

# Synthesis of $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ by the PVA-precursor method and charge–discharge characteristics of a lithium ion battery using this material as cathode

Ho-Jin Kweon <sup>a</sup>, Geun Bae Kim <sup>a</sup>, Hong Sup Lim <sup>a</sup>, Sang Sung Nam <sup>b</sup>, Dong Gon Park <sup>c,\*</sup>

<sup>a</sup> Samsung Display Devices Co., Ltd., ChunAn 330-300, South Korea

<sup>b</sup> Chemical Technology Division, Korea Research Institute of Chemical Technology, Taejon 305-600, South Korea

<sup>c</sup> Department of Chemistry, Sookmyung Women's University, Seoul 140-742, South Korea

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## Abstract

Polycrystalline powder of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was synthesized from poly(vinyl alcohol) gel (a PVA-precursor). The crystalline phase of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was developed without any minor phase above 600°C. The crystallization proceeded without any prominent heat event, which indicated homogeneous distribution of constituents and insignificant amount of diffusion barrier. The crystalline powder prepared from the PVA-precursor had relatively smaller particle size, larger surface area, and higher carbon content than the one prepared by the conventional solid state reaction. Charge–discharge property was studied by using a coin-type cell containing  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  as cathode material, and Li metal as the anode, in a potential range of 2.8–4.3 V. Initial discharge capacity (at a rate of C/10) of the cell was 170 mA h/g. At high rate of 1C, the cycling reversibility for the cell with  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared from the PVA-precursor was observed to be much better than that with the one prepared by the solid state reaction. After 90 continuous cycles at constant rate of 1C, the decrease of discharge capacity was less than 20 mA h/g in the case of the PVA-precursor method, whereas it was about 80 mA h/g for the solid state reaction. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Lithium ion battery; Cathode; Precursor; Electrochemical property

## 1. Introduction

Transition metal oxides with layered structure have attracted much interest, because of their possible use as electrode materials [1–3]. Especially, lithiated transition metal oxides, such as  $\text{LiMnO}_2$  [4],  $\text{LiMn}_2\text{O}_4$  [5],  $\text{LiCoO}_2$  [6], and  $\text{LiNiO}_2$  [7], have been studied extensively, because of their potential use as cathode materials for lithium secondary batteries.

$\text{LiCoO}_2$  and  $\text{LiNiO}_2$  are isostructural, having layer structure of  $\alpha\text{-NaFeO}_2$  type [8].  $\text{LiCoO}_2$  has been commercialized, whereas  $\text{LiNiO}_2$  has not, mostly because its preparation is easier and its reliability (safety) is better than  $\text{LiNiO}_2$  [9]. Even though it is harder to prepare,  $\text{LiNiO}_2$  has several advantages over  $\text{LiCoO}_2$ . Nickel is

cheaper than cobalt. If properly prepared, its specific capacity is higher than that of  $\text{LiCoO}_2$  [10]. Most of all, chemical potential of lithium in  $\text{LiNiO}_2$  is lower than that in  $\text{LiCoO}_2$ , thereby, contact oxidation of electrolyte can be less problematic for  $\text{LiNiO}_2$  than the former [11].

$\text{LiCoO}_2$  and  $\text{LiNiO}_2$  form complete solid solution ( $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ ), crystallizing into rhombohedral layer structure ( $R\bar{3}m$ ). Unit cell volume of  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$  is shown to decrease, as the value of  $y$  is increased [12]. Both nickel and cobalt in  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$  are in their oxidation state of III, and distributed homogeneously at 3a octahedral sites of cubic-close packed array of oxygen. Nickel in its oxidation state of II is considered to be impurity in  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ , frustrating two-dimensional layers of the crystal structure [13]. The generation of  $\text{Ni}^{+2}$  impurity is related to the presence of lithium deficiency. Cation disorder was related to the ratio of  $I(104)/I(003)$  which decreased as degree of disorder decreased [14]. Substitution of nickel by cobalt ( $0.2 < y < 1.0$ ) stabilized

\* Corresponding author. Tel.: +82-27109413; E-mail: dgpark@sookmyung.ac.kr

two-dimensional character of the layered structure of  $\text{LiNiO}_2$ , suppressing the generation of  $\text{Ni}^{+2}$  impurity [14,15]. Ratio of  $\text{Ni}^{2+}/\text{Ni}^{3+}$  was observed to be increased as the value of  $y$  decreased below 0.2, and concomitant increase in the ratio of  $I(104)/I(003)$  was observed [14,15].

$\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$  has usually been prepared by the conventional solid state reaction from various different precursors. The precursor may be a mixture of oxides, carbonates, hydroxides, or nitrates of constituent metal ions. Synthesis of  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$  from oxides or carbonates involves heat treatment at elevated temperature above  $800^\circ\text{C}$  with intermittent grindings [16]. When nitrates are used for the preparation, lithium deficiency and cation disorder may occur, since lithium nitrate is volatile above  $600^\circ\text{C}$  [14].

Performance of the lithium ion battery may be influenced greatly by not only the intrinsic property of  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ , but also the interactions among battery components. One of such interactions is oxidative degradation of nonaqueous electrolyte occurring at the interface of cathode and electrolyte. Therefore, physical characteristics, such as morphology and surface area of cathode materials, should give a great influence on the property of the battery [17,18]. Therefore, it would be desirable to control the physical characteristics of cathode materials during the synthetic process. As an effort to devise a new synthetic strategy to facilitate the tailoring of the physical properties, we tried to synthesize  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  from a precursor prepared by using an organic polymer as homogenizer. We report the synthesis of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  by the PVA-precursor method. Similar synthetic route was previously reported for the synthesis of single phase polycrystalline powder of  $(\text{Ln},\text{Sr})\text{CoO}_3$  [19]. Recently, the synthesis of  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCoO}_2$ , and  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  by the PVA-precursor method was reported as a communication by authors [20].

