

## Articles

### Synthesis of $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ by the PVA-precursor Method and the Effect of Air Flow During the Pyrolysis

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Polycrystalline powder of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was synthesized by pyrolyzing a powder precursor obtained by the PVA-precursor method. Coin cells of lithium-ion rechargeable battery were assembled, whose the cathodes were fabricated from the crystalline powders of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  synthesized by the method. The effect of synthetic variation on the property of the cell was tested by carrying out 100 consecutive cycles of charge-discharge on the cells. The property of the cell was largely influenced by the pyrolysis conditions applied for the synthesis of the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ . Depending on whether the pyrolysis was carried out in standing air or in the flow of dry air, the discharge capacity and cycle-reversibility of the cell varied in large extent. When the powder precursor was pyrolyzed in standing air, a minor phase of lithium carbonate was remained in the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ . The carbon containing powder precursor had to be pyrolyzed in the flow of dry air to eliminate the minor phase. In the flow of dry air, the lithium carbonate in the precursor was eliminated over 500–700 °C without any prominent heat event. By controlling the flow of air over the precursor during its pyrolysis, particle size could also be altered. The effect of flowing dry air, during first step pyrolysis or during second step heat treatment, on the property of the cell was discussed.

#### Introduction

As a portable energy source for small electronic devices, enormous amount of research effort has been focused on rechargeable lithium battery.<sup>1–4</sup> Many different solid compounds have been studied for being used as an electrode for the lithium battery.<sup>5–7</sup> Among the materials, lithiated transition metal oxides with a layered or spinel structure, such as  $\text{LiMn}_2\text{O}_4$ ,<sup>8–10</sup>  $\text{LiCoO}_2$ ,<sup>11–13</sup> and  $\text{LiNiO}_2$ <sup>14–16</sup> have been considered to be the most probable candidates for the cathode materials in the lithium rechargeable battery. Among those,  $\text{LiCoO}_2$  has been the first to be produced commercially in large quantity, mostly because it is easier to be synthesized than others. It is known that the synthesis of  $\text{LiNiO}_2$  is harder than  $\text{LiCoO}_2$ .<sup>15</sup> In spite of this synthetic obstacle,  $\text{LiNiO}_2$  has advantageous aspect that the chemical potential of lithium is lower in  $\text{LiNiO}_2$  than in  $\text{LiCoO}_2$ .<sup>17</sup> Therefore, contact oxidation of electrolyte at high electric potential shall be less problematic for  $\text{LiNiO}_2$  than for  $\text{LiCoO}_2$ . If properly prepared,  $\text{LiNiO}_2$  is also known to exhibit higher rechargeable capacity than  $\text{LiCoO}_2$ .<sup>18</sup>

Because  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$  are isostructural, they form complete solid solution of  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ . Introduction of Co into  $\text{LiNiO}_2$  reportedly stabilized two dimensional structure of  $\text{LiNiO}_2$ ,<sup>19</sup> facilitating the preparation of crystalline product. Powder of  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$  has been prepared by the conventional solid state reaction from a mixture of oxides, carbonates, or hydroxides. The preparation of  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$  by the conventional method involved heat treatment at the temperature higher than 800 °C for elongated time, with

intermittent grindings. Therefore, customizing physical characteristics of the crystalline product (such as particle size, morphology, or surface property) may be very limited. Recently, it was reported by others that  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$  could be prepared at 400–450 °C by using unusual precursor,  $\beta\text{-Ni}_{1-x}\text{Co}_x\text{OOH}$ .<sup>20</sup> Because not only the intrinsic property, but also such physical properties of the cathode material should have a significant influence on the performance of the battery,<sup>21,22</sup> it would be desirable if there were an easy way to control such physical properties of the cathode material during the synthetic process.

In an effort to devise a new synthetic route other than the conventional method, we applied the PVA-precursor method to the preparation of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ . The usefulness of the method in preparing mixed metal oxides was already well demonstrated in previous report by authors on the synthesis of  $(\text{Ln},\text{Sr})\text{CoO}_3$ .<sup>23</sup> It was shown that the crystalline structure and surface area of  $(\text{Ln},\text{Sr})\text{CoO}_3$  could be modified by controlling the pyrolysis conditions.<sup>24</sup>

As expected,  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  could easily be synthesized by the PVA-precursor method. But, unlike in the conventional solid state reaction, the synthetic progress was affected much by altering synthetic conditions. In this study, we report the synthesis of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  by the PVA-precursor method, and the effect of air flow during pyrolysis, on the property of the product.

#### Experimental Section

Nitrate salts of constituent metal ions, Li, Ni, and Co were

used in reagent grade and purchased from Junsei Co., Jpn. PVA with the degree of polymerization of 1500 was purchased from Junsei Co., Jpn. The PVA was used as gelling agent to replace water in the aqueous solution of constituent metal salts. An aqueous solution of constituent metal ions was prepared by dissolving  $\text{LiNO}_3$  (0.1 mole),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.085 mole), and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.015 mole) in 100 mL of distilled water. In a separate container, an aqueous solution of PVA was prepared by dissolving 8.8 g of PVA (when mole ratio of monomer units to metal ions was 1) in 200 mL of warm ( $\sim 80^\circ\text{C}$ ) distilled water. For convenience of description, the mole ratio of PVA (*i.e.* monomer units of vinyl alcohol) to metal ions will be designated as R from now on. A dark transparent solution mixture was obtained by combining those two aqueous solutions. The solution mixture was transformed into a gelatinous transparent gel by removing water via steady heating around  $70\text{--}80^\circ\text{C}$  in open air. No trace of precipitation was observed.

