

Electrochemical characteristics of $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ synthesized at 800 °C from the different combinations of carbonates and oxides

Myoung Youp Song^a, Ho Rim^b, Hye Ryoung Park^{c,*}

^aDivision of Advanced Materials Engineering, Hydrogen & Fuel Cell Research Center, Engineering Research Institute, Chonbuk National University, 567 Baekje-daero Deokjin-gu Jeonju, 561-756, Republic of Korea

^bASE Korea, 494 Munbal-dong Paju-si Gyeonggi-do, 413-790, Republic of Korea

^cSchool of Applied Chemical Engineering, Chonnam National University, 77 Yongbong-ro Buk-gu Gwangju, 500-757, Republic of Korea

Received 2 April 2013; accepted 9 April 2013

Available online 17 April 2013

Abstract

Cathode active materials with a composition of $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ were synthesized by a solid-state reaction method at 800 °C using Li_2CO_3 , NiO or NiCO_3 , and CoCO_3 or Co_3O_4 as the sources of Li, Ni, and Co, respectively. The electrochemical properties of the synthesized samples were then investigated. The structure of the synthesized $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ was analyzed, and the microstructures of the samples were observed. The curves of voltage vs. x in $\text{Li}_x\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_2$ for the first charge–discharge and the intercalated and deintercalated Li quantity Δx were studied. The $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ sample synthesized from Li_2CO_3 , NiCO_3 , and Co_3O_4 had the largest first discharge capacity (152 mAh/g), with a discharge capacity deterioration rate of 1.4 mAh/g/cycle.

© 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$; Solid-state reaction method; Various starting materials; Curve of voltage vs. x in $\text{Li}_x\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_2$; Discharge capacity

1. Introduction

Rapid development in portable electronic devices requires compact and light-weight batteries. Lithium secondary battery is one of the most interesting types of rechargeable battery. It has higher volumetric and gravimetric energy densities than other rechargeable batteries such as nickel–cadmium and nickel-metal hydride batteries. Lithium secondary battery has no memory effect, and only a slow self-discharge loss. Interest is also growing in using the lithium secondary battery for military, electric vehicle, and aerospace applications.

Materials which can intercalate and deintercalate Li ions are transition metal chalcogenides (TiS_2 , MoS_2 , and NbSe_3) and transition metal oxides (MnO_2 , V_6O_{13} , LiCoO_2 , LiNiO_2 , LiMnO_2 , and LiMn_2O_4).

Among these transition metal oxides, LiCoO_2 [1–5], LiNiO_2 [6–13], and LiMn_2O_4 [14–20] have been investigated by many researchers as cathode materials for lithium secondary batteries [21]. LiCoO_2 has a large diffusivity and a high operating voltage,

and it can be synthesized relatively easily. However, it has a disadvantage in that it contains an expensive element, Co. LiNiO_2 has a large discharge capacity [22], and is relatively excellent economically and environmentally. However, since Li and Ni have similar sizes ($\text{Li}^+ = 0.72 \text{ \AA}$ and $\text{Ni}^{2+} = 0.69 \text{ \AA}$), LiNiO_2 is usually obtained in non-stoichiometric compositions, $\text{Li}_{1-y}\text{Ni}_{1+y}\text{O}_2$ [23,24]. The Ni^{2+} ions in the lithium planes obstruct the movement of the Li^+ ions during intercalation and deintercalation [5,25].

The weaknesses of LiCoO_2 and LiNiO_2 were overcome by incorporating LiCoO_2 and LiNiO_2 phases into $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ compositions because the presence of cobalt stabilizes the structure in a strictly two-dimensional fashion, thus favoring good reversibility of the intercalation and deintercalation reactions [26–38]. Rougier et al. [26] reported that the stabilization of the two-dimensional character of the structure by cobalt substitution in LiNiO_2 is correlated with an increase in the cell performance, due to the decrease in the amount of extra nickel ions in the inter-slab space which impede the lithium diffusion. LiMn_2O_4 contains a relatively inexpensive element, Mn, and is environment-friendly, but its cycling performance is poor.

*Corresponding author. Tel.: +82 62 530 1885; fax: +82 62 530 1889.

E-mail address: hyrpark@naver.com (H.R. Park).

To synthesize $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ by the solid-state reaction method [26–30,32–34,37–40], different starting materials have been used by researchers. $\text{LiOH} \cdot \text{H}_2\text{O}$ or Li_2CO_3 , NiO or NiCO_3 , and Co_3O_4 or CoCO_3 have been used as starting materials by some researchers [37,38,40].

In this work, $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ cathode materials were synthesized by a solid-state reaction method at 800°C using Li_2CO_3 , NiO or NiCO_3 , and CoCO_3 or Co_3O_4 as the sources of Li, Ni, and Co, respectively. The electrochemical properties of the synthesized samples were then examined. The structure of the synthesized $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ was analyzed, and the microstructures of the samples were observed. The curves of voltage vs. x in $\text{Li}_x\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_2$ for the first charge–discharge and the intercalated and deintercalated Li quantity Δx were studied.

