



# Synthesis and characterization of $\text{LiNiO}_2$ cathode material prepared by an adipic acid-assisted sol–gel method for lithium secondary batteries

Yun Sung Lee<sup>a</sup>, Yang Kook Sun<sup>b</sup>, Kee Suk Nahm<sup>a,\*</sup>

<sup>a</sup>*School of Chemical Engineering and Technology, College of Engineering, Chonbuk National University, Chonju 561-756, South Korea*

<sup>b</sup>*Central Research Institute of Chemical Technology, Samsung Advanced Institute of Technology, 103-12, Moonji-Dong, Yusong-Gu, Daejeon 305-380, South Korea*

Received 5 October 1998; accepted 25 October 1998

## Abstract

$\text{LiNiO}_2$  ( $R\bar{3}m$ ) powders were synthesized by a sol–gel method using adipic acid as a chelating agent. Highly crystallized  $\text{LiNiO}_2$  was synthesized in oxygen at a calcination temperature of 750°C for 14 h when molar ratio of adipic acid to total metal ions was 1.0. The intensity ratio of (003)/(104) peaks of XRD spectrum for the synthesized material was 1.67. The  $\text{LiNiO}_2$  powders were monodispersed particulate with the average size of approximately 1–2  $\mu\text{m}$ . The electrochemical test of a half cell fabricated using the  $\text{LiNiO}_2$  powders revealed that the cell had a high initial discharge capacity of 158 mAh  $\text{g}^{-1}$ , but it showed very fast capacity fading just after several tens of charge/discharge cycles. © 1999 Published by Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium nickel oxides; Sol–gel method; Chelating agent; Adipic acid; Precalcination temperature

**PACS:** Batteries; 84.60.D; Chemical composition materials; 81.05; 82.80

## 1. Introduction

The layered oxide  $\text{LiMO}_2$  ( $M = \text{Co}, \text{Ni}, \text{Cr} \dots$ ) have been proposed as cathode materials for lithium secondary batteries [1–3]. Although  $\text{LiCoO}_2$  has been known as the best cathode material for lithium-ion batteries, which produces the best performance,  $\text{LiNiO}_2$  is generally accepted as an attractive cathode material because of its various advantages such as lower cost, higher discharge capacity, better rever-

sibility [4–6]. Transition metal ions such as nickel and cobalt ions are surrounded by six oxygen atoms forming  $\text{LiNiO}_2$  infinite slabs by edge-sharing of the  $\text{NiO}_2$  layers in octahedral sites. The ideal layered  $\text{LiNiO}_2$  structure has a close-packed oxygen array, which is slightly distorted from cubic close packing. Therefore,  $\text{LiNiO}_2$  phase has a rhombohedral structure with a  $R\bar{3}m$  space group and the parameters of the unit cell are usually defined in terms of the hexagonal setting. However, it has been reported that the synthesis of stoichiometric  $\text{LiNiO}_2$  is difficult because a high temperature treatment of  $\text{LiNiO}_2$  results in the decomposition of  $\text{LiNiO}_2$  into

\*Corresponding author. Tel.: +82-652-2702311; fax: +82-652-2702306; e-mail: nahmks@che.chonbuk.ac.kr

$\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  ( $x > 0$ ), which has a partially disordered cation distribution at the lithium sites [7]. It has been well known that the synthetic condition gives great impact on the electrochemical characteristics of cathode materials [8].

In this work, a sol–gel method has been used for the preparation of stoichiometric  $\text{LiNiO}_2$  with high electrical performance. Among the solution methods used for the synthesis of  $\text{LiNiO}_2$ , a sol–gel method has some advantages such as good stoichiometric control, production of submicronized particles, lower calcination temperature. We have investigated the optimum condition by examining the effects of the molar ratio of adipic acid to total metal ions and calcination temperature on the physicochemical properties and enhancement of charge/discharge behavior of  $\text{LiNiO}_2$  powders.

## 2. Experimental

$\text{LiNiO}_2$  powders were prepared along a synthetic procedure as shown in Fig. 1. A stoichiometric

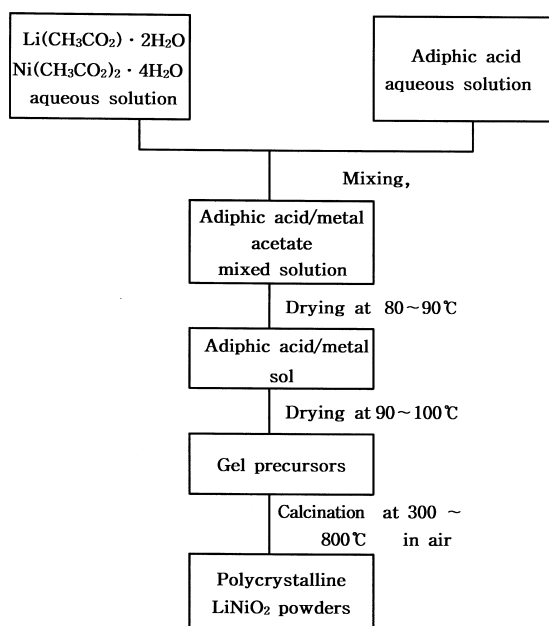


Fig. 1. Synthetic procedure of polycrystalline  $\text{LiNiO}_2$  powders by the adipic acid-assisted sol–gel method.