## 2. Experimentals

Nitrate salts of Li, Ni, and Co in reagent grade were purchased from Junsei, Japan. Poly(vinyl alcohol) (PVA) was purchased from Junsei, and degree of polymerization was 1500.

Polycrystalline powder of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was synthesized via the PVA-precursor method by using PVA as a gelling agent. In a 500-ml container,  $\text{LiNO}_3$  (6.89 g, 0.1 mol),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (24.72 g, 0.085 mol), and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (4.37 g, 0.015 mol) were dissolved in 100 ml of distilled water. In a separate container, 4.4 g of PVA was dissolved in 200 ml of warm distilled water. Mole ratio of PVA formula units to total metal ions was 0.5. These two aqueous solutions were combined and well mixed into a dark transparent solution. Water was removed by heating the solution around  $70\text{--}80^\circ\text{C}$  in open air. As water content diminished, the solution turned into a very

viscous gelatinous mass. This organic gel (PVA-precursor) was still transparent, and no trace of precipitation was observed in it. The PVA-precursor was transferred into an oversized alumina crucible, and heated to  $300^\circ\text{C}$  at a rate of  $1^\circ/\text{min}$  (first step heating) in air. Duration at  $300^\circ\text{C}$  was 3 h. The gel transformed into a very fine dark powder upon being heated. By heating this powder at  $750^\circ\text{C}$  for 12 h in air, the polycrystalline powder of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was obtained. In order to see if post-heat-treatment could influence the property of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ , the polycrystalline powder was further heated at  $500\text{--}600^\circ\text{C}$  for 10 h in a flow of air.

For comparison,  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was also synthesized by the solid state reaction. A powder mixture of  $\text{Ni}(\text{OH})_2$  and  $\text{Co}(\text{OH})_2$  was dispersed in 150 ml of distilled water, and was milled (Attrito-milling) into a slurry in a Teflon jar with  $\text{ZrO}_2$  balls which were mechanically rotated in 450 rpm for 1 h. By separating it from the balls, the slurry was collected using a sieve. The slurry was dried in an oven at  $120^\circ\text{C}$  for 24 h, and ground into powder by using a mortar. To the powder,  $\text{LiOH}$  was added and well-mixed by grinding them together in a mortar. The precursor (ground into powder) was obtained by heating the powder mixture at  $500^\circ\text{C}$  for 5 h in air. A sample of crystalline  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was obtained by heating the precursor at  $750^\circ\text{C}$  for 12 h in air. In order to see the effect of post-annealing, the crystalline powder was further heated at  $500\text{--}600^\circ\text{C}$  for 10 h in a flow of air.

Powder X-ray diffraction (PXRD) pattern was taken from powder samples by using Philips X'pert diffractometer. Silicon powder (Aldrich) was used as an internal standard for the calculation of lattice parameters. Simultaneous differential thermal (DTA) and thermo-gravimetric analysis (TGA) was carried out with Setram TG-DTA92 in a flow of dry air (30 ml/min). Heating rate was  $3^\circ\text{C}/\text{min}$ . Surface area of the powder was measured by BET method by using Micromeritics ASAP-2400. Adsorbed volatiles were removed from the surface by heating the powder at  $300^\circ\text{C}$  for 3 h under vacuum before measurement. SEM micrographs of the powder were taken by using Philips XL-30.

Electrochemical property of the crystalline product was studied by obtaining charge–discharge cycle curves from a coin-type cell of the lithium ion battery [21], which was assembled by using crystalline product of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  as the cathode material of the cell. The powder sample of crystalline  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  synthesized was well-mixed with PVDF binder and Super P carbon, and casted into a tape. From the tape, a circular disk of 1.6 cm diameter was cut out and used as the cathode of the coin cell. Metallic lithium was used as the anode of the cell, and the electrolyte was  $\text{LiPF}_6$  dissolved in EC/DMC(1:1) [22]. The charge–discharge cycles were carried out in a constant current mode. The rate was varied from C/10 to 1C with cut-off voltages of 2.8 and 4.3 V for discharge and charge. The cells were charged and discharged step-

wise, initially at C/10 for 2–3 cycles, at C/5 for five cycles, and then at 1C for a total of 100 cycles.

### 3. Results and discussion

A main concern in obtaining mixed metal oxides, as a single-phase product could be how to deal with the formation of minor phases during the heat treatment of solid reactants. Minor phases might be developed mainly due to variation of local stoichiometry from the desired value (compositional inhomogeneity). In conventional solid state reaction, solid reactants (oxides, carbonates, or coprecipitated hydroxides) are simply heated at high temperature for an extended period until minor phases disappear by diffusion reaction among grains. In many occasions, intermittent grindings and mixings were involved to remove diffusion barrier around grains, which could lace the product with inadvertent impurities. Theoretically, a best way to avoid this situation would be to keep the composition of the reactants as homogeneous as possible.

