solution (0.01 mol) according to Eq. (3). This calculation also explains why the other 130 °C reactions in a smaller bottle and with larger amounts of reagents fail to synthesize pure LiCoO_2 . Of course, Eq. (3) is not the only way to oxidize Co^{2+} ; H_2O can function as an oxidizing agent as in the following equation:



Thus, the formation of LiCoO_2 in the hydrothermal reactions in autoclaves can be explained by this reaction coupled with the Eq. (1) as well as due to the dissolved O_2 and O_2 in the free volume.

Since the reaction temperature of 130 °C can be easily achieved in aqueous solutions with high KOH concentration (12 M) without the help of an autoclave, we have explored the possibility of reflux reactions for the synthesis of LiCoO_2 . In fact, we have found that the reflux temperature

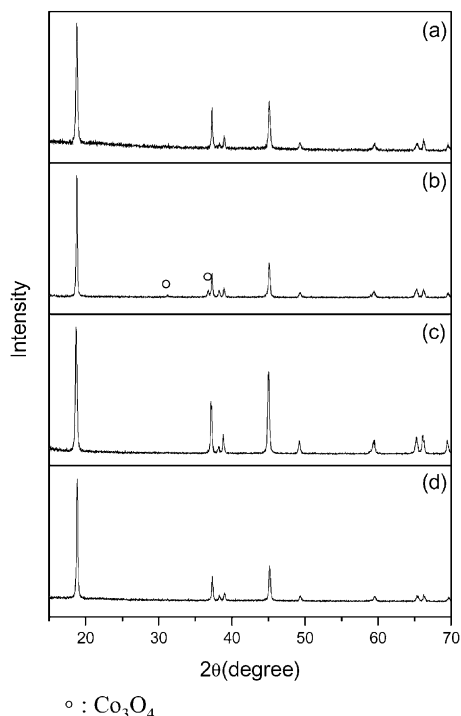


Fig. 2. X-ray powder patterns of LiCoO_2 samples from reflux reactions between Co(OH)_2 and LiOH for 48 h under an O_2 flow at (a) 130°C , (b) 130°C (in air), (c) 180°C , and (d) 200°C .

can be raised up to 200°C . Indeed, a reflux reaction at 130°C under an O_2 flow (rxn 4) produced a single phased LiCoO_2 (Fig. 2a). As can be found in the reaction conditions in Table 1, this reflux reaction used the similar conditions as the 130°C hydrothermal reaction except for the O_2 flow in the reflux reaction. On the contrary, a reflux reaction in air instead of an O_2 flow always produced samples contaminated by Co(OH)_2 and Co_3O_4 impurities (rxn 5) (Fig. 2b).

These results at 130°C of the hydrothermal and reflux reactions clearly show that the control of the oxidation potential is crucial for the synthesis of pure LiCoO_2 .

As long as the high oxidation potential is maintained by flowing O_2 , changing the reaction temperature does not influence the purity of the final product (Fig. 2c and d). The lattice parameters of these samples are identical within experimental error limits, indicating that they have the same compositions. The particles sizes are not influenced by the reaction temperature significantly as evidenced by the peak widths of the XRD patterns ($\text{FWHM} = 0.24^\circ$ for the 130°C sample to 0.22° for the 200°C sample) and the SEM images of the samples. Fig. 3 shows the SEM image of the sample from a 200°C reflux reaction (rxn 7); the particles have a uniform size distribution at around 100 nm with well-developed crystallite faces, indicating good crystallinity. Note that the 180 and 200°C reflux reaction (rxns 6 and 7) produced a pure LiCoO_2 sample, contrary to the hydrothermal reaction at 150 and 200°C (rxns 2 and 3), again, because of the insufficient amount of oxidizing agent in the latter two cases.

In order to have an effective oxidizing environment by simply flowing O_2 , the control of pH is very important, as is well known from the Pourbaix diagram [21]. According to this relationship, the high oxidation state of a metal ion is stabilized at the high pH and high oxidation potential regime. The minimum oxidation potential to stabilize a certain high oxidation state of a metal decreases as pH increases. Therefore, if a stronger oxidizing environment than 1 atm O_2 is used the pH of the solution can be lowered. In the present study, we have used a 12 M KOH solution ($\text{pH} = 15.1$) for all the reactions because the combination of this pH and O_2 flow appears to be close to the boundary between the Co^{3+} and Co^{2+} stability regions. Replacing KOH with LiOH hampers the reaction because the lower

