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Synthesis of lithium $LiNi_{1-y}Co_yO_2$ from lithium carbonate, nickel oxide and cobalt carbonate and their electrochemical properties

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Abstract

$LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) were synthesized by solid state reaction method at 800 °C and 850 °C from Li_2CO_3, NiO and $CoCO_3$ as starting materials. The electrochemical properties of the synthesized $LiNi_{1-y}Co_yO_2$ were investigated. As the content of Co decreases, particle size decreases rapidly and particle size gets more homogeneous. When the particle size is compared at the same composition, the particles synthesized at 850 °C are larger than those synthesized at 800 °C. Among $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) synthesized at 850 °C, $LiNi_{0.7}Co_{0.3}O_2$ has the largest intercalated and deintercalated Li quantity Δx at the first charge–discharge cycle, followed in order by $LiNi_{0.9}Co_{0.1}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$. $LiNi_{0.7}Co_{0.3}O_2$ synthesized at 850 °C has the largest first discharge capacity (142 mAh/g), followed in order by $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C (113 mAh/g), and $LiNi_{0.5}Co_{0.5}O_2$ synthesized at 800 °C (109 mAh/g).

Keywords: $LiNi_{1-y}Co_yO_2$; Solid state reaction method; Voltage vs. x in $Li_xNi_{1-y}Co_yO_2$ curve; Discharge capacity

1. Introduction

$LiCoO_2$ [1–4], $LiNiO_2$ [5–13], and $LiMn_2O_4$ [14–20] have been studied by many researchers as cathode materials for lithium secondary batteries [21]. $LiMn_2O_4$ is relatively inexpensive and environment-friendly, but its cycling performance is poor. $LiCoO_2$ has a large diffusivity and a high operating voltage, and its preparation is easy. However, it has a disadvantage that it contains an expensive element, Co.

$LiNiO_2$ is a very promising cathode material since it has a large discharge capacity [22] and is relatively excellent from the viewpoints of economics and environment. However, due to the similarity of Li and Ni ionic sizes ($Li^+ = 0.72$ Å and $Ni^{2+} = 0.69$ Å), the $LiNiO_2$ is practically obtained in the non-stoichiometric compositions, $Li_{1-y}Ni_{1+y}O_2$ [23,24], and the Ni^{2+} ions in lithium planes obstruct the movement of the Li^+ ions during charge and discharge [25,26].

The shortcomings of $LiCoO_2$ and $LiNiO_2$ can be overcome by incorporating these phases into $LiNi_{1-y}Co_yO_2$ 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 [25,27–35]. Rougier et al. [25] 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. Kang et al. [35] investigated the structure and electrochemical properties of the $Li_xCo_yNi_{1-y}O_2$ ($y = 0.1$, 0.3, 0.5, 0.7 and 1.0) system synthesized by solid state reaction with various starting materials to optimize the characteristics and synthetic conditions of the $Li_xCo_yNi_{1-y}O_2$. The first discharge capacities of $Li_xCo_yNi_{1-y}O_2$ were 60–180 mAh/g depending on synthetic conditions.

In this work, $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) cathode materials were synthesized by solid state reaction method at different temperatures using Li_2CO_3, NiO and $CoCO_3$ as starting materials. The electrochemical properties of the synthesized samples were then investigated.