The synthesis of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  by the PVA-precursor method was schematically described in Fig. 1. In the method, main effort was to keep the composition of reactants in the maximal homogeneous state. The aqueous solution of PVA was prepared in separate vessel, because it took long time to complete the dissolution in minimum amount of water. Warming (approx.  $80^\circ\text{C}$ ) of the solution could accelerate the step. Upon combining the aqueous solutions of metal salts and PVA, metal ions would be complexed to hydroxyl side groups of PVA [23]. This complex formation should keep the homogeneous distribution of the constituents during removal of water. Upon evaporation of water from the mixture, it became very viscous and gelatinous. In this stage, when most of water was removed, it could be considered that metal ions were dissolved in polymer matrix instead of water. The gel was transparent, which suggested that fractional precipitation of

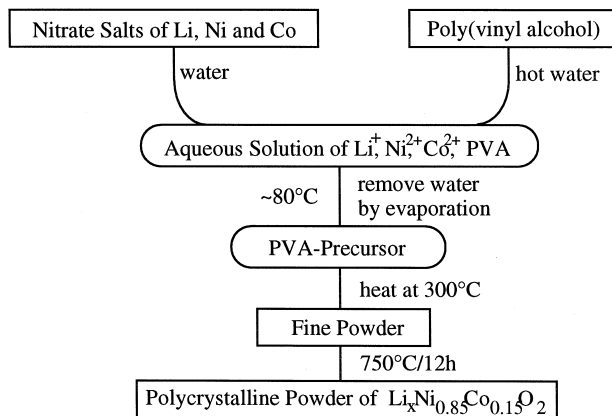


Fig. 1. Schematic diagram of the synthesis of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  by the PVA-precursor method. Rectangular containment indicates solid state, and the rounded one solution state.

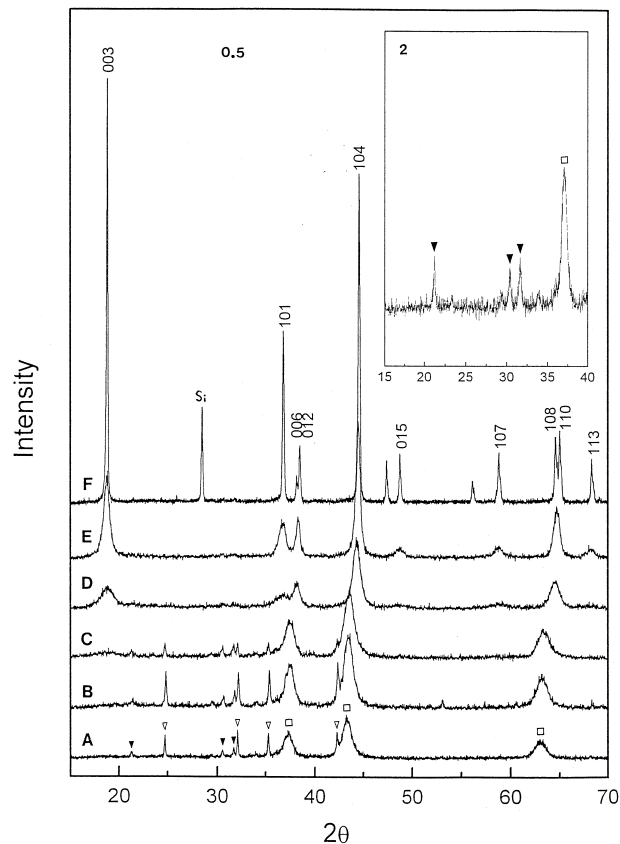


Fig. 2. PXRD patterns in series, for the samples prepared by heating (at a rate of  $3^\circ\text{C}/\text{min}$ ) the precursor at designated temperatures: (A)  $300^\circ\text{C}$  for 3 h, (B)  $400^\circ\text{C}$  for 5 min, (C)  $500^\circ\text{C}$  for 5 min, (D)  $600^\circ\text{C}$  for 5 min, (E)  $700^\circ\text{C}$  for 5 min, and (F)  $750^\circ\text{C}$  12 h in air. The polymer to metal mole ratio was 0.5. The PXRD pattern in the inset is for the precursor heated at  $300^\circ\text{C}$  for 3 h, when the polymer to metal mole ratio was 2. The designation of the symbol is as follows: Si standard (★),  $\text{Li}_2\text{CO}_3$  (▼),  $\text{LiNO}_3$  (▽), and NiO (□).

metal salts (segregation) was blocked by the complex formation, thereby enhancing homogeneous distribution of constituent ions. If aqueous solution of reactants was dried without PVA in it, the reactants would precipitate out from solution as water evaporated. In most cases, they precipitated fractionally, because of difference in their solubility products, thereby causing segregation.

PXRD patterns in Fig. 2 showed the formation of crystalline  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  from the PVA-precursor as it was heat treated in air. The gel was transformed into powder by pyrolyzing polymer matrix at  $300^\circ\text{C}$  in air, in order to facilitate handling of the precursor. As shown in Table 1, it had a small amount of carbonaceous residue (1.8% by weight) which originated from organic polymer. The powder had large surface area ( $27\text{ m}^2/\text{g}$ ), which might be utilized as a means of controlling the morphology of final product. Use of a polymer as gelling agent has been demonstrated by others in synthesizing various mixed metal oxides [24–27]. The use of PVA as homogenizing agent was also demonstrated in the syntheses of mixed metal oxides. In the syntheses of other mixed metal oxides,

Table 1  
Characteristics of the solid samples

	PVA-precursor method		Solid state (hydrates)
	Amorphous	Crystalline	
Surface area (m <sup>2</sup> /g)	27.2	2.56	1.82
Carbon content (%w)	1.84	0.69	negligible
Li stoichiometry (x)	–	0.85	0.84

such as LiCoO<sub>2</sub> [20], <sup>1</sup> LiMn<sub>2</sub>O<sub>4</sub> [20,28], (Ln,Sr)CoO<sub>3</sub> [19,23], by the PVA-precursor method, powder samples obtained by pyrolyzing the precursor at 300°C consisted mostly of amorphous phase. On the contrary, the powder obtained at 300°C by pyrolyzing the PVA-precursor to Li<sub>x</sub>Ni<sub>0.85</sub>Co<sub>0.15</sub>O<sub>2</sub> was crystalline. Crystalline phase of Li<sub>2</sub>CO<sub>3</sub>, LiNO<sub>3</sub>, and NiO were observed (Fig. 2A). Apparently, NiO was semicrystalline by seeing the broadness of diffraction peaks: the crystalline domain of NiO calculated by Scherer's equation was 10 nm [29]. On the contrary to the other mixed metal oxides [20,23,28], raising the amount of PVA relative to metal ions in the precursor (up to 4) did not eliminate the formation of crystalline Li<sub>2</sub>CO<sub>3</sub> and NiO at 300°C, although LiNO<sub>3</sub> didn't form when PVA to metal mole ratio was higher than one (see the inset of Fig. 2).