amount of Li ( $\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$ ) and Ni acetate ( $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , Kanto Chemical Co., Reagent grade) salts corresponding to a cationic ratio of  $\text{Li}/\text{Ni} = 1:1$  was dissolved in DI water. The dissolved solution was sufficiently mixed with an aqueous solution of adipic acid ( $\text{C}_6\text{H}_{10}\text{O}_4$ , Shimakyu's Purechemical Co., EP grade) and evaporated at  $90^\circ\text{C}$  for 12 h in a dry oven to be a transparent sol. The sol was dried at  $90\text{--}100^\circ\text{C}$  for 24 h in a vacuum dryer to yield gel precursors. In order to eliminate organic contents, the gel precursors were precalcined at a temperature of  $400^\circ\text{C}$  for 10 h in air or oxygen. For the preparation of the gel precursors at different molar ratios of adipic acid to total metal ions, the same procedure was repeated at various molar ratios of 0.5, 1.0, 1.5, and 2.0. The decomposed powders were slightly ground and then calcined again at  $700\text{--}800^\circ\text{C}$  for 10 h in air or in  $\text{O}_2$  to obtain pure  $\text{LiNiO}_2$  powders.

The thermal decomposition behavior of the gel precursors was examined with thermogravimetric analyzer (TGA, DuPont, TA2000) and differential thermal analysis (DTA, Dupont, TA 2000). Powder X-ray diffraction (XRD, D/Max-3A, Rigaku) using  $\text{Cu K}\alpha$  radiation was used to identify the crystalline phase of the materials calcined at various temperatures. The particle morphology of gel precursors obtained after the calcination was observed using a scanning electron microscope (SEM; GEOL, JSM 6400).

The electrochemical properties of  $\text{LiNiO}_2$  powders were determined in  $\text{Li}/\text{polymer electrolyte}/\text{LiNiO}_2$  cells. The polymer electrolyte was made from PAN (polyacrylic acid), plasticized by a 1:1 mixture of ethylene carbonate (EC) and propylene carbonate (PC) containing 1 M  $\text{LiClO}_4$  (Mitsubishi). The polymer electrolyte consisted of 12 wt% PAN, 40 wt% EC, 40 wt% PC, and 8 wt%  $\text{LiClO}_4$ . The cathode was prepared by mixing as-synthesized  $\text{LiNiO}_2$ , acetylene black (Super P), and polymer electrolyte at  $110^\circ\text{C}$  with a weight percent ratio of 60:32:8, following the coating of the resultant paste on Al foil current collector. The polymer electrolyte sandwiched by the two electrodes was sealed in a metallized plastic bag in an argon-filled dry box. The charge–discharge cycling was galvanostatically performed at a current density of  $0.05 \text{ mAh cm}^{-2}$  with cut-off voltages of 3.0–4.3 V (vs  $\text{Li}/\text{Li}^+$ ).

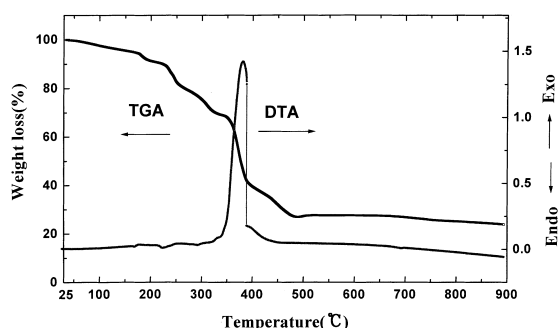


Fig. 2. Thermogravimetric and differential thermal analyses for the gel precursors preheated in a vacuum dryer at 100°C prior to thermal analysis in air at the heating rate of 5°C min<sup>-1</sup>.

### 3. Results and discussion

Fig. 2 shows TGA and DTA patterns for gel precursors prepared by sol–gel method when the molar ratio of adipic acid to total metal ions is 1.0. The weight loss of the gel precursors is terminated at about 500°C with four discrete regions of the weight loss occurred at 30–240, 240–350, 350–400, and 400–500°C, respectively. The weight loss in the temperature range of 30–240°C is due to the desorption of water. The weight loss due to the removal of adipic acid is observed in the temperature range of 240–350°C. But the weight loss in the temperature range of 350–400°C is attributed to the decomposition of metal acetate. Although not illustrated in this paper, we observed thermal behaviors for adipic acid and metal acetates, respectively, using TGA and DTA. TGA showed that adipic acid was quickly evaporated in the temperature range of 265–320°C, whereas metal acetate was steadily decomposed in the temperature range of 280–390°C. For the mixture of metal acetates and adipic acid, however, it is considered that adipic acid participates in the synthetic reaction at a certain temperature to accelerate the decomposition rate of metal acetates as observed in Fig. 2, resulting in the formation of LiNiO<sub>2</sub>. DTA analysis reveals the evolution of an sharp exothermic peak at about 380°C, indicating the rapid decomposition of metal acetate. The combustion of remaining organic compounds occurs in the temperature range of 400–500°C.