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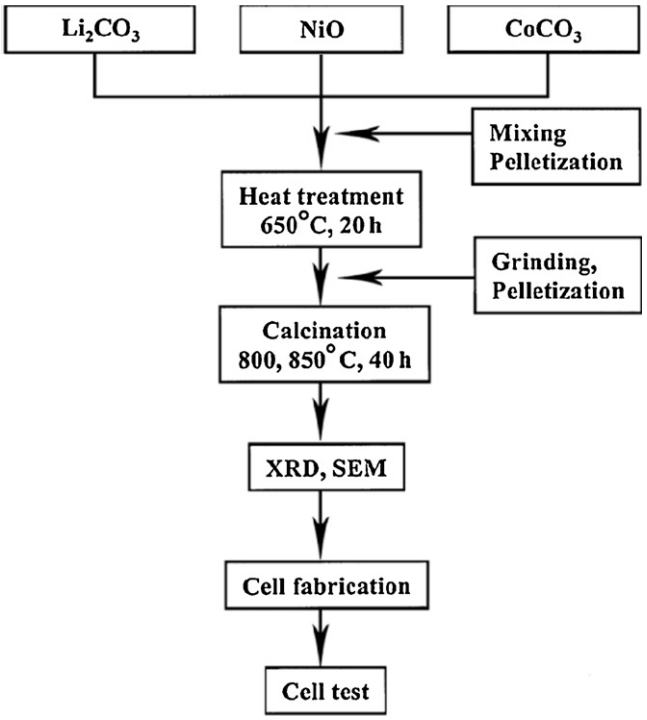

Fig. 1. Experimental procedure for $LiNi_{1-y}Co_yO_2$ synthesis from Li_2CO_3, NiO and $CoCO_3$ and characterization.

2. Experimental

Li_2CO_3, NiO and $CoCO_3$ were used as starting materials to synthesize $LiNi_{1-y}Co_yO_2$ by the solid-state reaction method. All the starting materials (with the purity 99.9%) were purchased from Aldrich Co.

The experimental procedure for $LiNi_{1-y}Co_yO_2$ synthesis from Li_2CO_3, NiO and $CoCO_3$ and characterization is given schematically in Fig. 1. The mixture of starting materials in the compositions of $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) was mixed sufficiently and pelletized. This pellet was heat treated in air at 650 °C for 20 h. It was then ground, mixed, pelletized and calcined at 800 °C or 850 °C for 20 h. This pellet was cooled at a cooling rate of 50 °C/min, ground, mixed and again pelletized. It was then calcined again at 800 °C or 850 °C for 20 h.

The phase identification of the synthesized samples was carried out by X-ray diffraction (XRD) analysis using Cu Kα radiation (Mac-Science Co., Ltd.). The scanning rate was 16°/min and the scanning range of diffraction angle (2θ) is $10^\circ \leq 2\theta \leq 70^\circ$. The morphologies of the samples were observed using a scanning electron microscope (SEM).

The electrochemical cells consisted of $LiNi_{1-y}Co_yO_2$ as a positive electrode, Li foil as a negative electrode, and electrolyte of 1 M $LiPF_6$ in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). A 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, positive electrode, and the electrolyte, the cell was assembled. 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 μA/cm^2 in a voltage range of 3.2–4.3 V.

3. Results and discussion

XRD patterns of $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) powders calcined at 800 °C or 850 °C for 40 h using $LiOH{\cdot}H_2O$, NiO and Co_3O_4 as starting materials were identified as corresponding to a α-$NaFeO_2$ structure with a space group of $R\bar{3}m$.

SEM micrographs of $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) synthesized from Li_2CO_3, NiO and $CoCO_3$ at 800 °C showed that the particle sizes were not homogeneous and $LiNi_{0.5}Co_{0.5}O_2$ had the largest particles. As the content of Co decreased, particle size decreased from $y = 0.5$ to $y = 0.3$ and increased from $y = 0.3$ to $y = 0.1$.

Fig. 2 exhibits SEM micrographs of $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) synthesized from Li_2CO_3, NiO and $CoCO_3$ at