This gel could be directly heated to high temperature to get crystalline product. But, to enhance handling convenience, the gel was transformed into a powder precursor by being heated at  $300^\circ\text{C}$  for 3h in standing air. The powder precursor was very fine and had very dark color of almost black. Crystalline products of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  were obtained by pyrolyzing the powder precursor under different conditions. In this study, observation was restricted to the influence of the air flow over the powder precursor to the quality of the crystalline products. One step pyrolysis was carried out in a flow of air at a rate of 1 L/min in a tube furnace equipped with a quartz tubing (100 cm long, 30 cm diameter). For comparison, the pyrolysis was also carried out in a box furnace in standing air (ambient air). Two step heat treatment was also carried out in order to see if minor phase could be removed at low temperature. The crystalline powder of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  which contained a minor phase was obtained by first step pyrolysis at  $750^\circ\text{C}$  for 12h in standing air. After the solid sample was transferred into the tube furnace, it was heated at  $500^\circ\text{C}$  for 10h, in a flow of air at a rate of 1 L/min. For all the heat treatment, the heating ramp was maintained at a rate of  $3^\circ\text{C}/\text{min}$ .

Powder X-ray diffraction (PXRD) patterns were taken from powder samples by using Philips X'pert diffractometer. For a few samples, Si powder (Aldrich Co.) was mixed as an internal standard. The SEM micrographs of powder samples were taken with Philips XL-30 scanning electron microscope. Simultaneous differential thermal (DT) and thermogravimetric (TG) analyses were carried out with Setram TG-DTA92. The heating ramp was maintained at a rate of  $3^\circ\text{C}/\text{min}$  in a flow of air at a rate of 30 mL/min. The specific surface area was measured by BET method by using Micromeritics ASAP-2400. The elemental analysis on residual carbon was performed by combustion method, and on metal constituents by ICP/MS.

Several coin cells of lithium rechargeable battery were assembled.<sup>25</sup> The cathode of the cells was fabricated by using a circular disk of 1.6 cm diameter which was cut out from a casted tape of a mixture of activated carbon (conduc-

tor), binder, and the powder of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  synthesized by the PVA-method. The electrolyte was  $\text{LiPF}_6$  dissolved in a 1 : 1 mixture of EC and DMC. The anode of the cell was metallic lithium. The continuous cycles of charge and discharge were carried out with the cell in constant current mode. The range of electric potential measurement was restricted within 1.5V, from lower limit of 2.8V to higher limit of 4.3V. The electrochemical process was cut off at the limit, and reversed immediately. Because our main concern was on the performance of the battery in a relatively severe condition of high rate, the cell was pre-conditioned at a rate of C/10 and C/5.

## Results and Discussion

Figure 1 describes the synthesis of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  by the PVA-precursor method. Constituent metal ions were provided from nitrate salts. PVA was dissolved in luke warm distilled water in a separate vessel, and combined with a solution of metal salts. Upon combining those two solutions, metal ions would be complexed to hydroxyl side groups of PVA.<sup>24</sup> By removing water by slow evaporation, a clear gel was obtained. This process corresponds to the exchange of solvent from water to PVA. The matrix of polymeric gel blocked the progress of fractional precipitation which should have occurred if the aqueous solution had been dried up without PVA. By preventing the constituent ions from forming fractional precipitates, compositional homogeneity was maximized.

Upon being heated at  $300^\circ\text{C}$  in standing air, the gel was transformed into fine dark powder which was much easier to handle than the gel. Fractional precipitation occurred during the pyrolysis, when the matrix of PVA was burnt off. Because the pyrolysis should proceed almost instanta-

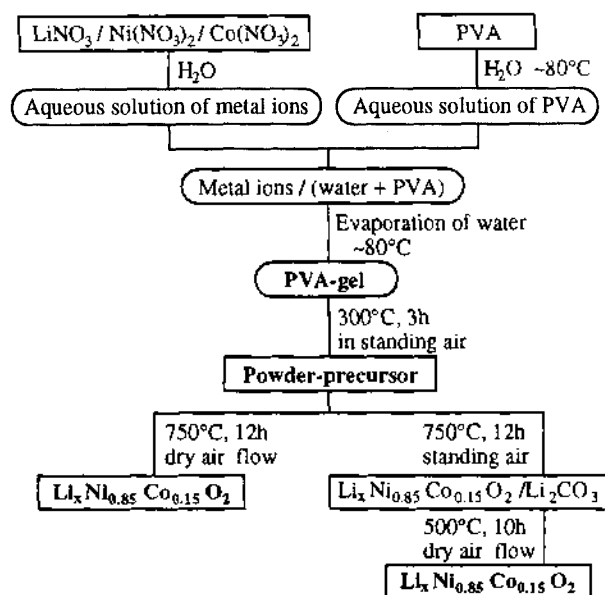
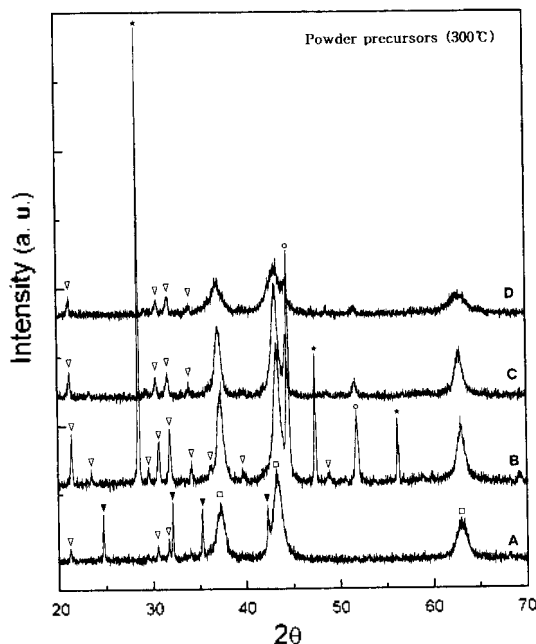


Figure 1. Schematic outline of the preparation of polycrystalline powder of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ . Rectangular containment represents solid state, and the round one solution state.

