

# LiNi<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub> prepared at low temperature using $\beta$ -Ni<sub>1-x</sub>Co<sub>x</sub>OOH and either LiNO<sub>3</sub> or LiOH

Y. Fujita \*, K. Amine, J. Maruta, H. Yasuda

Fundamental Technology Laboratory, Corporate R&D Center, Japan Storage Battery Co., Ltd., Nishinosho, Kisshoin, Minami-ku, Kyoto 601, Japan

Accepted 13 January 1997

## Abstract

LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> has been prepared at 400 °C by using  $\beta$ -Ni<sub>1-y</sub>Co<sub>y</sub>OOH and either LiNO<sub>3</sub> or LiOH. The mechanism of these reactions was clarified by differential thermal and thermogravimetric analyses. The material prepared with LiNO<sub>3</sub> is well crystallized because LiNO<sub>3</sub> melts and then reacts with the oxyhydroxide in a viscous state. However, when LiOH is used, a solid–solid diffusion reaction takes place and leads to a material with broad X-ray diffraction peaks. The electrochemical characteristics of these materials were evaluated and compared with those prepared by the usual processes at high temperature. © 1997 Elsevier Science S.A.

**Keywords:** Lithium; Nitrogen; Cobalt oxyhydroxide; Low temperature preparation; High coulombic efficiency

## 1. Introduction

The LiNi<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub> system has been extensively studied as an electrode for lithium secondary batteries [1–4]. This material is also a strong potential candidate to replace the actually commercialized LiCoO<sub>2</sub> because of its low cost and high specific capacity. However, the preparation of this material is reported to take place at a very high temperature and under oxygen stream because of the difficulty of oxidizing divalent nickel and cobalt used in the starting precursors [2–4]. In this case, a stoichiometric composition is very difficult to obtain and the material forms a solid solution Li<sub>1-x</sub>Ni<sub>1+x-y</sub>Co<sub>y</sub>O<sub>2</sub> with a partial cationic disorder distribution at the lithium site. The lithium deficiency in this case is probably caused by the partial evaporation of lithium precursor during the high temperature preparation. As a result, the electrochemical performances of the material degraded significantly when the degree of disorder increases. One way to compensate for the lithium loss during the high temperature preparation is the use of excess lithium. However, the final product has to be washed with water to eliminate impurities related to unreacted lithium-based material. This washing process may affect the reversible capacity of the material. The second way to prevent the lithium evaporation is lowering the preparation temperature. In this study, we report a

new process for the preparation of LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> with limited cobalt doping ( $0 \leq y \leq 0.15$ ) at 400 °C.

## 2. Experimental

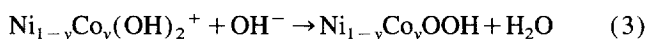
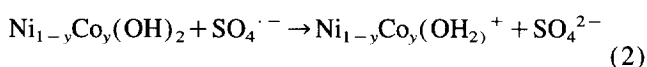
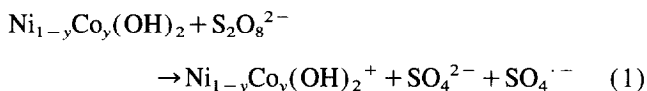
LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> ( $0 \leq y \leq 0.15$ ) was prepared by using the  $\beta$ -phase of Ni<sub>1-y</sub>Co<sub>y</sub>OOH and either LiNO<sub>3</sub> or LiOH as the starting materials.  $\beta$ -Ni<sub>1-y</sub>Co<sub>y</sub>OOH was initially prepared by oxidizing Ni<sub>1-y</sub>Co<sub>y</sub>(OH)<sub>2</sub> (Tanaka Chemical), co-precipitated by adding an alkaline solution to a solution of nickel salt and cobalt salt, in NaOH and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> [5] in the 5–80 °C temperature range. A stoichiometric mixture of  $\beta$ -Ni<sub>1-y</sub>Co<sub>y</sub>OOH and either LiNO<sub>3</sub> or LiOH was then strongly ground before being pelletized and heated under either a flow of oxygen (20%) and argon (80%) or air at ~400 °C for 24 h.

The test electrode was prepared by forming a paste made of the active material, acetylene black, poly(vinylidene difluoride) (PVDF) solution and NMP solvent. The paste was then coated on an aluminium mesh before being dried at 80 °C for ~1 h. The electrochemical performances of LiNi<sub>1-y</sub>Co<sub>y</sub>O<sub>2</sub> were evaluated in a glass cell containing a lithium foil anode, a lithium reference electrode and an electrolyte consisting of 1 M LiClO<sub>4</sub> dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1). The cells were cycled between the voltage limits of 4.3 to 3.0 V at a current density of 0.5 mA/cm<sup>2</sup> during both charge and discharge.