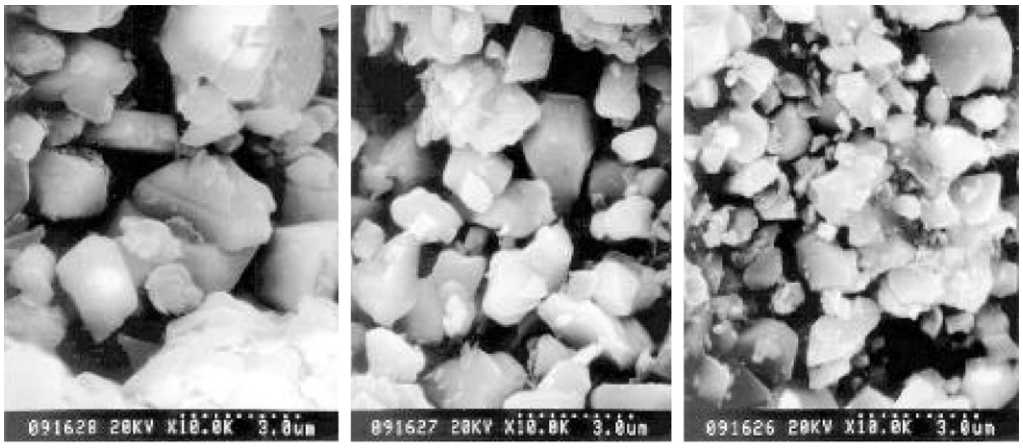

Fig. 2. SEM micrographs of $LiNi_{1-y}Co_yO_2$ synthesized from Li_2CO_3, NiO and $CoCO_3$ at 850 °C; (a) $y = 0.5$, (b) $y = 0.3$, and (c) $y = 0.1$.

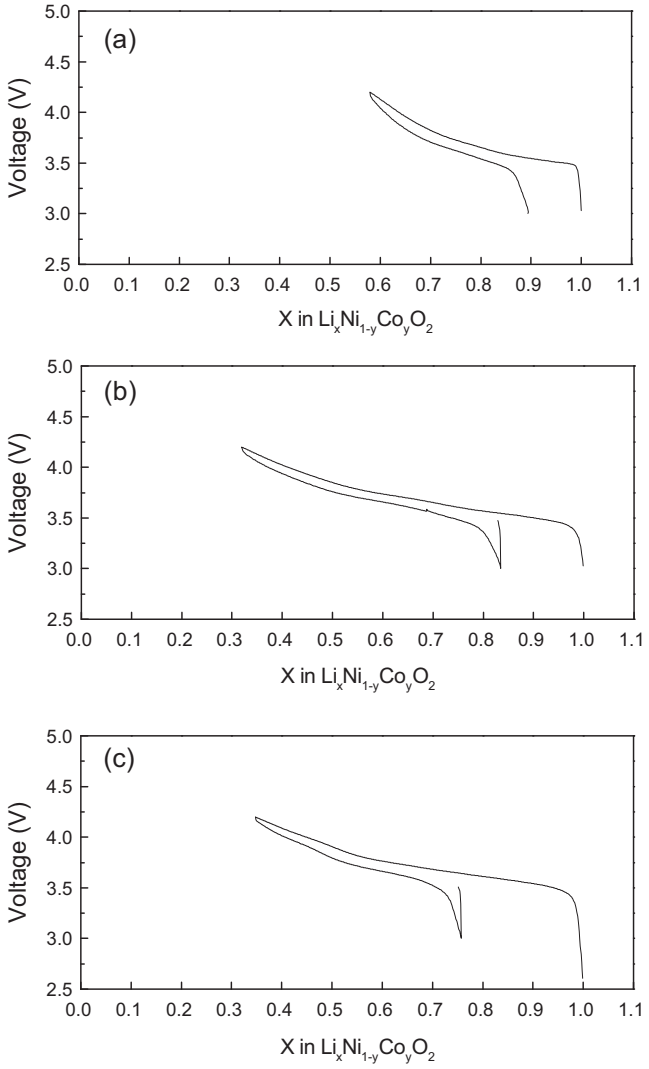

Fig. 3. Voltage vs. x in $Li_xNi_{1-y}Co_yO_2$ curves for the first charge–discharge at a current density of 200 μA/cm^2 of $LiNi_{1-y}Co_yO_2$ synthesized at 850 °C; (a) $y = 0.5$, (b) $y = 0.3$, and (c) $y = 0.1$.

850 °C. The particles have round surfaces. As the content of Co decreases, particle size decreases rapidly and particle size gets more homogeneous. When the particle size is compared at the same composition, the particles synthesized at 850 °C were larger than those synthesized at 800 °C.