To investigate the effect of precalcination tem-

perature on the crystalline phase of LiNiO<sub>2</sub> powders, the gel precursors were prepared at a molar ratio of adipic acid to total metal ions of 1.5. The gel-precursors were precalcined at 300°C for 10 h in air prior to the calcination. Fig. 3 shows XRD spectra for the gel-derived materials prepared at calcination temperatures of 600–800°C. The figure shows that the intensity of (003) peak is much weaker than that of (104) even though the calcination temperature is elevated up to 800°C. This indicates that LiNiO<sub>2</sub> powders with poor crystallinity is synthesized at the precalcined temperature of 300°C. It has been reported that the intensity ratio of (003) and (104) peaks is a key parameter that indicates the degree of the displacement of nickel and lithium ions. Ohzuku et al. [9] reported that the intensity ratio of (003) and (104) peaks should be more than 1.2 to enhance the electrode performance of LiNiO<sub>2</sub> and the extent of the splitting of (108) and (110) peaks is a reliable quantitative criterion for the determination of electrochemical activity of LiNiO<sub>2</sub> when the intensity ratio of (003) and (104) peaks is more than 1.2. On the other hand, Nitta et al. [10] estimated the electrochemical characterization of LiNiO<sub>2</sub> cathode material on the basis of the intensity ratio of (006) and (101) peaks. They proposed that the intensity ratio should be lower than 1.0 and high discharge capacities can be obtained at the intensity ratios of 0.34–

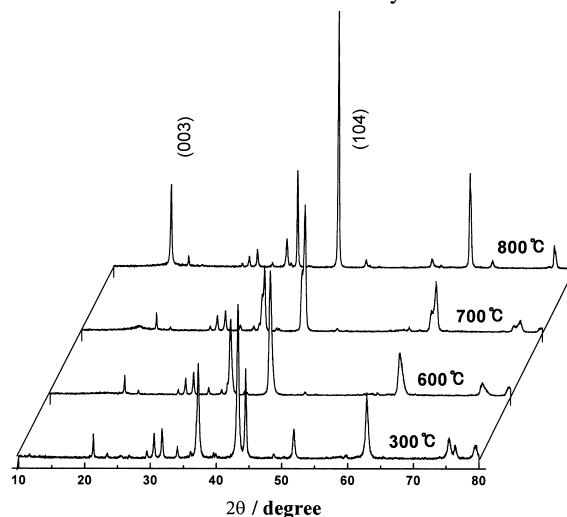


Fig. 3. X-ray diffraction patterns of LiNiO<sub>2</sub> powders calcined at various temperatures in air when molar ratios of adipic acid to total metal ions was 1.5. The gel precursors were preheated at 300°C in air.

0.4. For the preparation of crystalline  $\text{LiNiO}_2$ , we examined the intensity ratios of (003) and (104) peaks, and (101) and (006) as well as the degree of splitting of (108) and (110) peaks appeared on XRD spectrums for the prepared samples. All the peaks appeared from XRD spectrum for  $\text{LiNiO}_2$  are identified in Fig. 8.

For the gel-precursors precalcined at  $400^\circ\text{C}$ , however, the intensity ratio of (003) and (104) peaks rises to 1.2 at the calcination temperature of  $800^\circ\text{C}$  although XRD spectrum obtained at  $700^\circ\text{C}$  shows low intensity ratio of (003) and (104) peaks as shown in Fig. 4. Various impurities such as  $\text{LiOH}$ ,  $\text{LiNiO}_3$  and  $\text{Li}_2\text{O}$  are observed at  $2\theta = 20\text{--}35^\circ$  from XRD spectra at  $600$  and  $700^\circ\text{C}$ . This indicates that  $\text{LiNiO}_2$  with  $R\bar{3}m$  phase can be synthesized at temperatures ranges of  $700\text{--}800^\circ\text{C}$  for the precalcination temperature of  $400^\circ\text{C}$ . This is also supported from the evolution of an sharp exothermic peak at  $380^\circ\text{C}$  in DTA curve of Fig. 2. It means that the crystalline  $\text{LiNiO}_2$  powders are synthesized at the decomposition temperatures above  $380^\circ\text{C}$  and the crystallinity of  $\text{LiNiO}_2$  is enhanced with the increased calcination temperature. Therefore the decomposition of the gel-precursors was carried out at  $400^\circ\text{C}$  for 10 h in air throughout this experiment.

The gel precursors were prepared at various molar

ratios of 0.5, 1.0, 1.5 and 2.0 to investigate the effect of the quantity of chelating agent on the formation mechanism and structural difference of  $\text{LiNiO}_2$  phase. After the gel precursors were precalcined at  $400^\circ\text{C}$  in air, the sample powders were slightly ground and calcined for 14 h at different temperatures in air or oxygen. When the gel precursors were calcined at the temperature ranges of  $700\text{--}800^\circ\text{C}$ , XRD spectra showed that highly crystalline  $\text{LiNiO}_2$  phase with a rhombohedral structure was synthesized independent of the molar ratio of adipic acid to total metal ions.