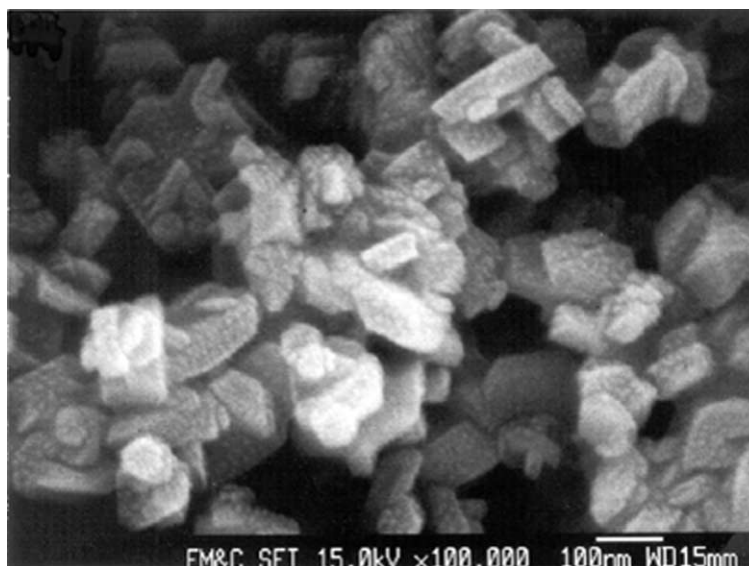
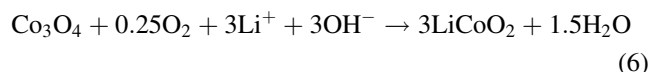
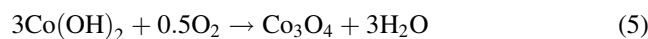


Fig. 3. Scanning electron microscope image of a LiCoO_2 sample synthesized from a reflux reaction of Co(OH)_2 and LiOH at 200°C for 48 h.

solubility of LiOH prohibits the required minimum pH. Similarly, using NH_4OH instead of KOH cannot work because it is a weak base. However, if a stronger oxidation environment than 1 atm O_2 is used less harsh pH conditions may be enough. As reported by Tabuchi et al. NaClO_3 can be a good oxidizing agent for this purpose [16], although they employed much higher concentration of NaOH than in the present study.

In order to observe the progress of the LiCoO_2 formation during the reflux reactions, some reactions at 130°C under an O_2 flow were carried out for varied lengths of reaction time. The product from a 6 h reflux (rxn 8) shows large amounts of Co_3O_4 and $\text{Co}(\text{OH})_2$ mixed with a small amount of LiCoO_2 in the XRD pattern (Fig. 4a). Longer refluxing time of 12 h (rxn 9) increases the amount of LiCoO_2 but still with the impurities (Fig. 4b); it takes more than 24 h to get a phase pure LiCoO_2 sample. Therefore, the formation of LiCoO_2 from $\text{Co}(\text{OH})_2$ in this study occurs in the following two step redox reactions:



Upon heating at 90°C in air in a basic aqueous solution, $\text{Co}(\text{OH})_2$ can be converted into Co_3O_4 [27], explaining our observation of Co_3O_4 intermediate during the 130°C reactions.

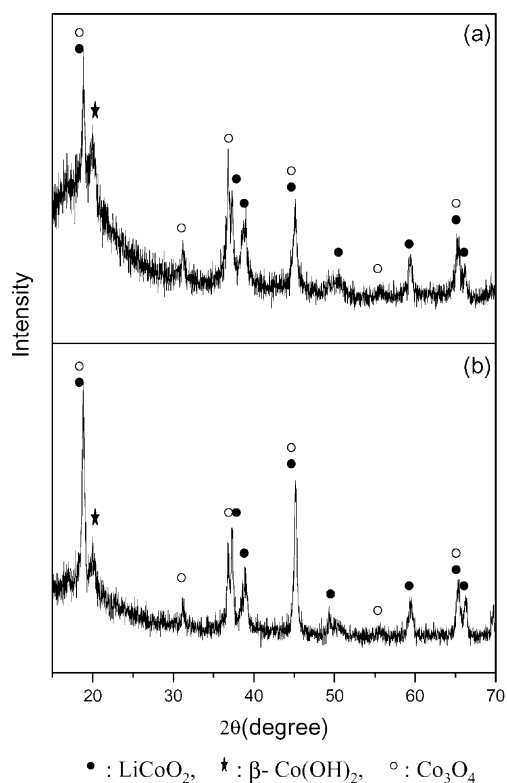


Fig. 4. X-ray powder patterns of LiCoO_2 samples from reflux reactions between $\text{Co}(\text{OH})_2$ and LiOH for at 130°C under an O_2 flow for (a) 6 h and (b) 12 h.