Predominant phase below 500°C was crystalline nickel oxide. Apparently, reaction among nickel oxide, lithium, and cobalt was not completed below 500°C. The broadness of the diffraction peaks was persistent even after the pattern started shifting toward Li<sub>x</sub>Ni<sub>0.85</sub>Co<sub>0.15</sub>O<sub>2</sub> as temperature was raised above 500°C, which suggested that the crystallinity of the product was still immature in time frame used in this study. Interestingly, no trace of minor phase was observed above 600°C, as the Li<sub>x</sub>Ni<sub>0.85</sub>Co<sub>0.15</sub>O<sub>2</sub> phase took its place.

DT and TGA traces by thermal analysis were shown in Fig. 3. Contrary to the syntheses of the other mixed metal oxides by the PVA-precursor method, where several prominent heat events (endotherms and exotherms) were observed during calcination [20,23,28], no such heat event was observed in the precursor to Li<sub>x</sub>Ni<sub>0.85</sub>Co<sub>0.15</sub>O<sub>2</sub>. An endothermic peak at 250°C was related to melting of LiNO<sub>3</sub> [14]. Some LiNO<sub>3</sub> was presumed to be volatilized above the temperature (~1% weight loss). Weight decrease of around 15% between 400 and 500°C was related mostly to decomposition of LiNO<sub>3</sub>. Subsequent weight loss above 500°C might be related to decomposition of Li<sub>2</sub>CO<sub>3</sub> and loss of carbonaceous residues. No other endothermic peak was observed except the one at 250°C, indicating that oxide phase above 600°C was single phase. Solid state reaction between cobalt-rich oxide phase and

nickel-rich oxide phase accompanied a broad endothermic peak around 600°C [14]. This observation also conformed to the PXRD results which revealed no minor phase above 600°C. The crystalline phase of Li<sub>x</sub>Ni<sub>0.85</sub>Co<sub>0.15</sub>O<sub>2</sub> was shown to develop immediately as LiNO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> were eliminated. There was not much heat flow during this process, indicating that the crystallization of Li<sub>x</sub>Ni<sub>0.85</sub>Co<sub>0.15</sub>O<sub>2</sub> proceeded without much energy consumption. Therefore, it could be presumed that the homogeneity attained in the gel was largely preserved in the solid sample. The nano domains of nickel oxides could be discrete ones in view of the observation that the broad diffraction peak of the nickel oxide never had chance to get sharper before it was consumed by the crystallization of Li<sub>x</sub>Ni<sub>0.85</sub>Co<sub>0.15</sub>O<sub>2</sub>.

The powder samples of the crystalline Li<sub>x</sub>Ni<sub>0.85</sub>Co<sub>0.15</sub>O<sub>2</sub> for the test cells were obtained by heating the precursor at 750°C for 12 h in air, and subsequently annealing at 500–600°C in a flow of air, if necessary. The cell parameters calculated by using LATT from the diffraction peaks were  $a = 2.868 \text{ \AA}$  and  $c = 14.162 \text{ \AA}$ . After heating the powder at 750°C for 12 h, the surface area was largely decreased to 2.56 from 27.2 m<sup>2</sup>/g (see Table 1), though it was still larger than that of the product synthesized by the solid state reaction. The amount of carbonaceous residue in the sample decreased after the heating, but it was not eliminated completely (around 0.6% left). The stoichiometry of Ni and Co was determined to be 0.85 and 0.15 by ICP/MS analysis for both of the materials prepared by the PVA-precursor method and the solid state reaction. But, the stoichiometry of lithium was analyzed to be less than 1. It was analyzed to be 0.85 by ICP/MS (see Table 1). The integrated intensity ratio of  $I(104)/I(003)$  in the PXRD pattern was calculated to be 0.996. Anticipated value, on the basis of the stoichiometry, was larger than 1, because the reported value of  $I(104)/I(003)$  was larger than 1 for the sample prepared via the solid state reaction, when mole ratio of Ni:Co was 0.85:0.15 [14]. It was suggested that orderliness of the two-dimensional layer

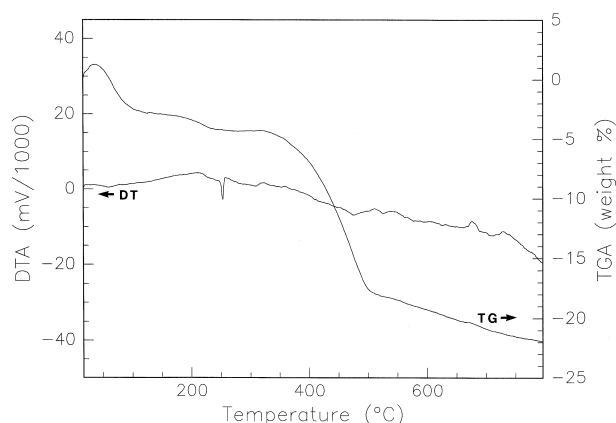


Fig. 3. TG/DT traces of the pyrolysis of the PVA-precursor to Li<sub>x</sub>Ni<sub>0.85</sub>Co<sub>0.15</sub>O<sub>2</sub> at a rate of 3°C/min in the flow of air (30 ml/min).