The gel precursors calcined at  $800^\circ\text{C}$  in air are crystallized into phase-pure  $\text{LiNiO}_2$  powders without any development of minor phases as shown in Fig. 5. The intensity ratio of (003)/(104) peaks of XRD spectrum for the sample synthesized is the highest value of 1.47 when the molar ratio of adipic acid to total metal ions is 1.5, but below 1.2 at the rest values of the molar ratio. With increasing the molar ratios of adipic acid to total metal ions, the crystallinity and intensity ratio of (003)/(104) peaks increase until the molar ratio increases up to 1.5, but decrease slightly when the molar ratio increases further. It is considered that the variation of the intensity ratio of (003)/(104) peaks with the amount of adipic acid used is mainly due to the role of adipic acid in the synthetic reaction. Adipic acid not only functions as a chelating agent but also accelerates the synthetic reaction of  $\text{LiNiO}_2$  with the evolution of large heat. Therefore, the produced amount of cross-linked gel precursors and the reaction heat increase with increasing the amount of adipic acid used in the synthesis of gel precursor. The cross-linked gel precursors may provide more homogeneous mixing of the cations and fewer tendencies for segregation during calcination, which strongly suppresses the formation of precipitates stemming the heterogeneity. This enhances the crystallinity of the prepared  $\text{LiNiO}_2$  powders. This is why the intensity ratio of (003)/(104) peaks increases with the amount of adipic acid used in the synthesis of  $\text{LiNiO}_2$ . If the excessive amount of adipic acid is used in the synthetic reaction, however, a negative effect will appear because the temperature rises too high in a short period of time and the partial pressure of oxygen in the gas phase decreases owing to the increase of organic com-

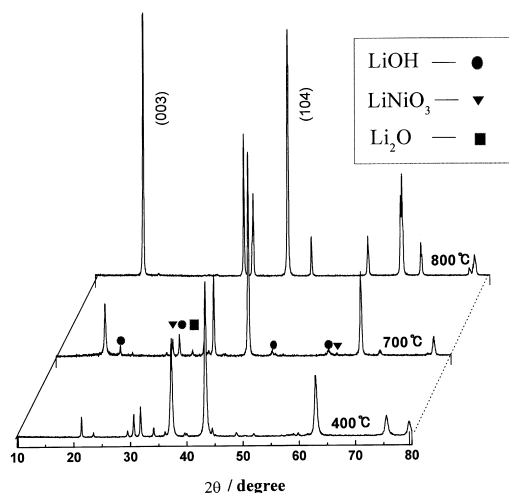


Fig. 4. X-ray diffraction patterns of  $\text{LiNiO}_2$  powders calcined at various temperatures in  $\text{O}_2$  when molar ratios of adipic acid to total metal ions was 1.5. The gel precursors were preheated at  $400^\circ\text{C}$  in air.

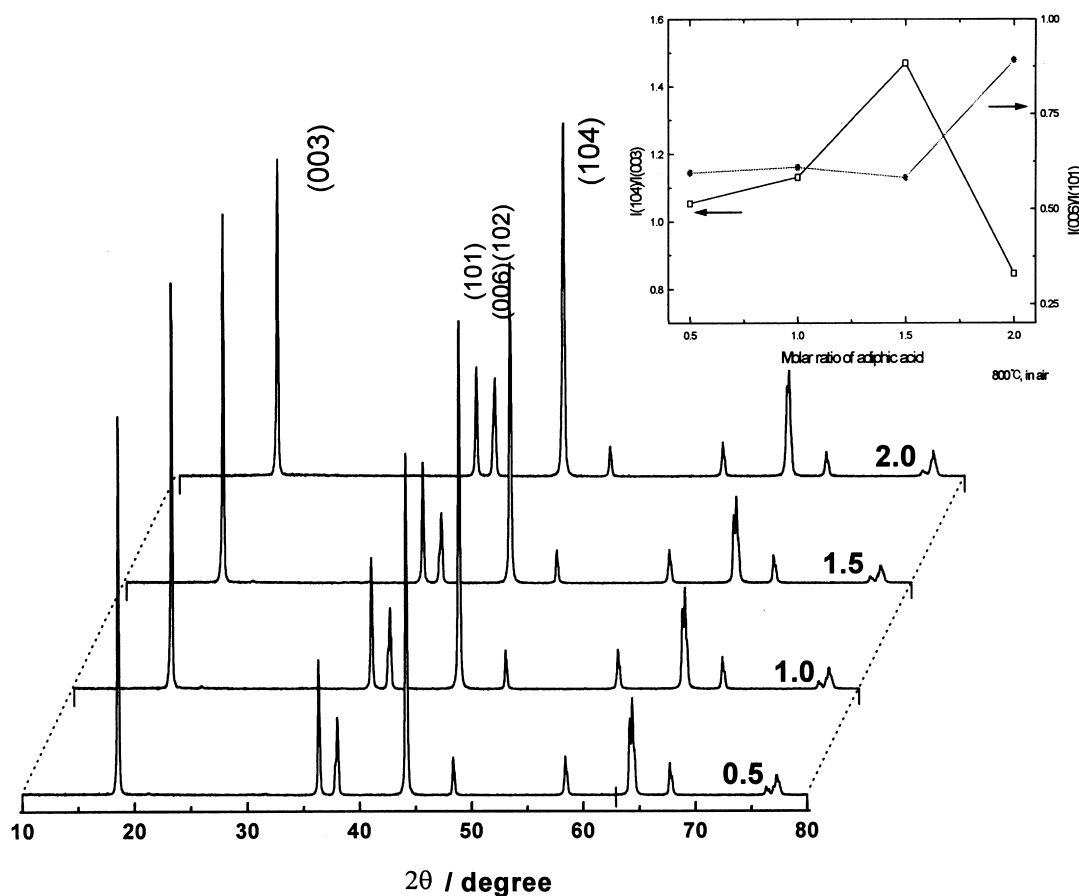


Fig. 5. X-ray diffraction patterns of  $\text{LiNiO}_2$  powders prepared at various molar ratios of adipic acid to total metal ions. The gel precursors were calcined at  $800^\circ\text{C}$  in air.