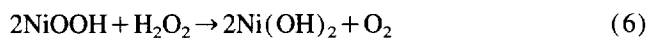
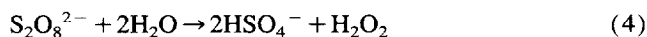
\* Corresponding author. Tel: (81) 75 316-3611. Fax: (81) 75-312-1261. E-mail: KYP01113@niftyserve.or.jp

### 3. Results and discussion

The preparation of  $\beta$ - $\text{Ni}_{1-y}\text{Co}_y\text{OOH}$  by oxidation of the corresponding hydroxide was carried out according to the following reactions:



When the oxidation takes place at 80 °C, a substitution of nickel with a limited amount of cobalt was necessary in order to stabilize the  $\beta$ -phase of the oxyhydroxide. Fig. 1(b) shows the X-ray diffraction pattern of  $\text{Ni}_{0.85}\text{Co}_{0.15}\text{OOH}$  obtained after oxidation of  $\text{Ni}_{0.85}\text{Co}_{0.15}(\text{OH})_2$  (Fig. 1(a)) at 80 °C. A pure  $\beta$ -phase was easily obtained with broad peaks. However, without cobalt doping and under the same oxidation condition, a mixture of nickel hydroxide and a small amount of  $\beta$ -phase denoted by (\*) was obtained (Fig. 1(c)). In this case,  $\beta$ - $\text{NiOOH}$  formed after the oxidation was immediately reduced by  $\text{H}_2\text{O}_2$  at 80 °C according to the following reactions:



After having optimized the preparation condition by lowering the oxidation temperature to around 5 °C, the reducing power of  $\text{H}_2\text{O}_2$  diminished and a pure  $\beta$ - $\text{NiOOH}$  without cobalt doping was prepared (Fig. 1(d)). The oxidation of the hydroxide form was also confirmed by titration of the oxidized material with  $\text{KMnO}_4$  and EDTA which gave an average valency of (+3) for both the Ni and the Co ions.

Fig. 2 shows the XRD patterns of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared from the  $\beta$ - $\text{Ni}_{1-y}\text{Co}_y\text{OOH}$  and  $\text{LiNO}_3$  process at 400

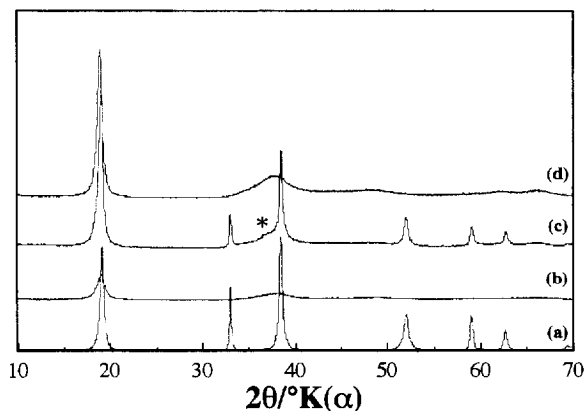


Fig. 1. XRD patterns of: (a)  $\text{Ni}_{0.85}\text{Co}_{0.15}(\text{OH})_2$ ; (b)  $\beta$ - $\text{Ni}_{0.85}\text{Co}_{0.15}\text{OOH}$  obtained after oxidation at 80 °C; (c)  $\text{Ni}(\text{OH})_2$  oxidized at 80 °C, and (d)  $\beta$ - $\text{NiOOH}$  obtained after oxidation at 5 °C.

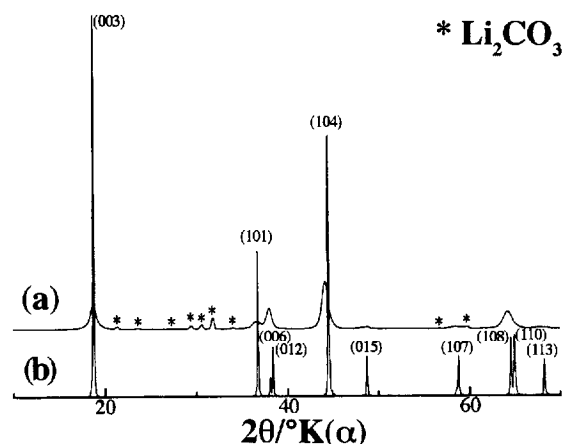


Fig. 2. XRD patterns of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared from  $\beta$ - $\text{Ni}_{0.85}\text{Co}_{0.15}\text{OOH}$  and  $\text{LiNO}_3$  at 400 °C under: (a) air, and (b) oxygen and argon flow.