Voltage vs. x in $Li_xNi_{1-y}Co_yO_2$ curves at a current density of 200 μA/cm^2 for the first charge–discharge of $LiNi_{1-y}Co_yO_2$ synthesized at 850 °C are shown in Fig. 3. The curves exhibit small polarizations, which are the changes in potentials for deintercalation and intercalation of lithium atoms. First charge–discharge curves of $LiNi_{0.7}Co_{0.3}O_2$ exhibit quite long plateaus. Among $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) synthesized at 850 °C, $LiNi_{0.7}Co_{0.3}O_2$ has the largest intercalated and deintercalated Li quantity Δx, followed in order by $LiNi_{0.9}Co_{0.1}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$.

Fig. 4 presents voltage vs. x in $Li_xNi_{1-y}Co_yO_2$ curves for the first and second charge–discharge of $LiNi_{0.7}Co_{0.3}O_2$ synthesized at 800 °C and 850 °C. The $LiNi_{0.7}Co_{0.3}O_2$ synthesized at 850 °C shows a larger value of Δx than that of the $LiNi_{0.7}Co_{0.3}O_2$ synthesized at 800 °C.

First charge capacities at a current density of 200 μA/cm^2 in the voltage range of 3.0–4.3 V for $LiNi_{1-y}Co_yO_2$ synthesized at 800 °C and at 850 °C are shown in Fig. 5. $LiNi_{0.7}Co_{0.3}O_2$ synthesized at 850 °C has the largest first discharge capacity, followed in order by $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C, $LiNi_{0.5}Co_{0.5}O_2$ synthesized at 800 °C, $LiNi_{0.7}Co_{0.3}O_2$ synthesized at 800 °C, $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 800 °C, and $LiNi_{0.5}Co_{0.5}O_2$ synthesized at 850 °C.

Fig. 6 presents the variation of the first charge capacity with the value of y for $LiNi_{1-y}Co_yO_2$ synthesized at 800 °C and 850 °C. $LiNi_{0.7}Co_{0.3}O_2$ synthesized at 850 °C has the largest first discharge capacity (142 mAh/g), followed in order by $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C (113 mAh/g), $LiNi_{0.5}Co_{0.5}O_2$ synthesized at 800 °C (109 mAh/g), $LiNi_{0.7}Co_{0.3}O_2$ synthesized at 800 °C (103 mAh/g), $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 800 °C (98 mAh/g), and $LiNi_{0.5}Co_{0.5}O_2$ synthesized at 850 °C (95 mAh/g).

The variations of discharge capacity with number of cycles for $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) synthesized at 800 °C and for $LiNi_{1-y}Co_yO_2$ ($y = 0.3$ and 0.5) synthesized at 850 °C are shown in Fig. 7. $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C has the largest first discharge capacity (113 mAh/g), followed in order by $LiNi_{0.5}Co_{0.5}O_2$ synthesized at 800 °C (109 mAh/g), $LiNi_{0.7}Co_{0.3}O_2$ synthesized at 800 °C (103 mAh/g), $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 800 °C (98 mAh/g), and $LiNi_{0.5}Co_{0.5}O_2$