<sup>1</sup> The powder obtained by heating the PVA-precursor to LiCoO<sub>2</sub> was amorphous (PXRD analysis).

structure was somehow enhanced, despite of the lithium deficiency, when  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was synthesized by the PVA-precursor method, and the oxidation state of Ni was mostly III. We are currently investigating this peculiar reproducible observation. Since the amount of lithium

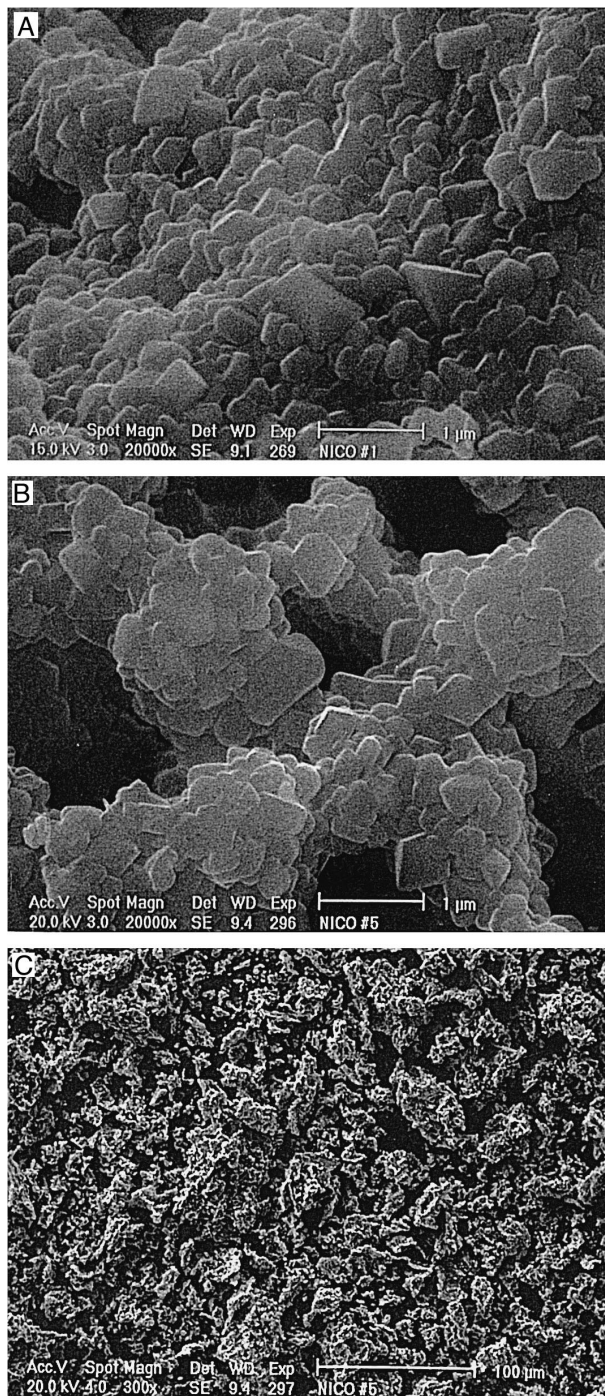


Fig. 4. SEM micrograph of the powder prepared by heating the PVA-precursor at 300°C for 3 h (A). The micrograph of the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared by heating the powder at 750°C for 12 h in air, and subsequent annealing at 500–600°C (B). Observation in low magnification shows the irregular formation of agglomerates (C).

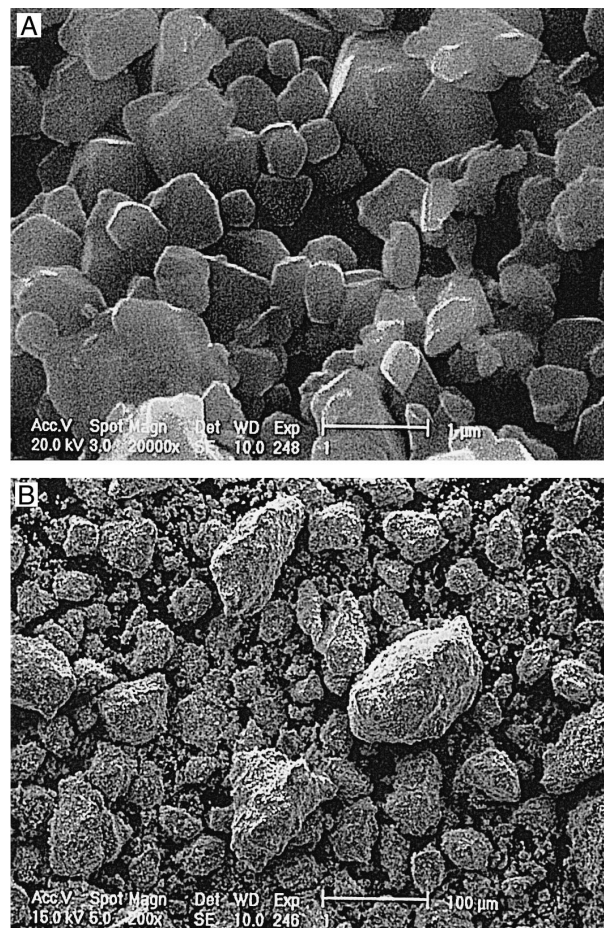


Fig. 5. SEM micrograph of the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared by the solid state reaction (A). Observation in low magnification shows roughly spherical feature of agglomerates (B).

added in reactants was stoichiometric, a part of lithium was presumed to be lost during the heat treatment. In order to get stoichiometric product, additional amount of lithium over the stoichiometric one had to be used.<sup>2</sup>

The SEM micrographs of the solid samples prepared by the PVA-precursor method are shown in Fig. 4. The fine powder obtained by heating the PVA-precursor at 300°C consisted of sub-micron particles whose crystalline facets were relatively well-defined (Fig. 4a). In most of previous studies, the powder precursors obtained by heating PVA-precursors at 300°C were amorphous, and looked like crumpled thin papers on micrographs [20,28]. In such amorphous precursors, the polymer (i.e., monomer unit) to metal mole ratio was higher than one. Therefore, one to one complex formation between polymer and metal ion

<sup>2</sup> By optimizing synthetic conditions and the stoichiometry of the constituents in  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ , we obtained a specific discharge capacity of 196 mA h/g at a rate of C/10; the accepted article will appear in March issue of the Journal of the Korean Electrochemical Society, 2 (1999) 5.