2. Experimental

Li_2CO_3 , NiO or NiCO_3 , and CoCO_3 or Co_3O_4 were used as starting materials in order to synthesize $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ by the solid-state reaction method. All the starting materials (with purities of 99.9%) were purchased from Aldrich Co.

Fig. 1 schematically shows the experimental procedure for the synthesis of $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ from Li_2CO_3 , NiO or NiCO_3 , and Co_3O_4 or CoCO_3 as the sources of Li, Ni, and Co, respectively, and the characterization of the synthesized samples. The mixture of the starting materials with the composition of $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ was sufficiently mixed and pelletized. The pellet was then heat-treated in air at 650°C for 20 h. It was then ground, mixed, pelletized, and calcined at 800°C for 20 h. Then, this pellet was cooled at a rate of $50^\circ\text{C}/\text{min}$, and then ground, mixed, and pelletized again. Finally, it was calcined again at 800°C for 20 h.

The phase identification of the synthesized samples was carried out by X-Ray Diffraction (XRD) analysis using $\text{Cu K}\alpha$ radiation (Mac-Science Co., Ltd.). The scanning rate was $16^\circ/\text{min}$, and the scanning range of the diffraction angle (2θ) was $10^\circ \leq 2\theta \leq 70^\circ$.

The morphologies of the samples were observed using a scanning electron microscope (SEM).

Electrochemical cells consisted of $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ as a positive electrode, Li foil as a negative electrode, and an electrolyte of 1 M LiPF_6 in a 1:1 (volume ratio) mixture of Ethylene Carbonate (EC) and Dimethyl Carbonate (DMC). Whatman glass-fiber was used as the separator. The cells were assembled in an argon-filled dry box. To fabricate the positive electrode, 89 wt% synthesized oxide, 10 wt% acetylene black, and 1 wt% Polytetrafluoroethylene (PTFE) binder were mixed in an agate mortar. By introducing Li metal, Whatman glass-fiber, the positive electrode, and the electrolyte, the cell was assembled. Fig. 2 shows a schematic diagram of the cell used in this work. The current-collectors were stainless-steel screws with a hole at the end to which a copper wire is connected. All the electrochemical tests were performed at room temperature with a potentiostatic/galvanostatic system (Mac-Pile system, Bio-Logic Co. Ltd.). The cells were cycled at a current density of $200 \mu\text{A}/\text{cm}^2$ in a voltage range of 3.2–4.3 V.

3. Results and discussion

The XRD patterns of the $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ and LiCoO_2 powders calcined at 800°C for 40 h using Li_2CO_3 , NiCO_3 , and CoCO_3 as starting materials are shown in Fig. 2. The peaks are identified as corresponding to those of the LiNiO_2 phase, which has $\alpha\text{-NaFeO}_2$ structure with a space group of $R\bar{3}m$. The fraction of each phase from the intensity ratios of the 003 and 104 peaks can be calculated since the 003 peak originates from the diffraction of only the $R\bar{3}m$ $\alpha\text{-NaFeO}_2$ structure while the 104 peak originates from the diffractions of both the $R\bar{3}m$ $\alpha\text{-NaFeO}_2$ and $\text{Fm}\bar{3}m$ NaCl structures. The value of the intensity ratio of the 003 and 104 peaks, I_{003}/I_{104} , for a completely stoichiometric composition LiNiO_2 was reported to be about 1.3 by Morales et al. [24]. Ohzuku et al. [39] reported that, as the intensity ratio of the 003 and 104 peaks increases, the degree of displacement of the nickel and lithium ions decreases. They also reported that electroactive LiNiO_2 showed a clear split of the (108) and (110) lines, which

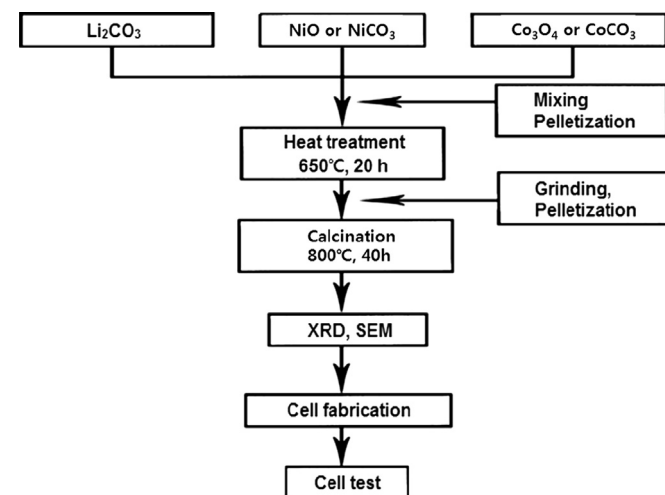


Fig. 1. Experimental procedure for $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ synthesis from Li_2CO_3 , NiO or NiCO_3 , and Co_3O_4 or CoCO_3 as the sources of Li, Ni, and Co, respectively, and the characterization of the synthesized $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$.