ponent gas produced during the decomposition of adipic acid. This explains the decrease of the intensity ratio of (003)/(104) peaks at the molar ratio of 2.0. On the other hand, the lowest intensity ratio of (006)/(101) peaks was observed at the molar ratio of 1.5. The intensity ratio of (006)/(101) peaks always varies in contrast with that of (003)/(104) as observed in Figs. 5–7. When the samples were prepared in  $\text{O}_2$ , however, the highest intensity ratio of (003) and (104) peaks of 1.67 is obtained at the molar ratio of adipic acid to total metal ions of 1.0 as shown in Fig. 6, which shows the formation of stoichiometric  $\text{LiNiO}_2$ . This means that the optimum molar ratio of adipic acid to total metal ions varies depending on the synthetic condition. Fig. 6 shows XRD patterns for the samples prepared as a function

of molar ratios of adipic acid to total metal ions at  $750^\circ\text{C}$  in  $\text{O}_2$ .

It has been reported that the deficiency of lithium ions in  $\text{LiNiO}_2$  is attributed to high vapor pressure of the lithium ions at high temperature ( $> 800^\circ\text{C}$ ) [11]. For the preparation of stoichiometric  $\text{LiNiO}_2$ , excessive lithium precursors should be used in the synthesis of  $\text{LiNiO}_2$ . Recently, some researchers have observed that the use of excessive lithium precursors was very effective to compensate the loss of lithium ion from  $\text{LiNiO}_2$  during the synthetic reaction [12]. In this work, gel-precursors were prepared with varying Li contents (1.0–1.05). Fig. 7 showed XRD patterns for  $\text{LiNiO}_2$  powders with various Li contents. XRD spectra show that the intensity ratio of (003) and (104) peaks decreases with increasing Li

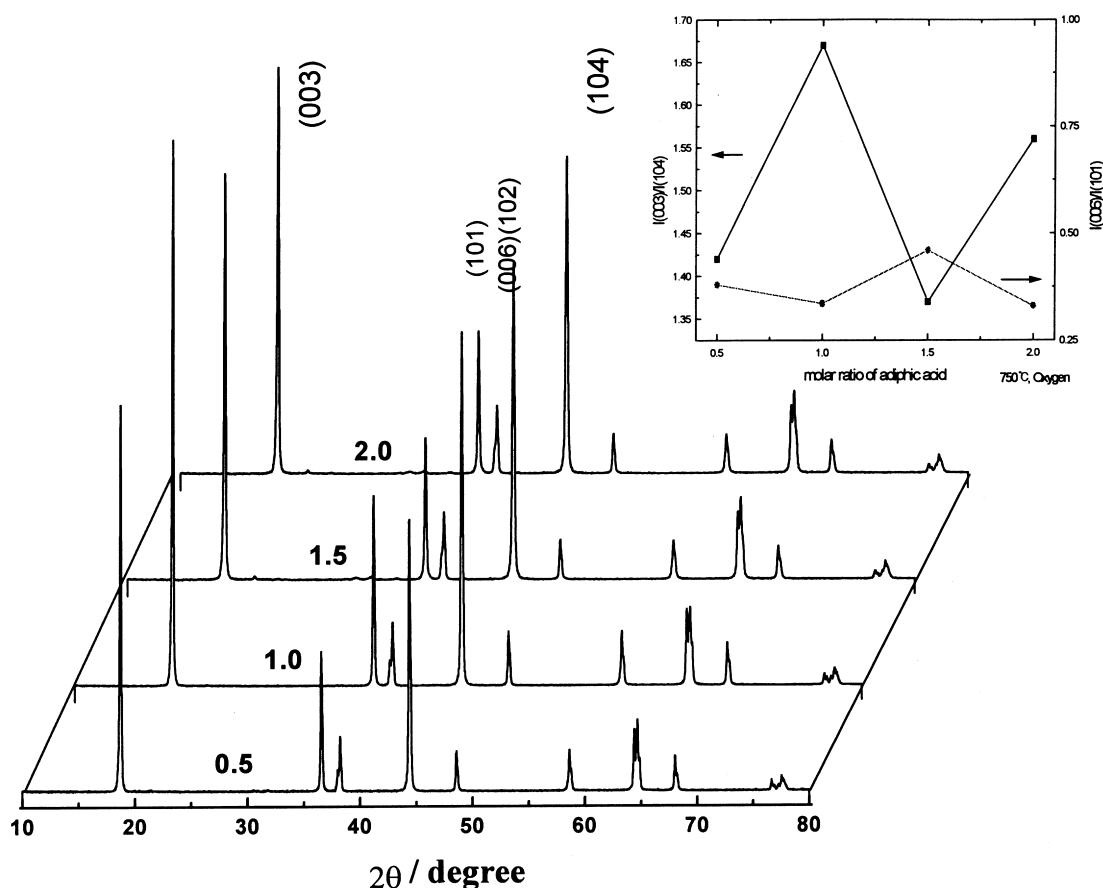


Fig. 6. X-ray diffraction patterns of  $\text{LiNiO}_2$  powders prepared at various molar ratios of adipic acid to total metal ions. The gel precursors were calcined at  $750^\circ\text{C}$  in  $\text{O}_2$ .