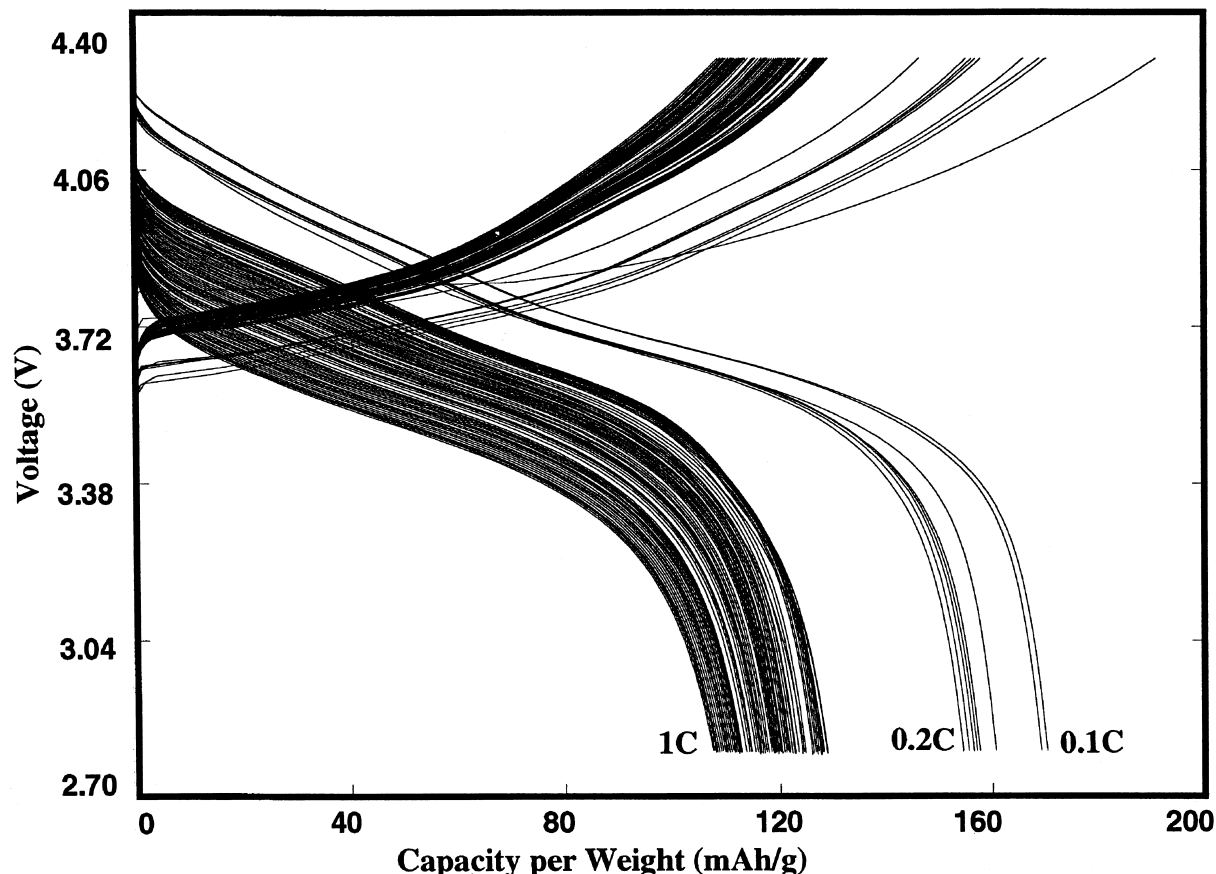


Fig. 6. The traces of continuous 100 cycles of charge and discharge carried out in a constant current mode on a test cell which was equipped with a cathode fabricated by using  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared by the PVA-precursor method. The operation was carried out stepwise at a rate of  $C/10$ ,  $C/5$ , and finally at  $1C$ .

was ensured. The excess amount of the polymer provided the source of the carbonaceous impurity in the powder. On the contrary, some metal ions should be rather free to move in the precursor to  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ , because polymer to metal mole ratio was less than 1 (0.5). In this case, only half of metal ions were allowed to be complexed to polymer. Presumably, the excess metal ions precipitated as a salt, which is consistent with  $\text{LiNO}_3$  diffraction peaks observed by PXRD (Fig. 2A). The  $\text{LiNO}_3$  diffraction peaks disappeared (inlet in Fig. 2), as polymer to metal mole ratio increased in the PVA-precursor.<sup>3</sup> The polycrystalline powder of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  consisted of sub-micron sized particles of approximately 200 nm (Fig. 4B). It appeared that some particles were fused together. The micrograph in Fig. 4C showed the agglomerates had rather irregular shape.