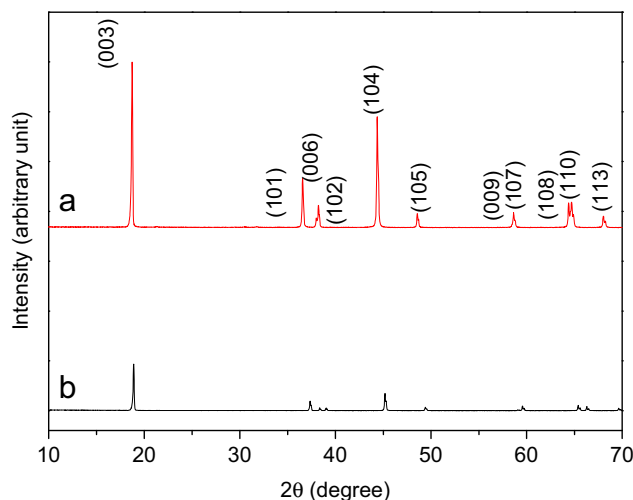


Fig. 2. X-ray ($\text{CuK}\alpha$) diffraction patterns of (a) $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ and (b) LiCoO_2 synthesized from Li_2CO_3 , NiCO_3 , and CoCO_3 .

appear in their XRD patterns at a diffraction angle near $2\theta=65^\circ$. The XRD pattern of the $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ powder synthesized using LiCO_3 , NiCO_3 , and CoCO_3 , exhibited in Fig. 2, shows that the intensity ratio of the 003 and 104 peaks is quite high and exhibits a clear split of the (108) and (110) lines.

Fig. 3 shows the SEM micrographs of the $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ synthesized at 800°C from combinations of starting materials: (a) Li_2CO_3 , NiO , and CoCO_3 , (b) Li_2CO_3 , NiCO_3 , and Co_3O_4 , (c) Li_2CO_3 , NiCO_3 , and CoCO_3 , and (d) Li_2CO_3 , NiO , and Co_3O_4 . The particles of sample (a), sample (c) and sample (d) are polygonal with quite flat surfaces. The particles of sample (d) are the largest, followed in order by sample (c) and sample (a). The particles of sample (b) are agglomerated.

The curves of voltage vs. x in $\text{Li}_x\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_2$ at a current density of $200\ \mu\text{A}/\text{cm}^2$ for the first charge–discharge of $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ synthesized at 800°C from combinations of starting materials are shown in Fig. 4, for: (a) Li_2CO_3 , NiO , and CoCO_3 , (b) Li_2CO_3 , NiCO_3 , and Co_3O_4 , (c) Li_2CO_3 ,

NiCO_3 , and CoCO_3 , and (d) Li_2CO_3 , NiO , and Co_3O_4 . Polarization is a change in the potentials for the deintercalation and intercalation of lithium atoms. The sample (d) has the smallest polarization, followed in order by sample (a), sample (b) and sample (c). The charge or discharge capacity is proportional to the value of Δx in $\text{Li}_x\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_2$. The sample (b) has the largest discharge capacity, followed in order by sample (d), sample (c) and sample (a).

Fig. 5 exhibits the curves of voltage vs. x in $\text{Li}_x\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_2$ for the first and second charge–discharge cycles for $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ synthesized at 800°C from Li_2CO_3 , NiCO_3 , and Co_3O_4 . The value of Δx for the second discharge is slightly smaller than that for the first discharge.

The variations of the discharge capacity with the number of cycles were investigated for two samples with relatively large first discharge capacities, a sample synthesized from Li_2CO_3 , NiCO_3 , and Co_3O_4 , and another sample synthesized from Li_2CO_3 , NiCO_3 , and CoCO_3 . A sample with the smallest first