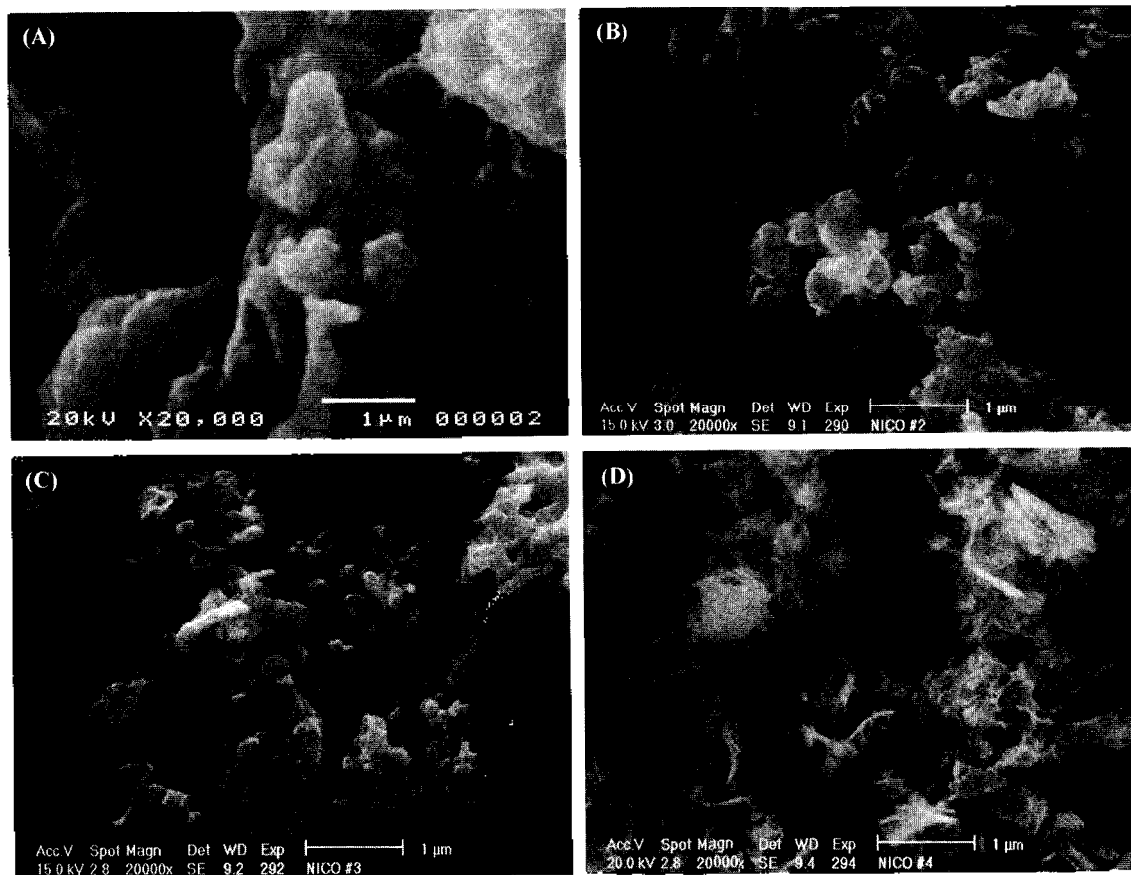
neously, the heterogeneous domain should be much more minute than in the case when large precipitates should form slowly by fractional precipitation in water. The PXRD pattern of the powder heated at 300 °C showed that it contained nickel oxides and lithium carbonate.

When  $R$  was 0.5 (less than one), the peaks for lithium nitrate were observed (Figure 2A). The observation of lithium nitrate indicated that autoignition, which should have consumed the nitrates,<sup>27</sup> did not proceed or partially proceeded, presumably because not all the lithium ions could be complexed to the PVA backbone. When  $R$  is 0.5, PVA can accommodate only half of the cations, assuming one to one complex formation. Nitrate salts will result from the cations which were left uncomplexed to PVA. Conforming to the reasoning, the lithium nitrate was eliminated when  $R$  was raised above 1, as shown in the Figure 2B, 2C, and 2D. Still, the peaks for lithium carbonate were persistent even when  $R=4$ . It was suggested that incomplete pyrolysis of PVA at 300 °C provided carbonaceous source for the formation of lithium carbonate. Therefore, it was anticipated that lithium carbonate would not be easily eliminated at low temperature if  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  were to be prepared by the PVA-precursor method.

By seeing the diffraction peaks were very broad, the domain of the crystalline NiO was considered to be very small (calculated to be around 10 nm, by Scherrer's



**Figure 2.** PXRD patterns of the powder precursor obtained by heating the PVA-gel at 300 °C. The mole ratio of PVA to metal ions ( $R$ ) was (A) 0.5, (B) 1, (C) 2, and (D) 4. The marks are for  $\nabla = \text{LiNO}_3$ ,  $\nabla = \text{Li}_2\text{CO}_3$ ,  $\circ = \text{Ni}_2\text{O}_3$ ,  $\square = \text{NiO}$ , and  $\star = \text{Si}$  standard.