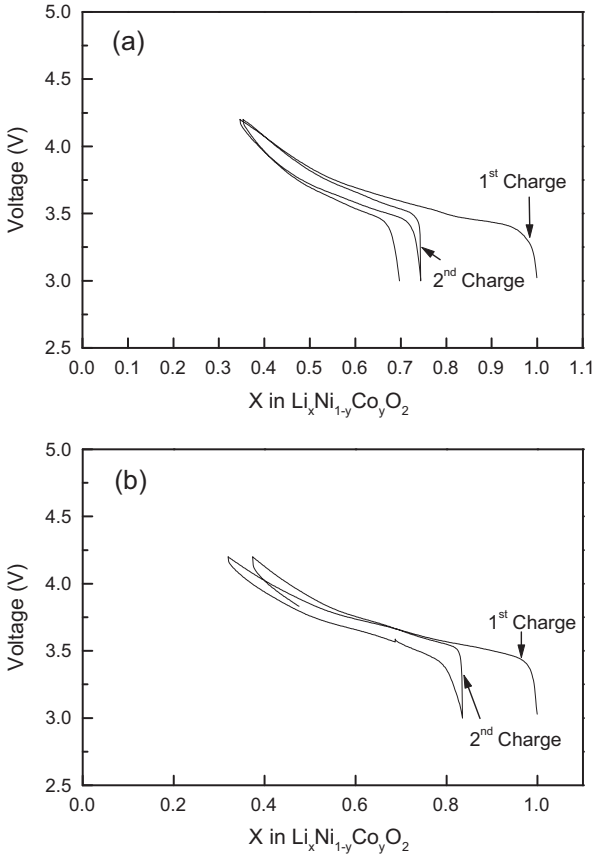

Fig. 4. Voltage vs. x in $Li_xNi_{1-y}Co_yO_2$ curves for the first and second charge–discharge of $LiNi_{0.7}Co_{0.3}O_2$ synthesized (a) at 800 °C, and (b) at 850 °C.

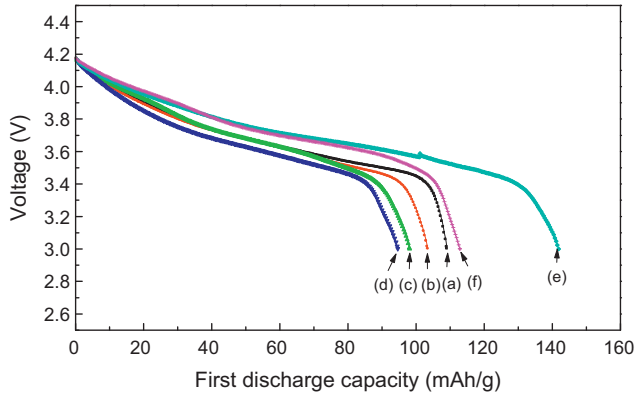

Fig. 5. First discharge capacity at a current density of 200 μA/cm^2 in the voltage range of 3.0–4.3 V for $LiNi_{1-y}Co_yO_2$ synthesized at 800 °C; (a) $y = 0.5$, (b) $y = 0.3$, and (c) $y = 0.1$, and at 850 °C; (d) $y = 0.5$, (e) $y = 0.3$, and (f) $y = 0.1$.

synthesized at 850 °C (95 mAh/g). $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) synthesized at 800 °C have very similar cycling behavior. $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) synthesized at 850 °C have better cycling performances than those synthesized at 800 °C. $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C with the largest discharge capacity has quite good cycling performance with the discharge capacity of 94 mAh/g at the fifth cycle.

The voltage vs. x in $Li_xNi_{1-y}Co_yO_2$ curves at a current density of 200 μA/cm^2 for the first charge–discharge of $LiNi_{1-y}Co_yO_2$ synthesized at 850 °C in Fig. 3 show that, as 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, which is revealed by the difference in Δx of the first charge and discharge curves, for all the samples. The lengths of plateaus in the charge and discharge curves are proportional to charge and discharge capacities. During the first charging, Li ions deintercalate not only from stable 3b sites but also from unstable 3b sites. After deintercalation from unstable 3b sites, the unstable 3b sites will be destroyed. This is considered to lead to smaller quantity of the intercalated Li ions by the first discharging than that of the deintercalated Li ions by the first charging.

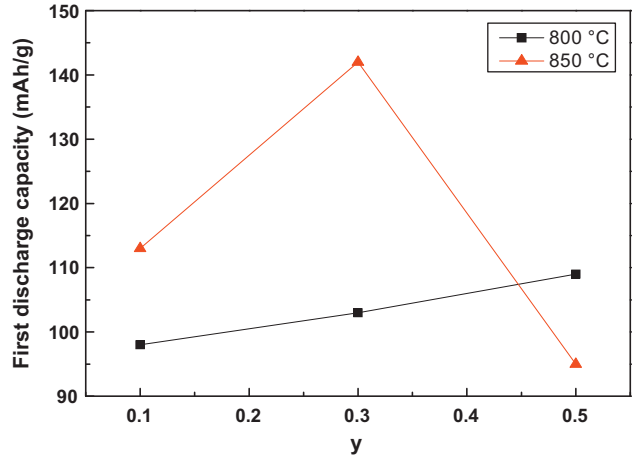

Fig. 6. Variations of the first charge capacity with value of y for $LiNi_{1-y}Co_yO_2$ synthesized at 800 °C and 850 °C.