Based on the experimentally [9–12,15,28–31] and theoretically [32] well established structural relationship between the spinel-structure and ordered $\alpha\text{-NaFeO}_2$ structure of Li_xCoO_2 and LiMnO_2 , we believed that the conversion of Co_3O_4 into LiCoO_2 in reaction (6) also occurs as a solid-to-solid transformation reaction, not involving a dissolution/recrystallization mechanism.

The lattice parameters of the compounds from the reflux reactions agree with those of stoichiometric LiCoO_2 in the literature. We have performed Rietveld structure refinements on the sample from rxn 7 (200°C reflux) and a commercial LiCoO_2 from a solid state reaction for a comparison sake (Fig. 5). The refined lattice parameters of the refluxed sample ($a = 2.8151(2)$ and $c = 14.049(1)$ Å) are identical to those of the solid state synthesized sample ($a = 2.8156(1)$ and $c = 14.0506(4)$ Å) within experimental errors. These values also agree well with those for the $x = 1.00$ compound of Li_xCoO_2 in the literature, indicating that the reflux reaction is an efficient way to synthesize stoichiometric

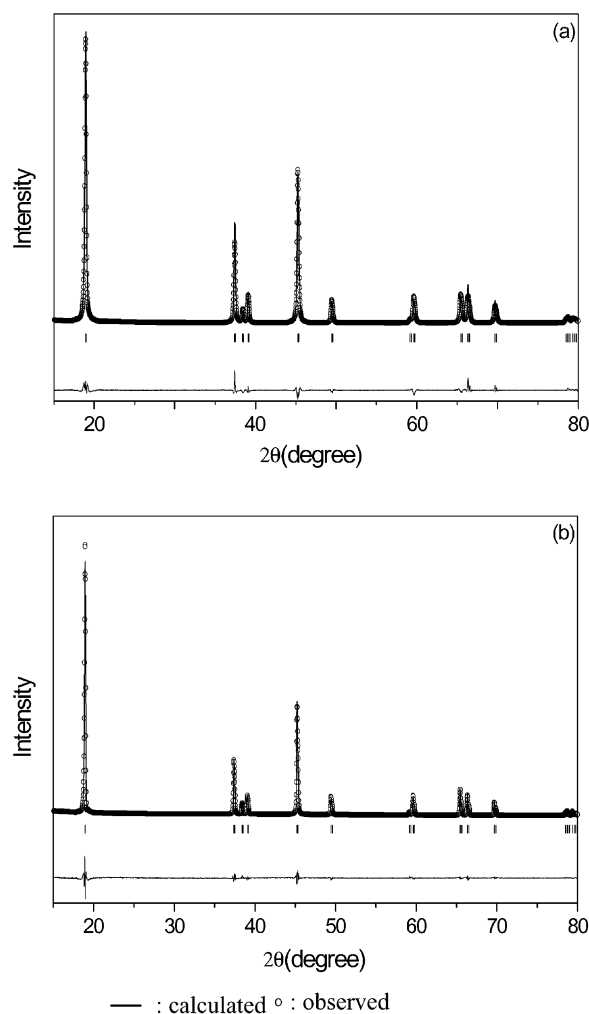


Fig. 5. Rietveld refinement results of LiCoO_2 samples (a) from a reflux reaction at 200°C under an O_2 flow for 48 h and (b) a solid state synthesis at high temperature (commercial sample).

LiCoO₂. For example, in their systematic study on Li_xCoO₂ with various *x*, Ménétrier and co-workers reported lattice parameters *a* = 2.8155(2) and *c* = 14.049(5) Å for the *x* = 1.0 compound [33,34], and a single crystal diffraction data on a stoichiometric LiCoO₂ was reported to have *a* = 2.8161(5) and *c* = 14.0536(5) Å [35].

As mentioned earlier, LiCoO₂ is reported to have two closely related structural modifications, layered-type HT and spinel related LT-LiCoO₂ [9–12,15,28–30]. The distinction between these two phase by XRD pattern is not easy because their powder patterns are almost identical, as demonstrated by Rossen et al. [30]. Kang et al. showed that the Raman spectroscopy can be a useful means to differentiate these two structures [15]. The factor group analyses on the space groups *R3m* and *Fd3m* (for the HT and LT phases, respectively) predict two and four Raman bands, respectively. They reported two strong Raman bands at 487 and 596 cm⁻¹ for the HT-LiCoO₂ and three Raman bands were observed at 447, 475 and 582 cm⁻¹ for the LT-LiCoO₂. Both of our LiCoO₂ from rxn 7 and a commercial LiCoO₂ show two strong bands at 484 and 593 cm⁻¹ in their Raman spectra (Fig. 6) in agreement with the assignment to the HT structure. It is interesting to note that all of the LiCoO₂ synthesized in aqueous media, including the hydrothermal in the literature and present reflux reactions, have the HT modification, despite that these methods use the lowest reaction temperature. Probably, the solution reactions provide a means for efficient material transportation, overcoming any diffusion barriers, to form the thermodynamically more stable phase.