**Figure 3.** SEM micrographs of the powder precursor obtained by heating the PVA-gel at 300 °C. The mole ratio of PVA to metal ions ( $R$ ) was (A) 0.5, (B) 1, (C) 2, and (D) 4.

equation<sup>28</sup>). The broadening of the peaks with the increase of R indicated that the crystallinity of the powder precursor decreased as more PVA was used in preparing the gel. Conforming to this PXRD observation, SEM images of the powder precursors, provided in Figure 3, showed that crystalline feature of the image was decreased as more PVA was used. Whereas crystalline facets were developed in the powder precursor which was obtained from the gel whose R was 0.5, they were no longer observable as the ratio was increased above 1. As R increased, the powder contained more of amorphous feature which resembled crumpled thin papers. The increase of this amorphous feature was suggested to be related to the increase of the residual carbon in the precursor powder (see the table below).

The crystalline powder of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was obtained by further heat treatment of the powder precursor at 750 °C for 12h in standing air, or in a flow of dry air at a rate of 1.0 L/min. The elemental analysis by ICP/MS showed that the stoichiometry of constituent transition metal ions was preserved. But, the stoichiometry of lithium was calculated to be 0.85–0.9. It was suspected that some lithium was lost by evaporation. Properties of solid products obtained by heating the gel were provided in the Table 1. The powder precursors had relatively large surface area. Upon being heated at 750 °C, the surface area largely decreased, though it was still higher than in the conventional solid state reaction.<sup>29</sup> The powder precursor also contained fair amount of residual carbon which originated from the organic polymer. The amount of residual carbon in the powder precursor roughly increased as more PVA was used in preparing the gel. Contrary to the incremental feature of the carbon content in the powder precursor, not much residual carbon was left in the crystalline product. This seemingly opposite trend was also observed in the previous study on the preparation of  $(\text{Ln},\text{Sr})\text{CoO}_3$  by the PVA-precursor method.<sup>23</sup>

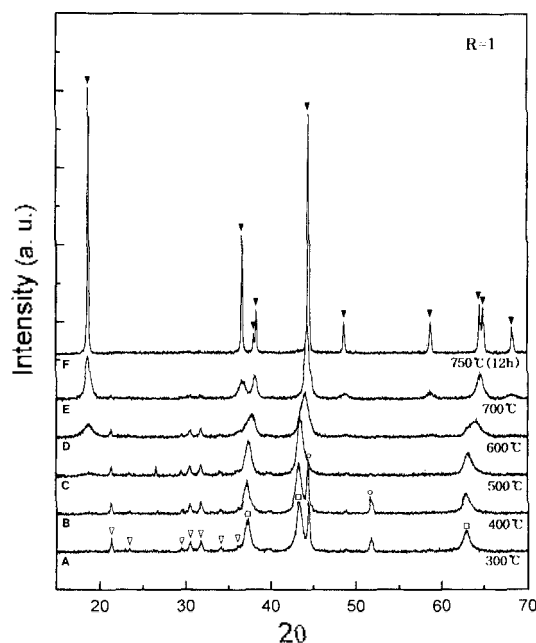
Because of this high content of residual carbon in the precursor, pyrolysis of the precursor had to be carried out in controlled manner. Because organic polymer was used in obtaining the gel, fair amount of residual carbon was inevitably left in the powder precursor, presumably as lithium carbonate, and some as elemental carbon. Eliminating the carbonaceous residue shall decide whether  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  can be synthesized as a single phase in an industrial quantity at low temperature. From a commercial point of view, the carbon residue in the sample could be a critical drawback in applying the PVA-precursor method for mass production.

Therefore, it would be desirable if the carbonaceous resi-

**Table 1.** Surface areas and carbon content of the solid samples obtained by heating the gel precursor at the designated temperature and time

	precursor (300 °C, 3h)				product (750 °C, 12h) <sup>*</sup>			
	R=0.5	1.0	2.0	4.0	R=0.5	1.0	2.0	4.0
surface area ( $\text{m}^2/\text{g}$ )	27	14	14	47	2.6	2.9	4.9	2.7
carbon content (wt%)	1.8	5.1	5.0	10.3	0.7	1.0	0.6	0.5

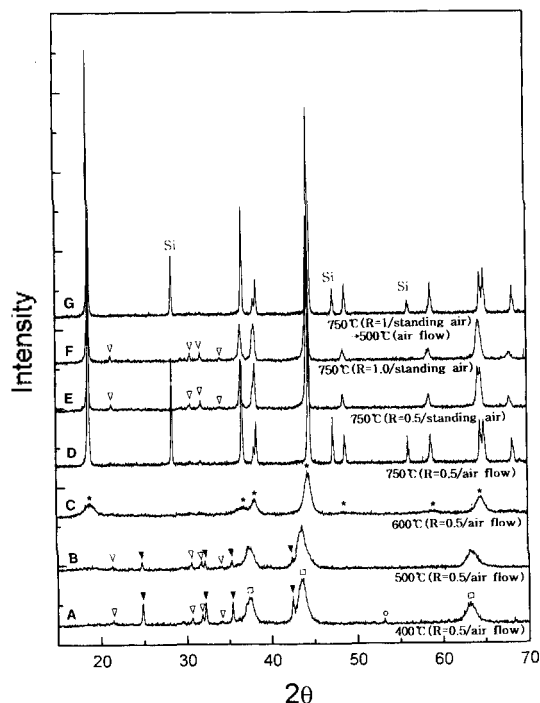
<sup>\*</sup>: Heated under the flow of air at a rate of 1.0 l/min.