°C under air (Fig. 2(a)) and a flow of oxygen and argon (Fig. 2(b)). The material prepared under air gives a mixture of  $\text{Li}_2\text{CO}_3$  denoted (\*) and a less-defined layered phase with very broad peaks. Whereas, the material prepared under a flow of oxygen and argon gives a highly crystallized pure layered phase with a hexagonal structure ( $a = 2.871 \text{ \AA}$ ,  $c = 14.19 \text{ \AA}$ ). In this case, the pattern shows a large integrated intensity ratio  $I_{(003)}/I_{(104)} = 1.49$  and a clear split of the (006) and (012) as well as (108) and (110) peaks which are indicative of less disorder in the structure.

Fig. 3 shows the XRD patterns of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared by the  $\text{LiOH}$  process at 450 °C under air (Fig. 3(a)) and a flow of oxygen and argon (Fig. 3(b)). In both cases, mainly pure layered phases were obtained with the patterns showing broad peaks. This result reveals that the particle size in these materials is rather small as confirmed by scanning electron microscopy (SEM) giving an average particle size of 0.1  $\mu\text{m}$ . When the material is prepared under air, small impurities related to unreacted  $\text{LiOH}$  are observed because of the limited reaction time. These impurities can be easily removed by washing the material with water. The integrated intensity ratio  $I_{(003)}/I_{(104)}$  was about 1.57 for the material prepared under oxygen and argon flow and a lower value of

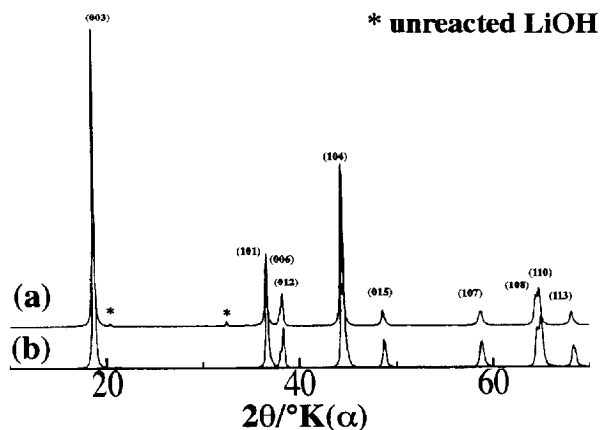


Fig. 3. XRD patterns of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared from  $\beta$ - $\text{Ni}_{0.85}\text{Co}_{0.15}\text{OOH}$  and  $\text{LiOH}$  at 450 °C under: (a) air, and (b) oxygen and argon flow.

1.13 for the one prepared under air reflecting the occurrence of some disorder within the structure.

The reaction mechanisms of materials prepared by the  $\text{LiNO}_3$  and  $\text{LiOH}$  processes were investigated by differential thermal (DTA) and thermogravimetric (TG) analysis. Fig. 4(a) shows the result of TG and DTA of the stoichiometric mixture of  $\beta\text{-Ni}_{0.85}\text{Co}_{0.15}\text{OOH}$  and  $\text{LiNO}_3$  under a flow of oxygen and argon. At least three endothermic peaks appear at a temperature lower than  $300^\circ\text{C}$ . This result indicates that several step reactions take place during the preparation process. The peak observed at  $90.7^\circ\text{C}$ , associated with a limited weight loss, corresponds to the elimination of the water molecule adsorbed by  $\text{LiNO}_3$ . The remaining other peaks are probably the result of partial decomposition, melting and reaction of the precursors. Therefore, the  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  synthesis reaction seems to proceed in a viscous state in which the starting materials keep mutually intimate contacts. In addition, taking into account that neither a DTA peak nor weight loss is observed over  $400^\circ\text{C}$ , it is concluded that the reaction is easily completed at  $400^\circ\text{C}$ . The sharp XRD peaks of the resulting material shown in Fig. 2(b) can be explained