Electrochemical analysis was performed on the sample from the 200 °C reflux reaction (rxn 7). The first charge-

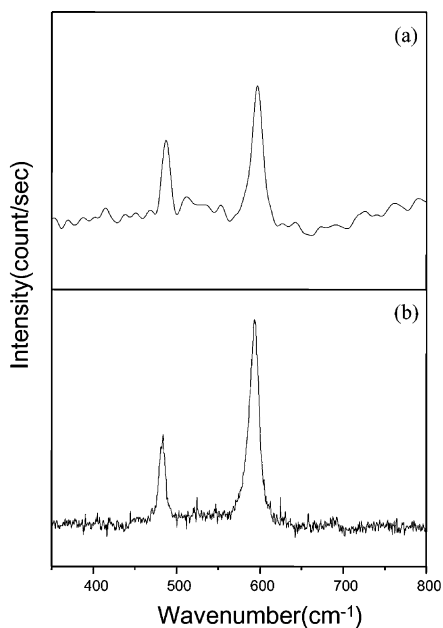


Fig. 6. Raman spectra of LiCoO₂ samples (a) synthesized from a reflux reaction of Co(OH)₂ and LiOH at 200 °C for 48 h and (b) a solid state reaction at high temperature (commercial sample).

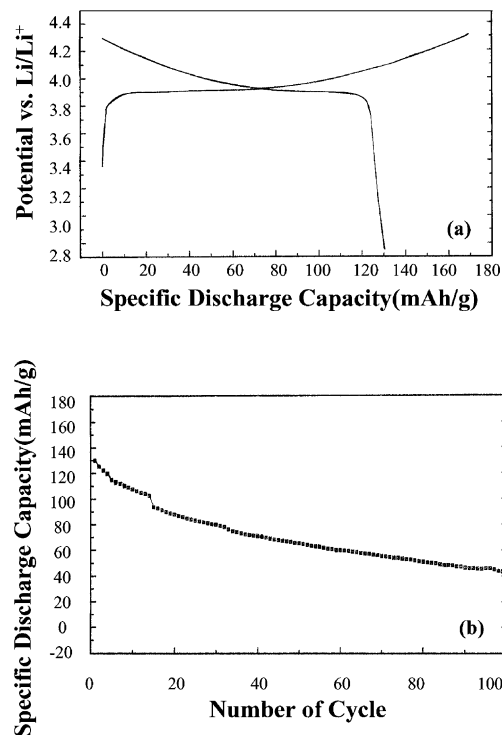


Fig. 7. (a) Charge and discharge characteristics and (b) the change of capacity as a function of the number of charge–discharge cycle for a LiCoO₂ synthesized from a reflux reaction of Co(OH)₂ and LiOH at 200 °C for 48 h.

discharge curves in Fig. 7a shows a charging capacity of 170 mAh/g, larger than many of the literature samples from low temperature reactions. However, it is reduced to 130 mAh/g from the second cycle, and to 42 mAh/g after 100 cycles (Fig. 7b), probably because of the small particle sizes. Clearly, this cycle life characteristics of the present material is not satisfactory for applications. However, note that these data are on a sample without any post-treatments such as heating or coating on the surface. Further studies to improve the cycleability of these materials by doping or coating are under progress.

4. Conclusion

We have synthesized LiCoO₂ powders using the reflux system by the reaction between Co(OH)₂ and LiOH·CH₂O in basic aqueous solution at temperature 130–200 °C under an O₂ atmospheric condition. We have demonstrated that the control of the oxidation potential is more important than temperature. Under suitably adjusted pH, temperature, reaction time, and oxidation potential, the products are pure stoichiometric LiCoO₂ in a uniform fine particle form with good crystallinity. This synthetic method has advantages over the reported hydrothermal method in many aspects. First, instead of the two step reactions of the reported method including the formation of CoOOH from compounds of divalent cobalt, the present method is a single

step reaction, simplifying the process and reducing the production cost. Second, because the control of the oxidation potential is more important than the reaction temperature, we could lower the synthesis temperature by up to 90 °C from the literature hydrothermal reactions. Third, the reflux reaction in the present study is much more easily adapted to a large-scale production than the hydrothermal reactions.

The same principle of this study can be applied to other metal ions, and we are currently working on the syntheses of LiMnO_2 in both the orthorhombic and layered structures and spinel-type LiMn_2O_4 .

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