**Figure 4.** PXRD patterns in series, for the samples obtained by heating the powder precursor at designated temperatures: (A) 300 °C for 3h, (B) 400 °C for 5 min, (C) 500 °C for 5 min, (D) 600 °C for 5 min, (E) 700 °C for 5 min, and (F) 750 °C for 12h. The polymer to metal mole ratio (R) was 1. The powder precursor was heated in the flow of dry air. The marks are for  $\nabla = \text{Li}_2\text{CO}_3$ ,  $\square = \text{NiO}$ , and  $\blacktriangledown = \text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ .

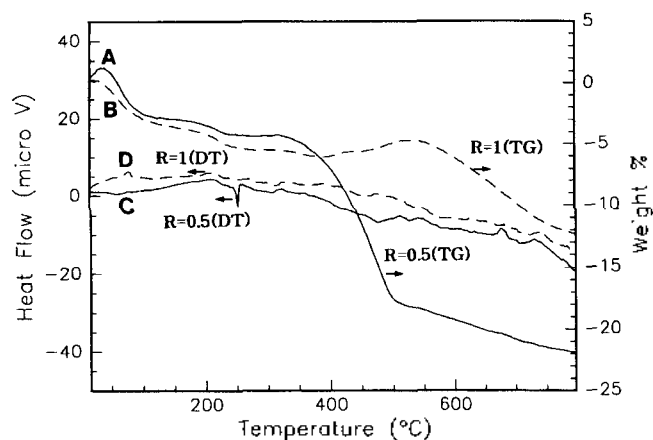
due could be eliminated from the sample at low temperature by using a cheapest possible way. The most crucial factor to achieve this goal was observed to be the flow of air over the precursor. Development of the crystalline phase of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was shown in Figure 4, where PXRD patterns were provided for a series of samples obtained by heating the powder precursor (R=1) at designated temperature. Dry air was passed over the samples while they were being heated. The peaks for  $\text{Ni}_2\text{O}_3$  disappeared around 500 °C. On the contrary, it was observed that lithium carbonate persisted up to 700 °C. When R was 0.5, it was observed that the peaks for lithium carbonate were not observed already from the sample heated at 600 °C (Figure 5C), if heated under the flow of dry air. It was also observed that lithium nitrate decomposed between 400 and 500 °C (Figure 5A and 5B). The diffraction peaks of NiO remained to be broad until they shifted gradually toward positions where diffraction peaks of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  should develop.

Whereas  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  could be obtained as a single phase in a flow of dry air, the minor phase of lithium carbonate persisted, when the precursor was heated in standing air. Assessing the splitting between (108) and (110) diffraction peaks around  $2\theta=64^\circ$ , crystallinity of the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  decreased as the minor phase of lithium carbonate was generated. Regardless of the amount of polymer used in preparing the gel, the lithium carbonate could not be removed below 800 °C without the flow of air (see Figure 5E and 5F). By seeing that lithium carbonate persisted further in the powder precursor with higher content of carbon (compare



**Figure 5.** PXRD patterns taken from the samples obtained by heating the powder precursors at designated temperatures and duration. The patterns from (A) to (E) are for  $R=0.5$ , and those from (F) and (G) are for  $R=1$ . For (A) to (D), the powder precursor was heated in the flow of dry air. For (E) and (F), the powder precursor was heated in standing air. For (G), the powder precursor was heated at 750 in standing air, then consecutively at 500 in the flow of dry air. The marks are for ▼ =  $\text{LiNO}_3$ , ∇ =  $\text{Li}_2\text{CO}_3$ , ○ =  $\text{Ni}_2\text{O}_3$ , □ =  $\text{NiO}$ , and ★ =  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ . Apparent shift of (G) was caused by taking the pattern in different scan range (instrumental cause).

those PXRD patterns for  $R=0.5$  and  $R=1$ , it appeared that gas product from pyrolysis of carbonaceous residue made local environment around the sample less favorable for complete decomposition of all the carbonate. Apparently, the crystallization was inhibited by the presence of lithium carbonate, thereby the peaks at high angle for  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  were not well separated. When the crystalline product with the minor phase of lithium carbonate was further heated at 500 °C for 10h (second-step heating) under the flow of dry air, the lithium carbonate could be removed, and crystallization of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was completed (Figure 5G). Elemental analyses by ICP/MS showed that lithium was not lost by this second step heat treatment, which indicated the minor phase was eliminated by reaction between two solid phases. This observation indicates that continuous provision of oxidizing environment is crucial in the pyrolysis of carbon-containing precursors prepared by the PVA-precursor method. In the previous study on  $(\text{Ln},\text{Sr})\text{CoO}_3$ , it was observed that local environment around the carbon-containing precursor could become even reducing, and caused the oxygen deficiency in the crystalline product.<sup>23</sup> In some occasions, the carbonate could not be eliminated completely even in the flow of dry air, as seen in Figure 5D. It was presumed that stoichiometry of Ni and Co was one other important fac-