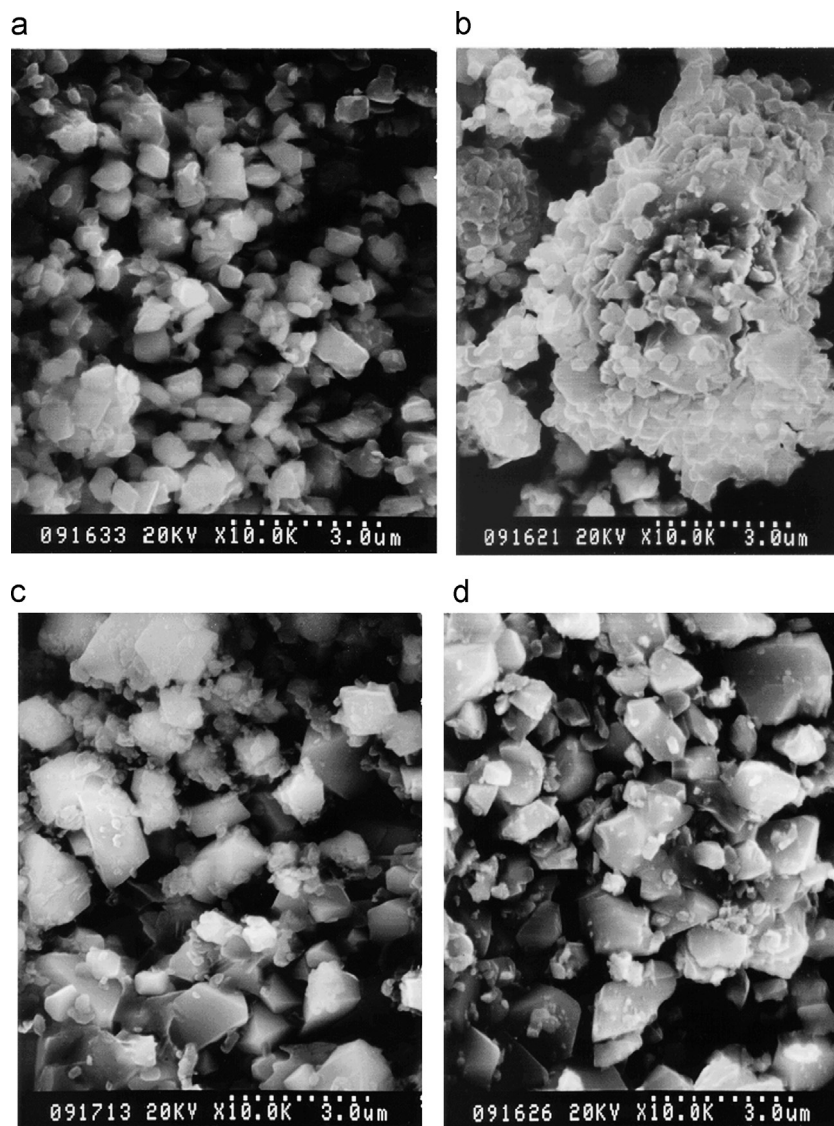


Fig. 3. SEM micrographs of the $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ synthesized at 800°C from combinations of starting materials: (a) Li_2CO_3 , NiO , and CoCO_3 , (b) Li_2CO_3 , NiCO_3 , and Co_3O_4 , (c) Li_2CO_3 , NiCO_3 , and CoCO_3 , and (d) Li_2CO_3 , NiO , and Co_3O_4 .