The SEM micrographs of polycrystalline powder of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared by the solid state reaction are

<sup>3</sup> Unpublished observations: The micrographs for the powder obtained by heating the PVA-precursor to  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  whose the polymer to metal mole ratio was higher than one revealed the particles with obscure feature (no prominent crystalline facets).

shown in Fig. 5. The size of the particle was about twice as large as that of the powder prepared by the PVA-precursor method (Fig. 5a). The particles formed agglomerates (Fig. 5b). The size of the agglomerates was not uniform. While the agglomerates prepared by the PVA-precursor method had irregular crumpled shape, those prepared by the solid state reaction were roughly spherical.

Samples obtained from the PVA-precursor had relatively high surface area and contained a small amount of carbonaceous residue [20]. Also, there are variety of synthetic factors that can be modified to manipulate the crystallization process, such as the kind of reactants and polymer-to-metal mole ratio. Compared with conventional solid state reaction, it might be easier to tailor the property of crystalline product via the PVA-precursor method. For example, it was observed that changing PVA to metal mole ratio, or PVA concentration of the PVA-gel could alter the particle size of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ .<sup>2</sup>

In Figs. 6 and 7, the traces of continuous 100 cycles of charge–discharge were shown for coin cells equipped with cathodes fabricated by using  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  synthesized in this study. Several features are distinctively comparable, such as the pattern of the drop in the electric potential (parallel vs. getting steeper), or the shape of the

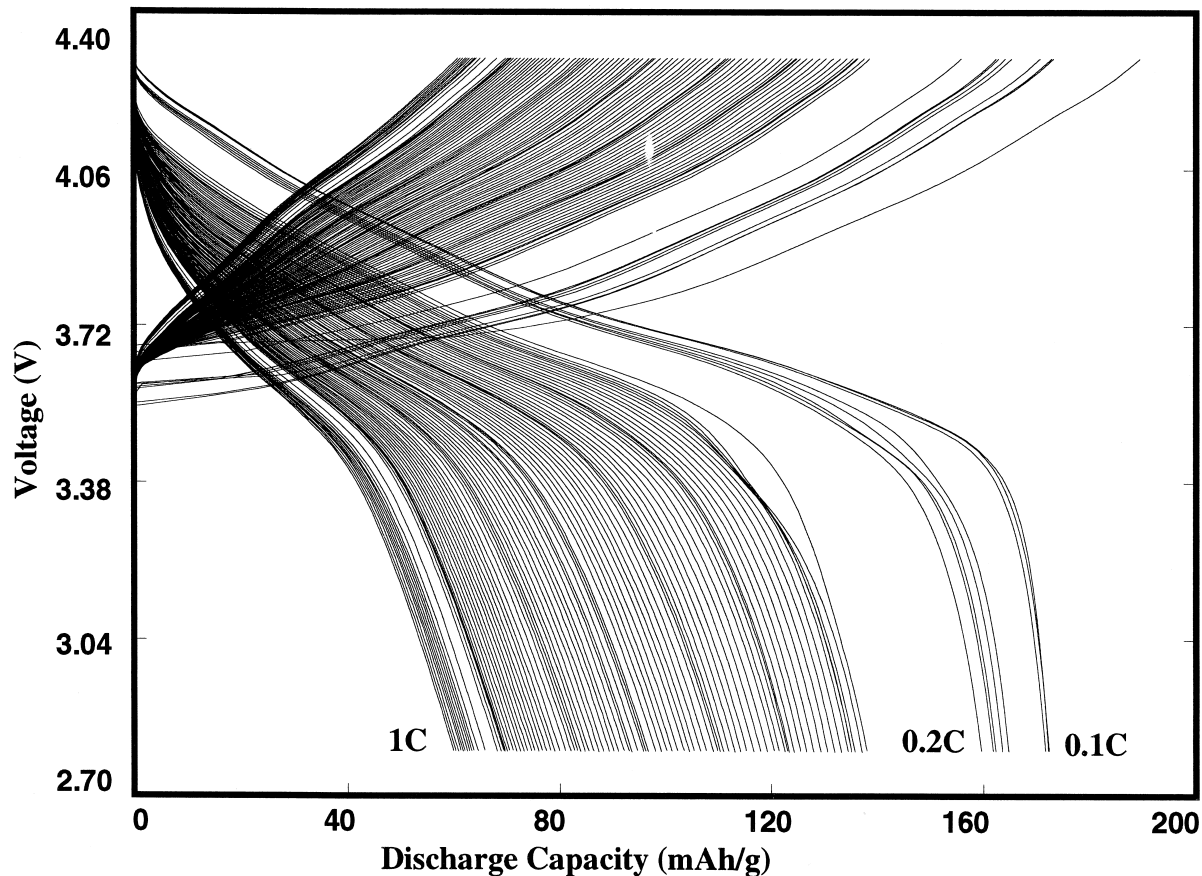


Fig. 7. The traces of continuous 100 cycles of charge and discharge carried out in a constant current mode on a test cell which was equipped with a cathode fabricated by using  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared by conventional solid state reaction. The operation was carried out stepwise at a rate of  $C/10$ ,  $C/5$ , and finally at  $1C$ .