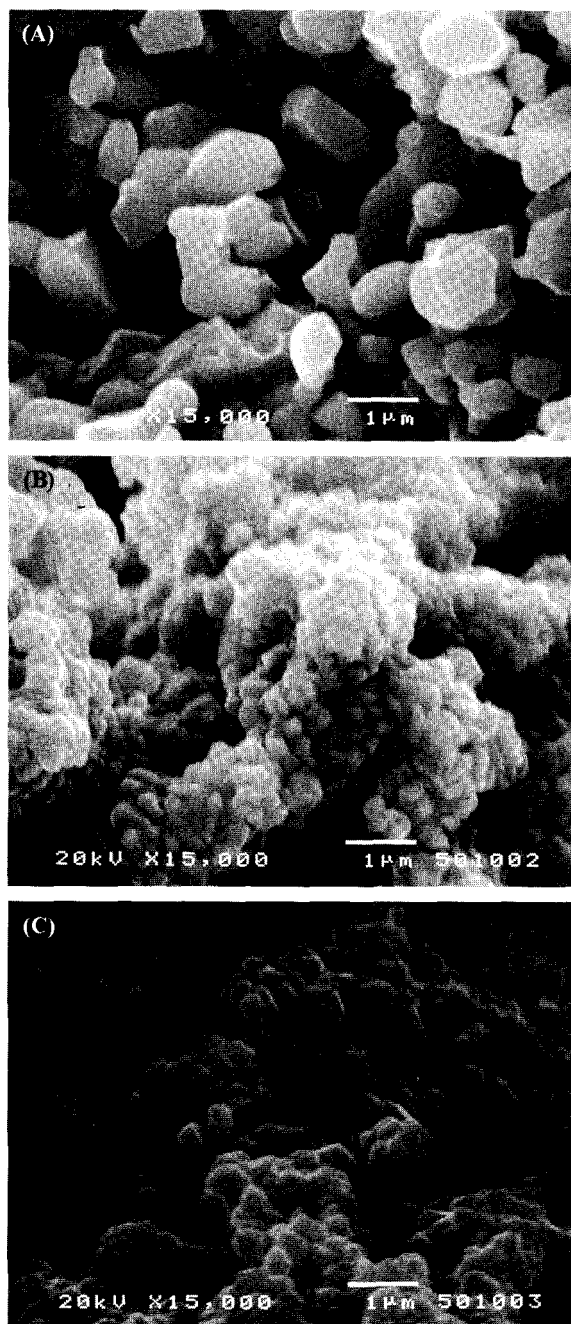


**Figure 6.** TGA traces of powder precursors, whose  $R$  was (A) 0.5, and (B) 1. DTA traces of powder precursors, whose  $R$  was (C) 0.5, and (D) 1. The measurements were carried out in the flow of dry air. The heating rate was 3/min.

tor to influence the elimination of the carbonate. This subject is on our pursue.

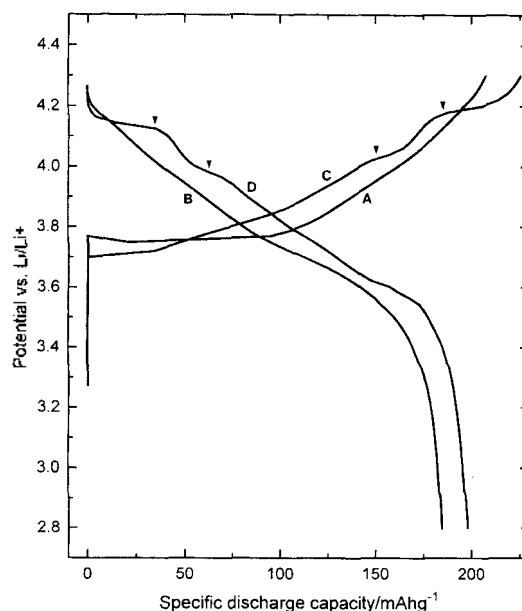
Thermal analyses (DT/TG) on the precursor powders, which were provided in Figure 6, conformed to the above PXRD observations. When  $R$  was 0.5, about 15% weight loss occurred between 400 and 500 °C where lithium nitrate was shown to disappear on the PXRD observation. This weight decrease was preceded by the endotherm of melting  $\text{LiNO}_3$  at 250 °C. Estimating from elemental analysis and the PXRD observations, further weight loss of around 2% between 500 and 600 °C was related to the decomposition of lithium carbonate. On the contrary, continuous weight loss of around 5% occurred above 500 °C when  $R$  was 1. The persistent observation of lithium carbonate by the PXRD observation and about 5% carbon content by elemental analysis indicated that this weight loss corresponded to the decomposition of lithium carbonate. Therefore, it appeared that lithium carbonate started decomposing around 500 °C in both cases, though it progressed further to higher temperature for the precursor with higher carbon content. Interestingly, the decomposition of lithium carbonate proceeded without any prominent heat event, which supported the view that it progressed over a range of temperature. This thermal behavior strongly suggests that kinetic factor may be important in the removal of lithium carbonate from the carbon-containing precursor under the flow of dry air. The fact that lithium carbonate could be removed by subsequent heating at 500 °C supports this suggestion. This observation indicated that we should be able to get the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  as a single phase at the temperature lower than 750 °C, if sufficient time was allowed for the complete removal of lithium carbonate under the flow of dry air.<sup>30</sup>

Figure 7 shows SEM images of the crystalline products of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  obtained by heating the powder precursors at different pyrolysis conditions. The average size of the particles was smaller for the carbonate-containing sample heated in standing air. The size of the particles appeared to be preserved after the lithium carbonate was removed by



**Figure 7.** SEM micrographs of the polycrystalline powder of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared by heating the powder precursor (A) at 750 °C for 12h in the flow of dry air, (B) at 750 °C for 12h in standing air, and (C) at 750 °C for 12h in standing air, followed by consecutive heat-treatment at 500 °C in the flow of dry air (two-step heat-treatment). The polymer to metal mole ratio (R) was 1.

consecutive heat treatment at 500 °C under the flow of dry air. It could not be known what was the role of the minor phase in the sample. But, it certainly appeared that particles got smaller if lithium carbonate was not removed while crystalline phase of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  formed around 500-600 °C. This interesting observation suggests that the size of the particle can be altered by following different routes of pyrolysis. If the powder precursor was heated stepwise at 750 °C in an ambient air, and consecutively at 500 °C in a flow of dry