contents in  $\text{LiNiO}_2$ . The ratios of  $I(003)/I(104)$  peaks are 1.54 and 1.14 for 1.0 and 1.05 of Li contents, respectively. The peaks of various impurities such as  $\text{LiOH}$ ,  $\text{Li}_2\text{O}$  and  $\text{LiNO}_3$  are observed from the XRD patterns for the lithium contents of 1.03 and 1.05. This result suggests that  $\text{LiNiO}_2$  prepared at the lithium content of 1.0 may be stoichiometric and is assumed to show good electrochemical properties. We have concluded that highly crystalline  $\text{Li}_{1.0}\text{NiO}_2$  powders could be synthesized in oxygen stream at  $750^\circ\text{C}$  for 14 h when the molar ratio of adipic acid to total metal ions is 1.0.

Oxygen flow rate in the calcination process is another parameter to determine the quality of  $\text{LiNiO}_2$  for lithium secondary batteries. Sato et al. [13] suggested that the flow rates of  $20\text{--}100\text{ ml min}^{-1}$

were the best flow rate of oxygen to synthesize crystalline  $\text{LiNiO}_2$  by a solid-state reaction when the time of heat treatment was 24–68 h. The effect of oxygen flow rate on the quality of  $\text{LiNiO}_2$  was examined as a function of oxygen flow rate.  $\text{LiNiO}_2$  powders were decomposed at  $400^\circ\text{C}$  for 10 h and the molar ratio of adipic acid to total metal ions was 1.0. The sample was calcined at  $750^\circ\text{C}$  under various oxygen flow rates of  $5\text{--}100\text{ ml min}^{-1}$ . Although the results of XRD patterns for the synthesized  $\text{LiNiO}_2$  have not been shown in this paper, the full width at the half maximum (FWHM) of (003) and (104) peaks decreased slightly with increasing oxygen flow rate in the given range. This indicates that the increase of oxygen flow rate does not influence the properties of  $\text{LiNiO}_2$  powders. Sato et al. also

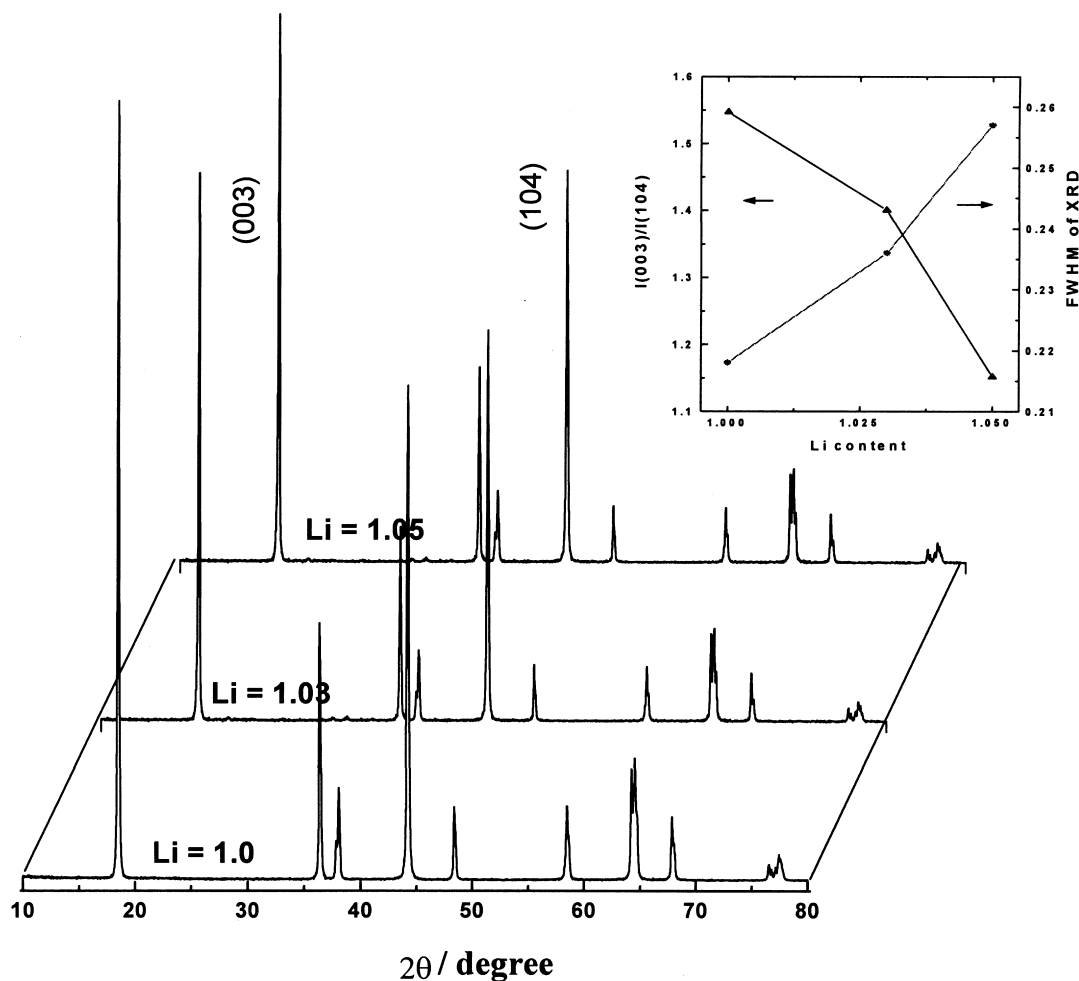


Fig. 7. X-ray diffraction patterns of  $\text{LiNiO}_2$  powders prepared at various Li contents. The gel precursors were calcined at  $800^\circ\text{C}$  in  $\text{O}_2$ .