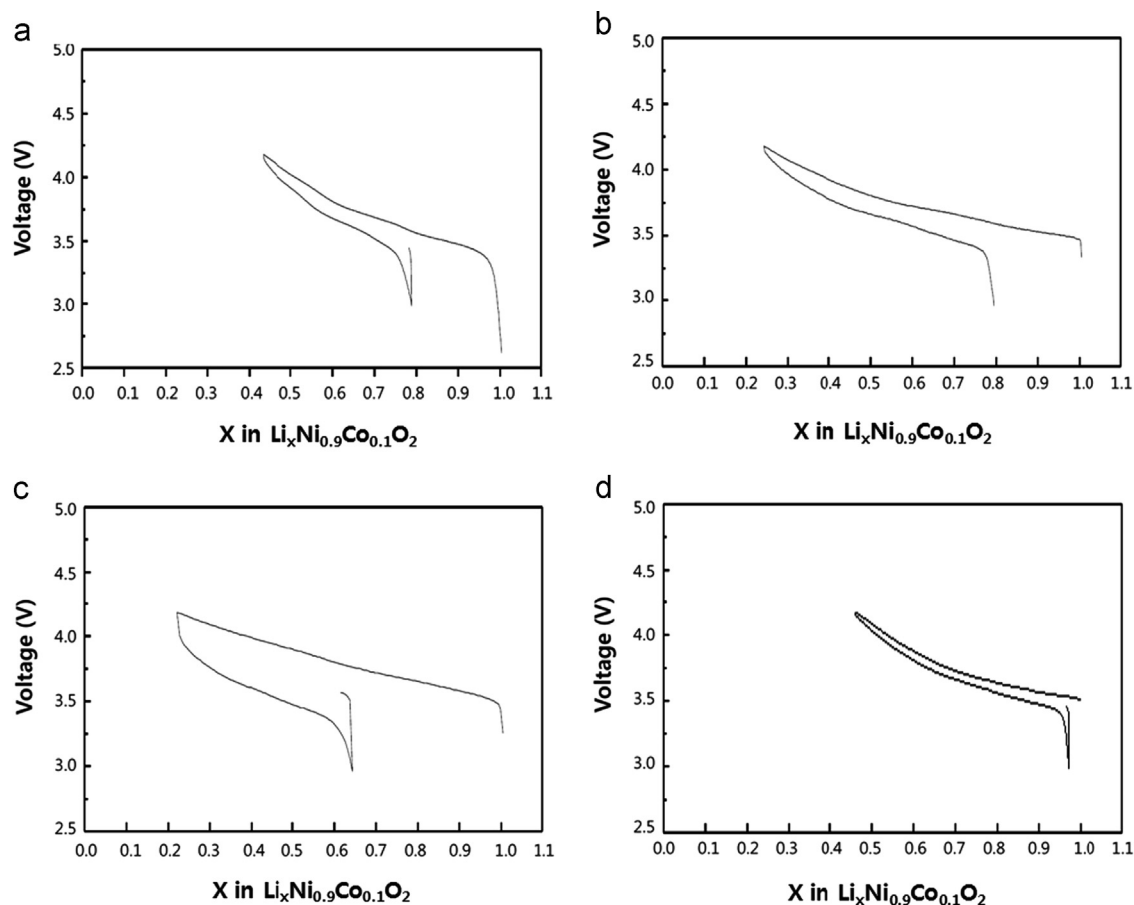


Fig. 4. Curves of voltage vs. x in $\text{Li}_x\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_2$ at a current density of $200 \mu\text{A}/\text{cm}^2$ for the first charge–discharge of $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ synthesized at 800°C from combinations of starting materials: (a) Li_2CO_3 , NiO , and CoCO_3 , (b) Li_2CO_3 , NiCO_3 , and Co_3O_4 , (c) Li_2CO_3 , NiCO_3 , and CoCO_3 , and (d) Li_2CO_3 , NiO , and Co_3O_4 .

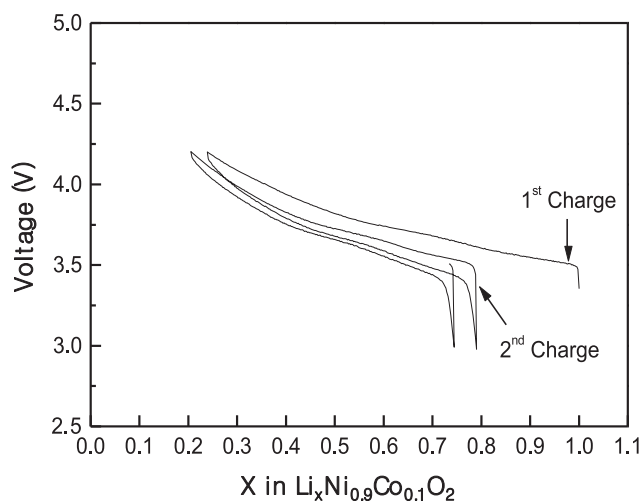


Fig. 5. Curves of voltage vs. x in $\text{Li}_x\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_2$ for the first and second charge–discharge cycles for $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ synthesized at 800°C from Li_2CO_3 , NiCO_3 , and Co_3O_4 .

discharge capacity synthesized from Li_2CO_3 , NiO , and CoCO_3 was also examined. The variations of the discharge capacity with the number of cycles for $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ synthesized at 800°C from (a) Li_2CO_3 , NiO , and CoCO_3 , (b) Li_2CO_3 ,

NiCO_3 , and Co_3O_4 , and (c) Li_2CO_3 , NiCO_3 , and CoCO_3 are shown in Fig. 6. The sample (b) has the largest first discharge capacity (152 mAh/g), followed in order by samples (c) (98 mAh/g), and (a) (146 mAh/g). The sample (b) has the best cycling performance, followed in order by the samples (c) and (a).

Fig. 7 shows the variations of the first-discharge capacity and the capacity deterioration rate of the $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ synthesized at 800°C with the following combinations of starting materials: (a) Li_2CO_3 , NiO , and CoCO_3 , (b) Li_2CO_3 , NiCO_3 , and Co_3O_4 , and (c) Li_2CO_3 , NiCO_3 , and CoCO_3 . The sample (b) has the largest first-discharge capacity, followed in order by sample (c) and sample (a). The sample (b) has the smallest capacity deterioration rate (1.4 mAh/g/cycle), followed in order by sample (c) (3.5 mAh/g/cycle), and sample (a) (6.2 mAh/g/cycle). The sample with a larger first-discharge capacity has a smaller capacity deterioration rate.

The curves of voltage vs. x in $\text{Li}_x\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_2$ at a current density of $200 \mu\text{A}/\text{cm}^2$ for the first charge–discharge of $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ in Figs. 4 and 5 show that, compared with the quantity of the deintercalated Li ions by the first charging, that of the intercalated Li ions by the first discharging is much smaller. During the first charging, Li ions deintercalate not only from stable 3b sites but also from unstable 3b sites. The destruction of

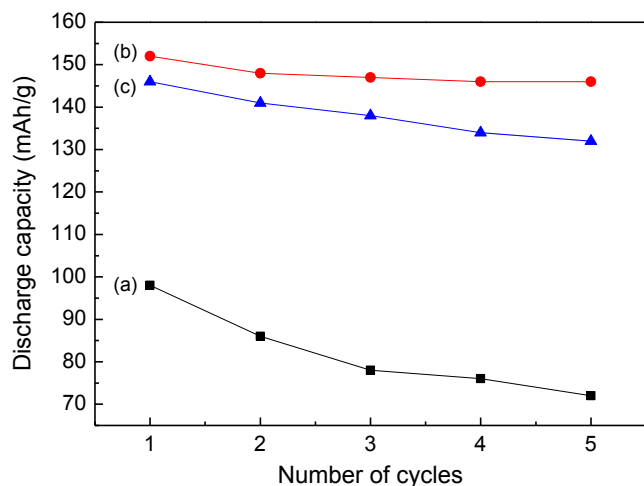


Fig. 6. Variations of the discharge capacity with the number of cycles for LiNi_{0.9}Co_{0.1}O₂ synthesized at 800 °C from (a) Li₂CO₃, NiO, and CoCO₃, (b) Li₂CO₃, NiCO₃, and Co₃O₄, and (c) Li₂CO₃, NiCO₃, and CoCO₃.