by the completion of reaction and the crystallization of the viscous material during the slow cooling process. When the synthesis of  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  is carried out under air,  $\text{LiNO}_3$  would melt, partially decompose and react with  $\text{CO}_2$  in the atmosphere, leading to the formation of the intermediary  $\text{Li}_2\text{CO}_3$ . Fig. 4(b) indicates that  $\text{Li}_2\text{CO}_3$  does not react completely with  $\beta\text{-Ni}_{1-y}\text{Co}_y\text{OOH}$  at  $400^\circ\text{C}$ , because a continuous weight loss is observed over this temperature. These phenomena would cause remaining of  $\text{Li}_2\text{CO}_3$  and broader X-ray diffraction peaks as shown in Fig. 2(a). Fig. 4(c) shows the results of TG and DTA of the stoichiometric mixture of  $\beta\text{-Ni}_{0.85}\text{Co}_{0.15}\text{OOH}$  and  $\text{LiOH}$  under a flow of oxygen and argon. The DTA curve exhibits only two endothermic peaks. The first sharp peak observed at  $73^\circ\text{C}$  is associated with the elimination of the water molecule adsorbed by  $\text{LiOH}$ . The second peak observed at  $243^\circ\text{C}$  corresponds to the generation reaction of  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ . In the TG curve, no weight loss is observed over  $400^\circ\text{C}$ . These facts indicate that the final product can be obtained at a temperature as low as  $450^\circ\text{C}$ . The less crystallinity of the resulting material by the  $\text{LiOH}$  process (Fig. 3(b)), in comparison with the material by the  $\text{LiNO}_3$  process, can be attributed to that  $\text{LiOH}$  does not melt and, thus, the reaction proceeds in the solid–solid state, unlike the solid–liquid state in the  $\text{LiNO}_3$  process. Contrary to the  $\text{LiNO}_3$  process, the possibility of the formation of intermediary  $\text{Li}_2\text{CO}_3$  when operating in air is very limited, because  $\text{LiOH}$  does not melt or decompose. Similar DTA and TG analyses were conducted by using  $\text{Ni}_{1-y}\text{Co}_y(\text{OH})_2$  or a mixture of  $\text{Ni}(\text{OH})_2$  and  $\text{Co}(\text{OH})_2$  instead of the oxyhydroxide form. The result shows that the hydroxide form does not react completely with either  $\text{LiNO}_3$  or  $\text{LiOH}$  at  $400^\circ\text{C}$ . In this case, a temperature higher than  $750^\circ\text{C}$  is needed to bring the reaction to completion. The temperature dependence for the completion of the reaction on starting materials results from the difference of the oxidation state of nickel in the material. As nickel in the hydroxide,  $\text{Ni}_{1-y}\text{Co}_y(\text{OH})_2$  or  $\text{Ni}(\text{OH})_2$  is in the divalent state, it must be oxidized to the trivalent state at the end of the reaction and, therefore, operated at such a higher temperature as  $750^\circ\text{C}$ . On the other hand, nickel in the oxyhydroxide,  $\text{Ni}_{1-y}\text{Co}_y\text{OOH}$  is already in the trivalent state, this starting material, therefore, leads easily to the final material even at such a temperature as low as  $400\text{--}450^\circ\text{C}$ .