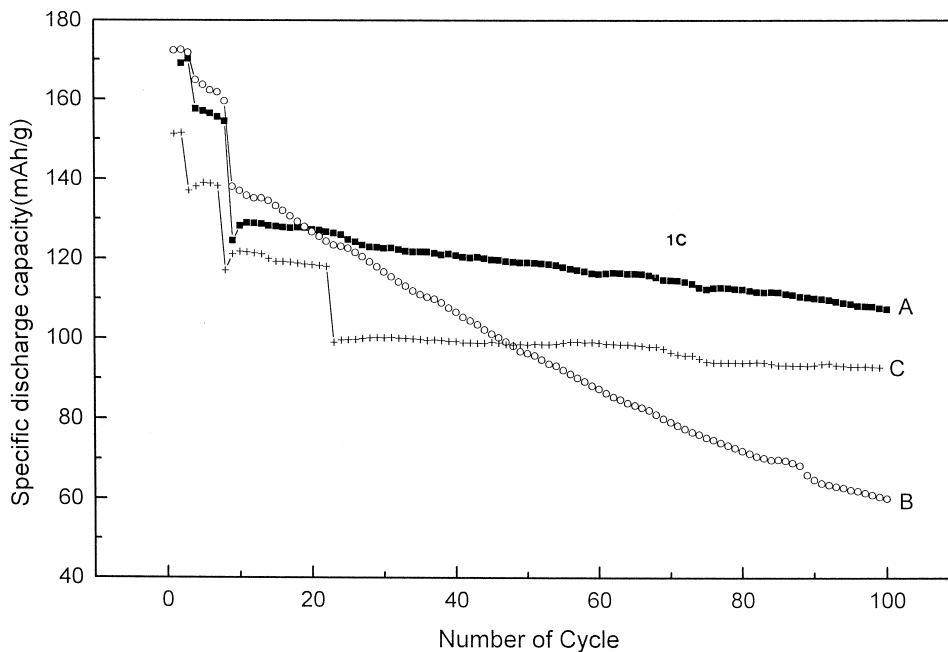


Fig. 8. The variation of discharge capacity of a coin cell equipped with a cathode made from  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  synthesized by the PVA-precursor method (A), or by conventional solid state reaction (B). When  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was obtained by heating the precursor only at  $750^\circ\text{C}$ , without being annealed, the reversibility of the cycle was very good, even though the initial discharge capacity was low (C).

charging curve (convex vs. concave, in the middle).<sup>4</sup> The drop of specific discharge capacity was compared in Fig. 8 for those cells. In fabricating the cells, all factors other than synthetic route to  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  (the PVA-precursor method vs. the solid state reaction) were identical.

For the PVA-precursor method, the test of the cell was carried out for both samples of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  which were either post-heated at 500°C or not (Fig. 8A vs. C). Annealing the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  (obtained by being heated at 750°C) at 500°C in the flow of air raised the initial discharge capacity of the cell in large extent, from 150 to 170 mA h/g. Apparently, this improvement by further heating was not observed for the sample prepared by the solid state reaction.<sup>5</sup> Considering the lithium stoichiometry was lower than 1.0 (see Table 1), the observed value of 170 mA h/g should be counted as being satisfactory in a practical term. Stoichiometric compensation during the synthetic process shall improve the capacity.<sup>2</sup>

It was observed that the property of the cell with the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared by the solid state reaction deteriorated fast as the cycle was repeated (Figs. 7 and 8B). The specific discharge capacity of the cell, which was 140 mA h/g initially at a rate of 1C (9th cycle), decreased down to 60 mA h/g after 90 cycles (100th cycle). On the contrary, the cell with the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared from the PVA-precursor exhibited very good cycle reversibility especially at high rate (Figs. 6 and 8A). The decrease of specific discharge capacity during consecutive 90 cycles (from 9th to 100th cycle) at a rate of 1C was less than 20 mA h/g. Fig. 8C also shows good cycle property of the cell with the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared without being annealed at 500°C. Even though initial capacity (150 mA h/g) was much lower, the cycle reversibility of the cell was much better than others at high rate. The decrease of the capacity was almost negligible at 1C. The PXRD patterns for those samples of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ , which were annealed or unannealed, had identical pattern and intensities, which strongly suggested that the physical property of the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  might be an important factor to affect the property of the cell.<sup>6</sup>

#### 4. Conclusion

Single-phase polycrystalline powder of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  was synthesized by the PVA-precursor method. PVA was used as gelling agent to keep constituent metal ions from precipitating into heterogeneous composition;

thereby maximizing homogeneity of the precursor before it was heated. The polymer precursor turned into very fine powder by being heated at 300°C in air. At above 500°C, the reaction to single phase  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  proceeded without any prominent heat event. At above 600°C,  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  contained single phase as observed by PXRD, and no other phase (minor phase) was observed. It appears possible that the single phase crystalline  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  may be synthesized at a temperature lower than 750°C.

Physical properties, such as surface area, morphology, and shape of the agglomerates of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  synthesized by the PVA-precursor method were drastically different from those prepared by the solid state reaction. It was suggested that manipulation of the properties through adjustment of the synthetic condition could be carried out much easier via the PVA-precursor method than via the solid state reaction.

By using the  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared from the PVA-precursor as the cathode material, test coin cells containing a Li anode were fabricated and tested. The initial capacity of the cell was 170 mA h/g at a rate of C/10. Considering the stoichiometry was set to  $y = 0.15$  in  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ , where lithium deficiency was expected to accompany the cation disorder [14], the capacity obtained for the cell should be considered to be more than expected. Because lithium stoichiometry did not reach 1 in this study (0.85), we expect further improvement by raising the lithium stoichiometry to ideal one, and by optimizing Ni to Co ratio.<sup>2</sup> Most of all, the reversibility of the charge–discharge cycle was very good even at high rate of 1C, when the cathode was fabricated by using  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared by the PVA-precursor method. Performance of the cell was greatly improved when annealing at 500°C was carried out for the polycrystalline product of  $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  synthesized by the PVA-precursor method. This improvement by annealing was not observed for the sample prepared via the solid state reaction.

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<sup>4</sup> We do not fully understand underlying reason for this apparent difference, which is reproducible result.

<sup>5</sup> The effect of annealing on the property of  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$  synthesized from the PVA-precursor was described in a separate article submitted to Bulletin of Korean Chemical Society.

<sup>6</sup> We are currently investigating the effect of particle morphology.



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