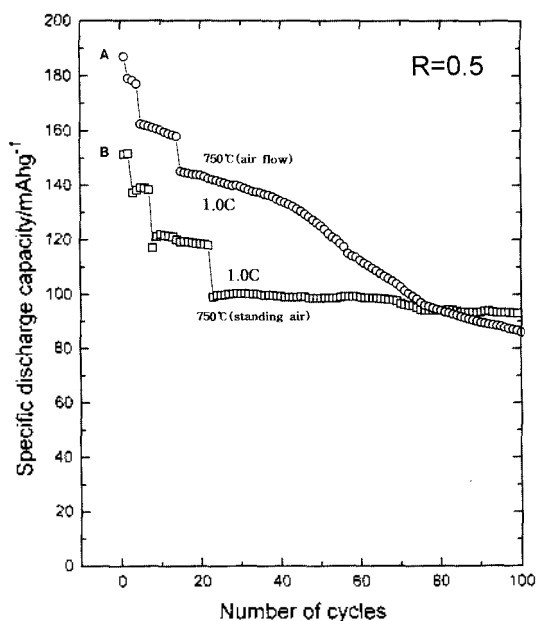


**Figure 8.** Trace of first cycle of charge-discharge of the cell with  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  as cathode material (A and B), compared to that of the cell with  $\text{LiNiO}_2$  as cathode material (C and D). The trace (A) and (C) are charging curves, and (B) and (D) are for discharging curves of the cell, in constant rate of  $C/10$ . Structural change was marked by ▼.

air, the size of the single phase product of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  came out to be smaller than that of the product obtained by heating the precursor only at 750 °C in a flow of air from the start.

Continuous cycles of charge and discharge in constant current mode were carried out on coin cells of lithium battery whose cathodes were made from the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  obtained by the PVA-precursor method. The first trace of the cycle (at a rate of  $C/10$ ) obtained from the cell with the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was compared with that from the cell with  $\text{LiNiO}_2$  synthesized by the citrate-precursor method,<sup>31</sup> in Figure 8. The initial capacity of the cell with the  $\text{LiNiO}_2$  was about 10 mAh/g higher than the counterpart. But, the trace showed the change of curvature in many places. A few major changes occurred around 4.15 and 4.0 V. This indicated the layers in the  $\text{LiNiO}_2$  experienced a few structural transitions during the electrochemical reaction.<sup>22,32</sup> The frequent structural transitions give negative influence on the integrity of the layer structure of the cathode material, which result in a poor cyclability of the cell. Contrary to the bumpy trace for the cell with the  $\text{LiNiO}_2$ , that with the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  exhibited smooth traces for both charge and discharge, which suggested no such structural transitions. Therefore, the stabilizing role of the cobalt mixed to the  $\text{LiNiO}_2$  was apparent not only in the  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$  synthesized by the solid state reaction,<sup>33</sup> but also in the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  synthesized by the PVA-precursor method.

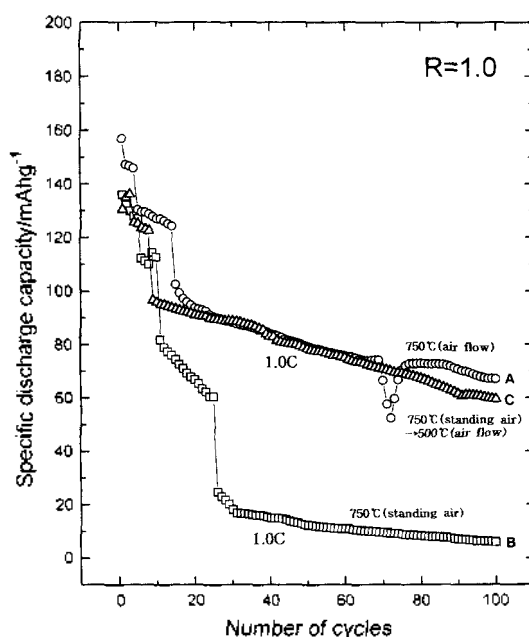
By keeping all the other factors same except the route how the powder precursors were pyrolyzed, the electrochemical properties of those crystalline powders of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  were compared, and shown in Figure 9 and 10. A few cycles



**Figure 9.** Cycle performance of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  heated in designated gas environment at 750 °C for 12h. R was 0.5.

at a rate of  $C/10$ ,  $C/5$ , and  $C/2$  were allocated for conditioning of the cell in the beginning. In Table 2, important capacity values were summarized: the initial discharge capacity at a rate of  $C/10$ , initial discharge capacity at a rate of  $1C$ , final discharge capacity at  $1C$ , and drop of the discharge capacity by consecutive operation of charge-discharge cycles at a rate of  $1C$ .

For the case when R was 0.5 (Figure 9), discharge capacity reached initially to 187 mAh/g, when the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was prepared in the flow of dry air. When it was prepared in standing air, the discharge capacity only reached to 135 mAh/g. Therefore, the initial capacity of the cell was improved in large extent when the pyrolysis of the powder precursor was carried out in the flow of air. Even though the initial discharge capacity was higher, the reversibility of the cycle was poorer, when it was compared to the case where standing air was used. The discharge capacity of the cell decreased rapidly down to ~80 mAh/g after 100 cycles. On the contrary, the reversibility of the cycle was exceptionally good at high rate of  $1C$ , when the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was prepared in standing air. Drop of the capacity was almost negligible after consecutive 80 cycles at the rate. Discharge



**Figure 10.** Cycle performance of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  heated in designated gas environment at 750 °C for 12h (A and B). Cycling behavior of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared by two step heating, at 750 °C in standing air then consecutively at 500 °C in the flow of dry air, was shown as (C). R was 1.0.

capacity at the rate was around 100 mAh/g which was practically acceptable, considering the stability of the cycle.