reported that the crystallinity of  $\text{LiNiO}_2$  enhanced significantly with increasing the flow rate of oxygen [13]. In our synthetic system, however,  $5 \text{ ml min}^{-1}$  of oxygen flow rate was enough to synthesize the crystalline  $\text{LiNiO}_2$  powders. This partly proves that the sol–gel method is more effective for the synthesis of the crystalline  $\text{LiNiO}_2$ . Fig. 8 shows a XRD spectrum for  $\text{Li}_{1.0}\text{NiO}_2$  prepared at the optimum synthetic condition in this experiment;  $750^\circ\text{C}$  of calcination temperature, 14 h of calcination time, oxygen atmosphere, the molar ratio of adipic acid to total metal ions of 1.0, and  $5 \text{ ml min}^{-1}$  of the oxygen flow rate.

SEM was used to characterize the morphology of

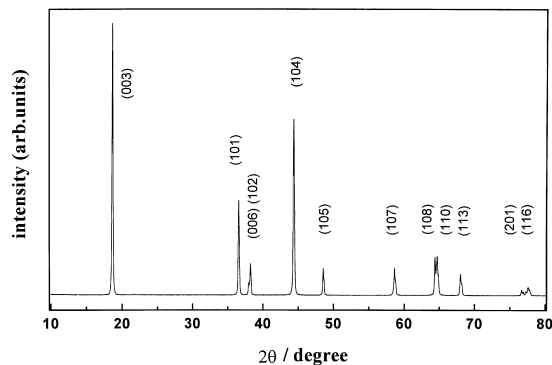


Fig. 8. X-ray diffraction pattern of  $\text{LiNiO}_2$  powders calcined at  $750^\circ\text{C}$ . The molar ratio of adipic acid to total metal ions was 1.0.

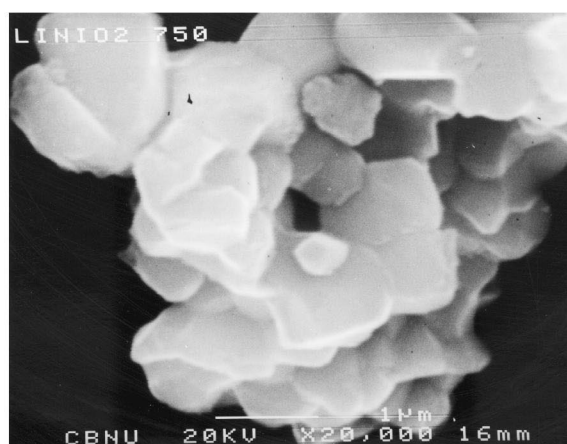
$\text{LiNiO}_2$  powders as a function of the calcination temperature. The gel precursors were prepared at the molar ratio of adipic acid to total metal ions of 1.0. Fig. 9 showed SEM micrographs for  $\text{LiNiO}_2$  powders calcined at different temperatures. The average particle size of the powders is about  $0.6\text{ }\mu\text{m}$  for the gel precursors calcined at  $400$  and  $700^\circ\text{C}$ , but increases suddenly to be about  $2\text{ }\mu\text{m}$  with a narrow particle-size distribution when the precursors were calcined at  $750$  and  $800^\circ\text{C}$ .

Fig. 10 is a plot of the discharge capacity vs the number of cycle for the  $\text{Li/PAN/LiNiO}_2$  fabricated using  $\text{LiNiO}_2$  powders synthesized at the best con-

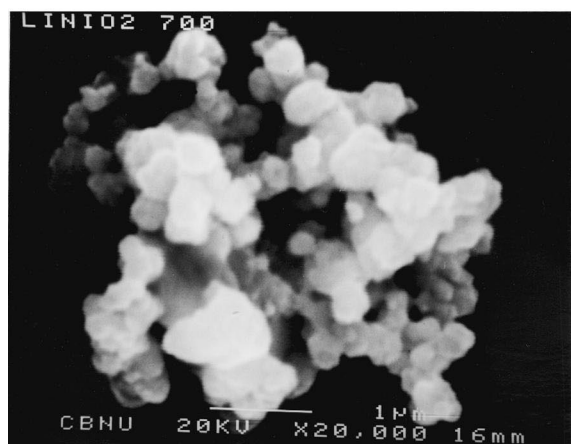
dition. The cell was cycled under a constant-charge capacity at a rate of  $0.05\text{ mAh cm}^{-2}$  between cut-off voltages of  $3.6\text{--}4.3\text{ V}$ . Although the cell delivers the initial capacity of  $158\text{ mAh g}^{-1}$ , but the capacity fading is accelerated very fast after 15 cycles. Many researchers have investigated the fading mechanism of the discharge capacity. Arai et al. [12] reported that the fast capacity fading of  $\text{Li}_{1-x}\text{NiO}_2$  is mainly attributed to the substitution of nickel ion in the lithium site which results in the disturbance of the diffusion of lithium ion in the charge/discharge processes. They proposed that the capacity fading can be reduced by limiting the first charging to