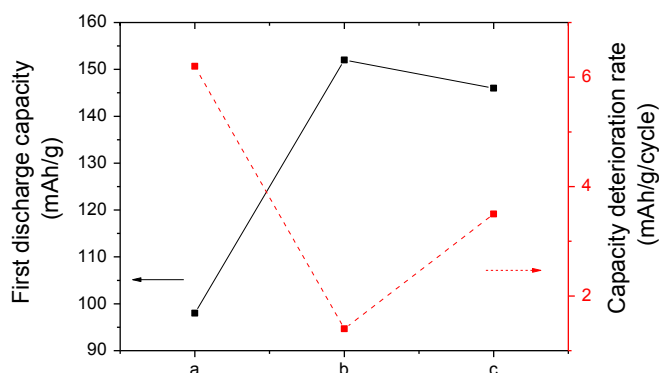


Fig. 7. Variations of the first discharge capacity and the capacity deterioration rate of the LiNi_{0.9}Co_{0.1}O₂ synthesized at 800 °C with the combination of starting materials: (a) Li₂CO₃, NiO, and CoCO₃, (b) Li₂CO₃, NiCO₃, and Co₃O₄, and (c) Li₂CO₃, NiCO₃, and CoCO₃.

the unstable 3b sites, after deintercalation from unstable 3b sites, is thought to lead to much smaller quantity of the Li ions intercalated by the first discharging than that of the Li ions deintercalated by the first charging.

In the curves of voltage vs. x in Li _{x} Ni_{0.9}Co_{0.1}O₂ at a current density of 200 μ A/cm² for the first charge–discharge cycle shown in Fig. 4(b) and for the first and second charge–discharge cycles shown in Fig. 5 of LiNi_{0.9}Co_{0.1}O₂ synthesized at 800 °C from Li₂CO₃, NiCO₃, and Co₃O₄, the charge–discharge curves exhibit quite long plateaus, where two phases co-exist [41]. During charging and discharging, LiNiO₂ goes reportedly through three or four phase transitions [39,42,43]. Song et al. [43] reported that $-dx/dV$ vs. V curves of LiNi_{1-y}Ti_yO₂ ($y=0.012$ and 0.025) for charging and discharging showed four peaks, revealing four phase transitions from hexagonal structure (H1) to monoclinic structure (M), from M to hexagonal structure (H2), from H2 to hexagonal structure (H2)+hexagonal structure (H3), and from H2+H3 to H3, or vice versa.

4. Conclusions

Cathode active materials with a composition of LiNi_{0.9}Co_{0.1}O₂ were synthesized by a solid-state reaction method at 800 °C using Li₂CO₃, NiO or NiCO₃, and CoCO₃ or Co₃O₄ as the sources of Li, Ni, and Co, respectively. The electrochemical properties of the synthesized samples were then investigated. The LiNi_{0.9}Co_{0.1}O₂ sample synthesized from Li₂CO₃, NiCO₃, and Co₃O₄ had the largest first discharge capacity (152 mAh/g), with a discharge capacity deterioration rate of 1.4 mAh/g/cycle. The curves of the voltage vs. x in Li _{x} Ni_{0.9}Co_{0.1}O₂ for the first charge–discharge of LiNi_{0.9}Co_{0.1}O₂ showed that after deintercalation from unstable 3b sites, the unstable 3b sites would be destroyed, leading to a smaller quantity of the Li ions intercalated by the first discharging than that of the Li ions deintercalated by the first charging. The sample with a larger first-discharge capacity had a smaller capacity deterioration rate.