When R was 1 (Figure 10), both initial discharge capacity and reversibility of the cycle were largely improved when the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was prepared under the flow of dry air. Initial discharge capacity increased from 135 to 159 mAh/g. The reversibility of the cycle at high rate of  $1C$  was very good.<sup>31</sup> Seemingly good reversibility observed in the trace of Figure 10B was caused by false impression. Because discharge capacity reached practical minimum of 10 mAh/g already at 30 cycles, it was considered that almost no electrochemical reaction was occurring there after. Therefore, reversibility should be assessed from the slope at a rate of  $C/2$  for the particular trace, which was not good when the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was prepared in standing air. For this particular case when R was 1.0, the performance of the cell was very poor, rendering it almost useless for any practical application. Therefore, flowing air during pyrolysis appears essential to get the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  in good quality.

**Table 2.** Comparison of the initial discharge capacity ( $C_{a_i}$ ) at  $C/10$ , the initial discharge capacity at  $1C$  ( $C_{a_i}(1C)$ ), the final discharge capacity at  $1C$  ( $C_{a_f}(1C)$ ), and the drop of the discharge capacity at  $1C$  ( $\Delta C_{a_i}(1C)$ )

pyrolysis condition	R=0.5				R=1			
	$C_{a_i}$	$C_{a_i}(1C)$	$C_{a_f}(1C)$	$\Delta C_{a_i}(1C)$	$C_{a_i}$	$C_{a_i}(1C)$	$C_{a_f}(1C)$	$\Delta C_{a_i}(1C)$
750 °C. 12h air flow	187	145	87	-58	157	100	68	-32
750 °C. 12h standing air	151	100	93	-7	136	80*	60*	-20*
750 °C. 12h standing air ↓	-	-	-	-	130	95	62	-33
500 °C, 10h air flow	-	-	-	-	130	95	62	-33

\*Because almost no electrochemical reaction occurred at  $1C$ , these values were assessed from the trace for the rate of  $C/2$ .

When lithium carbonate was removed from crystalline  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  by second step heat treatment at 500 °C under the flow of dry air, the performance of the cell improved in large extent, and neared to that of the cell with the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared under the flow of dry air from the start. Even though the initial discharge capacity was not increased much, the reversibility of the cycle became as good as that for the one where the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was prepared in the flow of air. It is presumed that incomplete crystallization of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ , which results from remaining minor phase of lithium carbonate, affects negatively on the initial performance of the battery, possibly by eliminating available sites for lithium. Once the phase of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was crystallized, it appeared that the site-availability was not improved by additional thermal processing. The additional thermal processing apparently influenced the reversibility of the cycle. But, there is no apparent clue on why the change of R leads to contradictory results on the reversibility of the cycle. This observation only indicates that there are many synthetic variations in the PVA-precursor method which can be manipulated to alter the characteristics of cathode material.

### Conclusion

The PVA-precursor method, the unconventional synthetic strategy developed by authors for the preparation of mixed metal oxides, was successfully applied in preparing single phase polycrystalline powder of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ . By using PVA as a gelling agent, constituent metal ions were homogeneously distributed in the organic gel. The powder precursor was obtained by pyrolyzing the organic gel at 300 °C. The precursor had large surface area and high content of residual carbon (about 2-10%) which increased as more PVA was used. As more PVA was used in preparing the precursor, its amorphous feature increased. The precursor contained crystalline lithium carbonate which had to be eliminated to obtain fully crystalline single phase product of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ . The most crucial condition to eliminate the lithium carbonate was flowing dry air over the precursor during pyrolysis. The lithium carbonate was eliminated below 700 °C if the pyrolysis was carried out in the flow of dry air, whereas it persisted to 800 °C in standing air. Decomposition of lithium carbonate occurred over a wide range of temperature from 500 to 700 °C without accompanying any prominent heat event, thereby, it could be removed at the temperature as low as 500 °C in the flow of dry air. Particle size of the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  could be controlled in some extent by following different routes of pyrolysis. In the flow of dry air, the pyrolysis of the precursor produced bigger particles than in standing air. The crystalline product of single phase  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  in small particle size could be obtained by two step heat-treatment: first step at 750 °C in standing air to get crystalline particles in small size, followed by second step heating at 500 °C to eliminate the minor phase of lithium carbonate from the particles.

Coin-type cells of lithium ion battery were assembled by

using cathodes fabricated from the crystalline product of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  synthesized by the PVA-precursor method. The lithium carbonate remaining in the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  inflicted detrimental influence on the initial performance of the cell. The initial discharge capacity decreased in large extent, when the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was prepared in standing air. But, the cycle-reversibility of the cell didn't exhibit a consistent trend. When R was 0.5, the cycle-reversibility appeared better, even though it appeared worse when R was 1, if the pyrolysis was carried out in standing air. The poor reversibility could be corrected by removing the lithium carbonate from the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  by second step heat treatment at 500 °C in the flow of dry air. After the treatment, the cycle-reversibility was improved in large extent, though the initial capacity was not.

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  30. We could synthesize the crystalline powder of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  without the minor phase of lithium carbonate at  $700^\circ\text{C}$  in the flow of dry air.
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  33. The reversibility for this particular case was much better than the cell with  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  synthesized from a mixture of metal hydroxides.<sup>29</sup> The drop of the discharge capacity at a rate of 1C was as large as 80 mAh/g (from 140 down to 60 mAh/g) for the cell with  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  synthesized from the mixture of metal hydroxides.
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