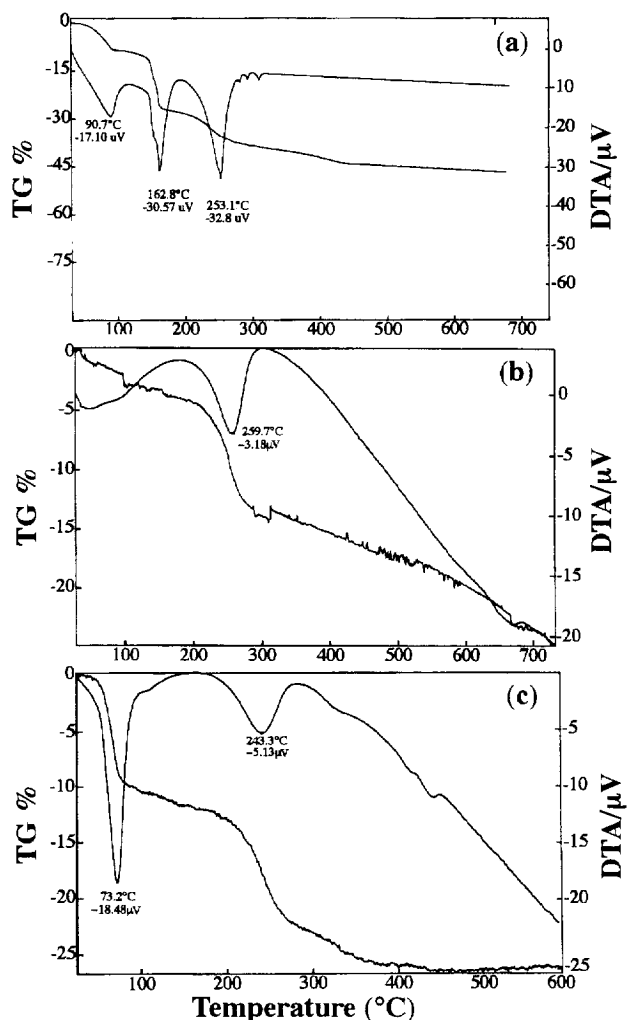


Fig. 4. DTA and TG curves of a stoichiometric mixture of  $\beta\text{-Ni}_{0.85}\text{Co}_{0.15}\text{OOH}$  and (a)  $\text{LiNO}_3$ , (b)  $\text{Li}_2\text{CO}_3$  and (c)  $\text{LiOH}$ .

#### 4. Electrochemical characteristics

Fig. 5 compares the charge and discharge characteristics of the first cycle of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared by the  $\text{LiNO}_3$  process (Fig. 5(a)) with the  $\text{LiOH}$  process (Fig. 5(b)). Both materials present a monotonous variation of the potential with the capacity, indicating the occurrence of a one-phase reaction during cycling. This result reveals that no structural transition from hexagonal to monoclinic takes place, unlike  $\text{LiNiO}_2$  prepared at a high temperature [6] where several structural transitions take place during cycling. These differences in the charge/discharge behavior can be

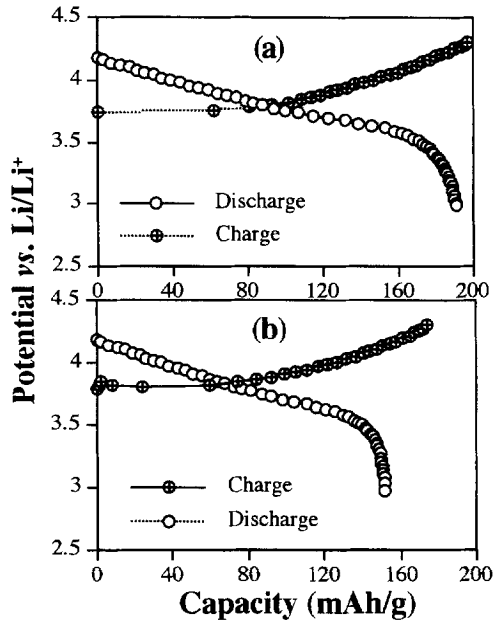


Fig. 5. Charge and discharge curves of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared from  $\beta\text{-Ni}_{0.85}\text{Co}_{0.15}\text{OOH}$  and (a)  $\text{LiNO}_3$  at  $400^\circ\text{C}$ , (b)  $\text{LiOH}$  at  $450^\circ\text{C}$ .  $\text{LiClO}_4/(\text{EC}+\text{DEC})$  was used as the electrolyte at a current density of  $0.5\text{ mA}/\text{cm}^2$ .

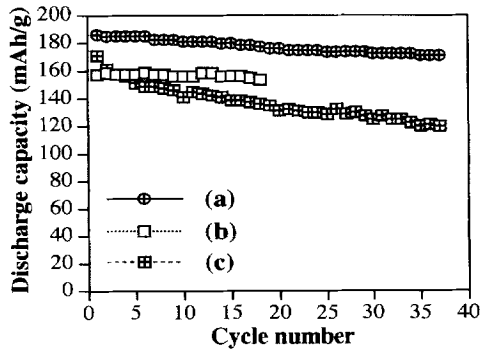


Fig. 6. Variation of the discharge capacity with cycle number of  $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$  prepared from  $\beta\text{-Ni}_{0.85}\text{Co}_{0.15}\text{OOH}$  and (a)  $\text{LiNO}_3$  at  $400^\circ\text{C}$ , (b)  $\text{LiOH}$  at  $450^\circ\text{C}$  and (c)  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  prepared from  $\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$  and  $\text{LiOH}$  at  $750^\circ\text{C}$ .