References

- [1] K. Ozawa, Lithium-ion rechargeable batteries with LiCoO₂ and carbon electrodes: the LiCoO₂/C system, *Solid State Ionics* 69 (1994) 212–221.
- [2] R. Alcántara, P. Lavela, J.L. Tirado, R. Stoyanova, E. Zhecheva, Structure and electrochemical properties of boron-doped LiCoO₂, *Journal of Solid State Chemistry* 134 (1997) 265–273.
- [3] Z.S. Peng, C.R. Wan, C.Y. Jiang, Synthesis by sol–gel process and characterization of LiCoO₂ cathode materials, *Journal of Power Sources* 72 (1998) 215–220.
- [4] W.D. Yang, C.Y. Hsieh, H.J. Chuang, Y.S. Chen, Preparation and characterization of nanometric-sized LiCoO₂ cathode materials for lithium batteries by a novel sol–gel method, *Ceramics International* 36 (1) (2010) 135–140.
- [5] S.K. Kim, D.H. Yang, J.S. Sohn, Y.C. Jung, Resynthesis of LiCo_{1-x}Mn_xO₂ as a cathode material for lithium secondary batteries, *Metals and Materials International* 18 (2) (2012) 321–326.
- [6] J.R. Dahn, U. von Sacken, C.A. Michael, Structure and electrochemistry of Li_{1±y}NiO₂ and a new Li₂NiO₂ phase with the Ni(OH)₂ structure, *Solid State Ionics* 44 (1990) 87–97.
- [7] J.R. Dahn, U. von Sacken, M.W. Juskow, H. Al-Janaby, Rechargeable LiNiO₂/carbon cells, *Journal of the Electrochemical Society* 138 (1991) 2207–2212.
- [8] B.H. Kim, J.H. Kim, I.H. Kwon, M.Y. Song, Electrochemical properties of LiNiO₂ cathode material synthesized by the emulsion method, *Ceramics International* 33 (2007) 837–841.
- [9] H.U. Kim, D.R. Mumm, H.R. Park, M.Y. Song, Synthesis by a simple combustion method and electrochemical properties of LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂, *Electronic Materials Letters* 6 (3) (2010) 91–95.
- [10] S.H. Ju, J.H. Kim, Y.C. Kang, Electrochemical properties of LiNi_{0.8}Co_{0.2-x}Al_xO₂ ($0 \leq x \leq 0.1$) cathode particles prepared by spray pyrolysis from the spray solutions with and without organic additives, *Metals and Materials International* 16 (2) (2010) 299–303.
- [11] S.N. Kwon, J.H. Song, D.R. Mumm, Effects of cathode fabrication conditions and cycling on the electrochemical performance of LiNiO₂ synthesized by combustion and calcination, *Ceramics International* 37 (5) (2011) 1543–1548.
- [12] M.Y. Song, C.K. Park, H.R. Park, D.R. Mumm, Variations in the electrochemical properties of metallic elements-substituted LiNiO₂ cathodes with preparation and cathode fabrication conditions, *Electronic Materials Letters* 8 (1) (2012) 37–42.
- [13] M.Y. Song, D.R. Mumm, C.K. Park, H.R. Park, Cycling performances of LiNi_{1-y}M_yO₂ (M=Ni, Ga, Al and/or Ti) synthesized by wet milling and solid-state method, *Metals and Materials International* 18 (3) (2012) 465–472.