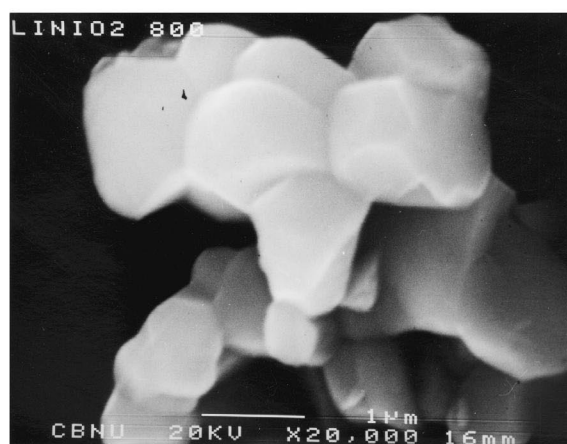
(a)



(c)



(b)



(d)

Fig. 9. Scanning electron micrographs of the  $\text{LiNiO}_2$  powders calcined at (a)  $400^\circ\text{C}$ , (b)  $700^\circ\text{C}$ , (c)  $750^\circ\text{C}$ , (d)  $800^\circ\text{C}$ .



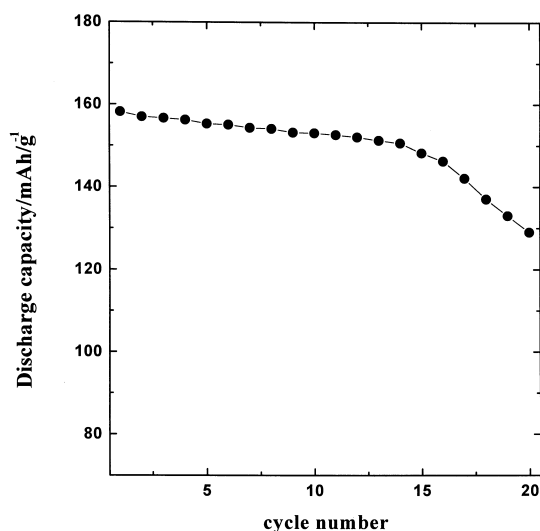


Fig. 10. A plot of specific discharge capacity vs number of cycles for the Li/PAN/  $\text{LiNiO}_2$  cells using  $\text{LiNiO}_2$  powders calcined at  $750^\circ\text{C}$ . The molar ratio of adipic acid to metal ions was 1.0. Cycling was carried out galvanostatically at constant charge/discharge current density of  $0.05 \text{ mA cm}^{-2}$  between 3.0 and 4.2 V.

$x = 0.8$ . Another possible reason for the fading was proposed to be due to the sublimation of lithium compounds in the process of calcination at high temperatures, which cause lithium deficiency and nickel substitution in the lithium site. At present, we suspect that the substitution of nickel ion in the lithium site might take place during the charge/discharge processes to deteriorate the reversibility of the electrode. In order to clarify the reason why the discharge capacity is faded so rapidly in our system, however, we believe further experiments are necessary in our future work.

#### 4. Conclusion

Stoichiometric  $\text{LiNiO}_2$  powders were synthesized by a sol–gel method using adipic acid as a chelating agent. The quality of the prepared samples were evaluated by measuring the intensity ratios of (003) and (104) peaks, and (101) and (006) as well as the degree of splitting of (108) and (110) peaks appeared on XRD spectrums. The crystallinity of  $\text{LiNiO}_2$  precalcined at  $300^\circ\text{C}$  was poor even the post-calcination was carried out at  $800^\circ\text{C}$ , while the

crystalline  $\text{LiNiO}_2$  was synthesized at  $400^\circ\text{C}$ . It was considered that adipic acid not only functions as a chelating agent but also accelerates the synthetic reaction of  $\text{LiNiO}_2$  with the evolution of large heat. When excessive lithium precursors were used for the preparation of  $\text{LiNiO}_2$ , various impurities such as  $\text{LiOH}$ ,  $\text{Li}_2\text{O}$  and  $\text{LiNO}_3$  were incorporated in  $\text{LiNiO}_2$  powders. The properties of  $\text{LiNiO}_2$  were very lightly influenced with  $\text{O}_2$  flow rate. The optimum synthetic condition of  $\text{LiNiO}_2$  was as follows; the calcination temperature of  $750^\circ\text{C}$ , calcination time of 14 h, oxygen atmosphere, the molar ratio of adipic acid to total metal ions of 1.0, and oxygen flow rate of  $5 \text{ ml min}^{-1}$ . The average particle size of  $\text{LiNiO}_2$  powders was about  $0.6 \mu\text{m}$  when calcined at 400 and  $700^\circ\text{C}$ , but increases suddenly to be about  $2 \mu\text{m}$  with a narrow particle-size distribution when the precursors were calcined at 750 and  $800^\circ\text{C}$ . The cell fabricated using  $\text{LiNiO}_2$  synthesized at the optimum condition delivered the initial capacity of  $158 \text{ mAh g}^{-1}$ , but the capacity fading was accelerated very fast after 15 cycles.

#### Acknowledgements

This work is supported by the academic research fund of Ministry of Education, Republic of South Korea.

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