attributed to both the low temperature preparation and the presence of limited cobalt doping in our materials which reinforce the covalency of the  $\text{Ni}_{1-y}\text{Co}_y\text{O}_2$  slabs, thus preventing the structural transitions. The material prepared from the  $\text{LiNO}_3$  process shows a high discharge capacity of  $190\text{ mAh/g}$  and high charge and discharge coulombic efficiencies of  $97\%$ . Whereas, the material prepared from the  $\text{LiOH}$  process shows relatively lower performances with a discharge capacity of  $157\text{ mAh/g}$  and a coulombic efficiency of  $89\%$ . Both materials exhibit very good cyclic reversibility (Fig. 6 (a), (b)) with a very limited loss in the discharge capacity when compared with  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  material (Fig. 6(c)) prepared by the usual process from  $\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$  and  $\text{LiOH}$  at  $750^\circ\text{C}$ . In order to confirm the occurrence of no structural transition in the low-temperature materials, a

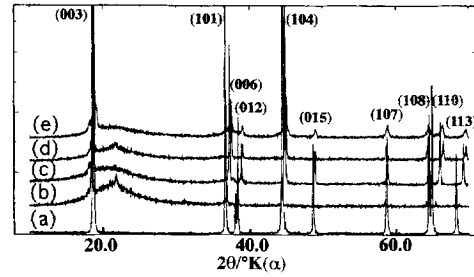


Fig. 7. XRD patterns of  $\text{Li}_{1-x}\text{Ni}_x\text{O}_2$  after extraction of lithium during charge: (a)  $x=0$ ; (b)  $x=0.3$ ; (c)  $x=0.5$ ; (d)  $x=0.7$ , and (e)  $x=0.8$ .

sequence of the powder XRD patterns of  $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  phases were taken after electrochemical de-intercalation of lithium during the charging process. Fig. 7 shows the patterns of  $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$  with ( $x=0, 0.3, 0.5, 0.7, 0.8$ ). All materials give a sharp peaks indicating the maintenance of good crystallinity during the electrochemical de-intercalation. This result indicates that the host framework remains stable during cycling. All X-ray patterns are easily indexed as a layered hexagonal structure without the appearance of peaks corresponding to the monoclinic phase. The finding that no structural transition from hexagonal to monoclinic occurs during the charging process corroborates very well the one-phase reaction observed in the corresponding charge and discharge curves. Furthermore, the (110) peak is shifted towards high angle diffraction during the lithium extraction, reflecting the decrease in the unit cell parameter  $a$ . This decrease is caused by the increasing strength of the covalency of  $\text{Ni}_{1-y}\text{Co}_y\text{O}_2$  sheet because  $\text{Ni}^{4+}$  and  $\text{Co}^{4+}$  have smaller ionic radius than  $\text{Ni}^{3+}$  and  $\text{Co}^{3+}$ . On the other hand, the (006) peak is shifted towards low diffraction angles, revealing the expansion of the  $c$ -unit parameter. This expansion is caused by the increase in the negative interaction between the oxygen of the adjacent layers after the lithium extraction.

## 5. Conclusions

$\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  with a pure layered phase was obtained even at  $400\text{--}450^\circ\text{C}$  by using  $\beta\text{-Ni}_{1-y}\text{Co}_y\text{OOH}$  and either  $\text{LiNO}_3$  or  $\text{LiOH}$  as the starting materials. This is attributed to the fact that nickel in the starting material is already trivalent, thus there is no need for the successive oxidation by a higher temperature process. The investigation of the reaction mechanism by DTA and TG analyses revealed that  $\text{LiNO}_3$  is more effective to complete the reaction at a low temperature than  $\text{LiOH}$ . The material prepared by the  $\text{LiNO}_3$  process in a gas mixture of oxygen ( $20\%$ ) and argon ( $80\%$ ) showed a very monotonous discharge/charge curve, a discharge capacity of  $190\text{ mAh/g}$  and a good cyclic reversibility with a very limited loss in the discharge capacity.

**References**

- [1] C. Delmas and I. Saadoune, *Solid State Ionics*, 53–56 (1992) 370–375.
- [2] C. Delmas and I. Saadoune and A. Rougier, *J. Power Sources*, 43–44 (1993) 595.
- [3] T. Ohzuku, U. Ueda and M. Nagayama, *Electrochim. Acta*, 38 (1993) 1159.
- [4] T. Ohzuku, H. Komori, M. Nagayama, K. Sawai and T. Hirai, *Chem. Express*, 6 (1991) 161.
- [5] V.O. Glemser and J. Einerhard, *Z. Anorg. Chem.*, 261 (1950) 26.
- [6] T. Ohzuku, A. Ueda and M. Nagayama, *J. Electrochem. Soc.*, 140 (1993) 1862.