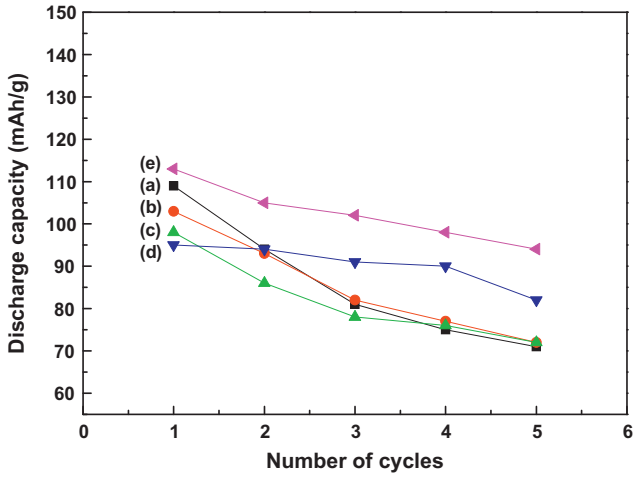

Fig. 7. Variations of discharge capacity with number of cycles for $LiNi_{1-y}Co_yO_2$ synthesized at 800 °C; (a) $y = 0.5$, (b) $y = 0.3$, and (c) $y = 0.1$, and at 850 °C; (d) $y = 0.5$, and (e) $y = 0.1$.

In the voltage vs. x in $Li_xNi_{1-y}Co_yO_2$ curves for the first and second charge–discharge of $LiNi_{0.7}Co_{0.3}O_2$ synthesized at 800 °C and 850 °C in Fig. 4, the charge–discharge curves exhibit quite long plateaus, where two phases co-exist [36]. Arai et al. [37] reported that, during charging and discharging, $LiNiO_2$ goes through three phase transitions; phase transitions from hexagonal structure (H1) to monoclinic structure (M), from monoclinic structure (M) to hexagonal structure (H2), and from hexagonal structure (H2) to hexagonal structure (H3) or vice versa. Ohzuku et al. [38] reported that, during charging and discharging, $LiNiO_2$ goes through four phase transitions; phase transitions from H1 to M, from M to H2, from H2 to hexagonal structures H2 + H3, and from H2 + H3 to H3 or vice versa. Song et al. [39] reported that $-dx/|dV|$ vs. V curves of $LiNi_{1-y}Ti_yO_2$ ($y = 0.012$ and 0.025) for charging and discharging showed four peaks, revealing the four phase transitions from H1 to M, from M to H2, from H2 to H2 + H3, and from H2 + H3 to H3 or vice versa.

4. Conclusions

$LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) were synthesized from Li_2CO_3, NiO and $CoCO_3$ as starting materials by solid state reaction method, in which mixtures with compositions of $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) were heat treated in air at 650 °C for 20 h, and then calcined at 800 °C or 850 °C for 40 h. As the content of Co decreases, particle size decreases rapidly and particle size gets more homogeneous. Among $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) synthesized at 850 °C, $LiNi_{0.7}Co_{0.3}O_2$ has the largest intercalated and deintercalated Li quantity Δx at the first charge–discharge cycle, followed in order by $LiNi_{0.9}Co_{0.1}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$. $LiNi_{0.7}Co_{0.3}O_2$ synthesized at 850 °C has the largest first discharge capacity (142 mAh/g), followed in order by $LiNi_{0.9}Co_{0.1}O_2$ synthesized at 850 °C (113 mAh/g), and $LiNi_{0.5}Co_{0.5}O_2$ synthesized at 800 °C (109 mAh/g). $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5)

synthesized at 850 °C have better cycling performances than those synthesized at 800 °C.

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