- [14] J.M. Tarascon, E. Wang, F.K. Shokoohi, W.R. Mckinnon, S. Colson, The spinel phase of LiMn_2O_4 as a cathode in secondary lithium cells, *Journal of the Electrochemical Society* 138 (1991) 2859–2864.
- [15] A.R. Armstrong, P.G. Bruce, Synthesis of layered LiMnO_2 as an electrode for rechargeable lithium batteries, *Letters to Nature, Nature* 381 (1996) 499–500.
- [16] M.Y. Song, D.S. Ahn, On the capacity deterioration of Spinel phase LiMn_2O_4 with cycling around 4 V, *Solid State Ionics* 112 (1998) 21–24.
- [17] M.Y. Song, D.S. Ahn, H.R. Park, Capacity fading of spinel phase LiMn_2O_4 with cycling, *Journal of Power Sources* 83 (1999) 57–60.
- [18] D.S. Ahn, M.Y. Song, Variations of the electrochemical properties of LiMn_2O_4 with synthesis conditions, *Journal of the Electrochemical Society* 147 (3) (2000) 874–879.
- [19] H.J. Guo, Q.H. Li, X.H. Li, Z.X. Wang, W.J. Peng, Novel synthesis of LiMn_2O_4 with large tap density by oxidation of manganese powder, *Energy Conversion and Management* 52 (4) (2011) 2009–2014.
- [20] C. Wan, M. Cheng, D. Wu, Synthesis of spherical spinel LiMn_2O_4 with commercial manganese carbonate, *Powder Technology* 210 (1) (2011) 47–51.
- [21] J.W. Park, J.H. Yu, K.W. Kim, H.S. Ryu, J.H. Ahn, C.S. Jin, K.H. Shin, Y.C. Kim, H.J. Ahn, Surface morphology changes of lithium/sulfur battery using multi-walled carbon nanotube added sulfur electrode during cyclings, *Korean Journal of Metals and Materials* 49 (2) (2011) 174–179.
- [22] Y. Nishida, K. Nakane, T. Satoh, Synthesis and properties of gallium-doped LiNiO_2 as the cathode material for lithium secondary batteries, *Journal of Power Sources* 68 (1997) 561–564.
- [23] P. Barboux, J.M. Tarascon, F.K. Shokoohi, The use of acetates as precursors for the low-temperature synthesis of LiMn_2O_4 and LiCoO_2 intercalation compounds, *Journal of Solid State Chemistry* 94 (1991) 185–196.
- [24] J. Morales, C. Perez-Vicente, J.L. Tirado, Cation distribution and chemical deintercalation of $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$, *Materials Research Bulletin* 25 (1990) 623–630.
- [25] B.J. Neudecker, R.A. Zuhre, B.S. Kwak, J.B. Bates, J.D. Robertson, Lithium manganese nickel oxides $\text{Li}_x(\text{Mn}_y\text{Ni}_{1-y})_{1-x}\text{O}_2$, *Journal of the Electrochemical Society* 145 (1998) 4148–4157.
- [26] A. Rougier, I. Saadoune, P. Gravereau, P. Willmann, C. Delmas, Effect of cobalt substitution on cationic distribution in $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ electrode materials, *Solid State Ionics* 90 (1996) 83–90.
- [27] C. Delmas, I. Saadoune, Electrochemical and physical properties of the $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ phases, *Solid State Ionics* 53–56 (1992) 370–375.
- [28] E. Zhecheva, R. Stoyanova, Stabilization of the layered crystal structure of LiNiO_2 by co-substitution, *Solid State Ionics* 66 (1993) 143–149.
- [29] C. Delmas, I. Saadoune, A. Rougier, The cycling properties of the $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ electrode, *Journal of Power Sources* 43–44 (1993) 595–602.
- [30] A. Ueda, T. Ohzuku, Solid-state redox reactions of $\text{LiNi}_{1/2}\text{Co}_{1/2}\text{O}_2$ (R3m) for 4 V secondary lithium cells, *Journal of the Electrochemical Society* 141 (1994) 2010–2014.
- [31] M. Menetrier, A. Rougier, C. Delmas, Cobalt segregation in the $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ solid solution: a preliminary ^7Li NMR study, *Solid State Communications* 90 (1994) 439–442.
- [32] R. Alcantara, J. Morales, J.L. Tirado, R. Stoyanova, E. Zhecheva, Structure and electrochemical properties of $\text{Li}_{1-x}(\text{Ni}_y\text{Co}_{1-y})_{1+x}\text{O}_2$ effect of chemical delithiation at 0 °C, *Journal of the Electrochemical Society* 142 (1995) 3997–4005.
- [33] B. Banov, J. Bourilkov, M. Mladenov, Cobalt stabilized layered lithium–nickel oxides, cathodes in lithium rechargeable cells, *Journal of Power Sources* 54 (1995) 268–270.
- [34] Y.M. Choi, S.I. Pyun, S.I. Moon, Effects of cation mixing on the electrochemical lithium intercalation reaction into porous $\text{Li}_{1-\delta}\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ electrodes, *Solid State Ionics* 89 (1996) 43–52.
- [35] S.J. Lee, J.K. Lee, D.W. Kim, H.K. Baik, S.M. Lee, Fabrication of thin film $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode for Li rechargeable microbattery, *Journal of the Electrochemical Society* 143 (1996) L268–L270.
- [36] D. Caurant, N. Baffier, B. Garcia, J.P. Pereira-Ramos, Synthesis by a soft chemistry route and characterization of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ ($0 \leq x \leq 1$) cathode materials, *Solid State Ionics* 91 (1996) 45–54.
- [37] H. Rim, H.R. Park, M.Y. Song, Synthesis of lithium $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ from lithium carbonate, nickel oxide and cobalt carbonate and their electrochemical properties, *Ceramics International* 38 (2012) 5987–5991.
- [38] H. Rim, H.R. Park, M.Y. Song, Electrochemical performance of cobalt-substituted lithium nickel oxides synthesized from lithium and nickel carbonates and cobalt oxide, *Ceramics International* 39 (2013) 917–923.
- [39] T. Ohzuku, A. Ueda, M. Nagayama, Electrochemistry and structural chemistry of LiNiO_2 (R3m) for 4 V secondary lithium cells, *Journal of the Electrochemical Society* 140 (1993) 1862–1870.
- [40] M.Y. Song, H. Rim, E. Bang, Electrochemical properties of cathode materials $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ synthesized using various starting materials, *Journal of Applied Electrochemistry* 34 (2004) 383–389.
- [41] W. Li, J.N. Reimers, J.R. Dahn, In situ x-ray diffraction and electrochemical studies of $\text{Li}_{1-x}\text{NiO}_2$, *Solid State Ionics* 67 (1993) 123–130.
- [42] H. Arai, S. Okada, H. Ohtsuka, M. Ichimura, J. Yamaki, Characterization and cathode performance of $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ prepared with the excess lithium method, *Solid State Ionics* 80 (1995) 261–269.
- [43] M.Y. Song, D.S. Lee, H.R. Park, Electrochemical properties of $\text{LiNi}_{1-y}\text{Ti}_y\text{O}_2$ and $\text{LiNi}_{0.975}\text{M}_{0.025}\text{O}_2$ (M=Zn, Al, and Ti) synthesized by the solid-state reaction method, *Materials Research Bulletin* 47 (2012) 1021–1027.