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Comparison of lithium nickel cobalt oxides synthesized from NiO, Co_3O_4, and $LiOH{\cdot}H_2O$ or Li_2CO_3 by solid-state reaction method

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Abstract

$LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) cathode materials were synthesized by the solid-state reaction method at different temperatures from $LiOH{\cdot}H_2O$, NiO and Co_3O_4 and from Li_2CO_3, NiO and Co_3O_4 as the starting materials. The physical and electrochemical properties of the synthesized samples were then compared. Among $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) synthesized for 40 h from $LiOH{\cdot}H_2O$, NiO and Co_3O_4, and from Li_2CO_3, NiO and Co_3O_4, $LiNi_{0.5}Co_{0.5}O_2$ synthesized from Li_2CO_3, NiO and Co_3O_4 at 800 °C has relatively large first discharge capacity and relatively good cycling performance. This sample is considered the best one with relatively good electrochemical properties.

Keywords: $LiNi_{1-y}Co_yO_2$; Solid-state reaction method; $LiOH{\cdot}H_2O$ or Li_2CO_3; Degree of displacement of the nickel and lithium ions; Discharge capacity; Capacity fading rate

1. Introduction

$LiCoO_2$ [1–3], $LiNiO_2$ [4–8], and $LiMn_2O_4$ [9–14] have been investigated as cathode materials for lithium secondary batteries [15]. $LiMn_2O_4$ is relatively cheap 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.

$LiNiO_2$ has a large discharge capacity [16] and is relatively excellent from the viewpoints of economics and environment. It is thus considered a very promising cathode material. However, since the sizes of Li and Ni ions ($Li^+ = 0.72$ Å and $Ni^{2+} = 0.69$ Å) are similar, the $LiNiO_2$ is practically obtained in the non-stoichiometric composition, $Li_{1-y}Ni_{1+y}O_2$ [17,18]. The Ni^{2+} ions in the lithium planes obstruct the movement of the Li^+ ions during charge and discharge [19,20].

Since the presence of cobalt stabilizes the structure in a strictly two-dimensional fashion, incorporation of $LiCoO_2$ and $LiNiO_2$ phases into $LiNi_{1-y}Co_yO_2$ favors good reversibility of the intercalation and deintercalation reactions [19,21–28]. Rougier et al. [19] 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.

In our previous work [29], we studied the electrochemical properties of the cathode materials, $LiNi_{1-y}Co_yO_2$, synthesized from $LiOH{\cdot}H_2O$ or Li_2CO_3, NiO or $NiCO_3$, and Co_3O_4 or $CoCO_3$ by the solid-state reaction method. The cathode materials, $LiNi_{1-y}Co_yO_2$, synthesized from $LiOH{\cdot}H_2O$, NiO and Co_3O_4, and from Li_2CO_3, NiO and Co_3O_4 showed relatively good electrochemical properties.

In this work, $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) cathode materials were synthesized by the solid-state reaction method at different temperatures from $LiOH{\cdot}H_2O$, NiO and Co_3O_4, and from Li_2CO_3, NiO and Co_3O_4 as the starting materials. The physical and electrochemical properties of the synthesized samples were then compared.

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2. Experimental

$LiOH{\cdot}H_2O$ (High Purity Chemical Laboratory Co., purity 99%), Li_2CO_3 (High Purity Chemical Laboratory Co., purity 99%), NiO (High Purity Chemical Laboratory Co., purity 99.9%) and Co_3O_4 (High Purity Chemical Laboratory Co., purity 99.9%) were used as the starting materials in order to synthesize $LiNi_{1-y}Co_yO_2$ by the solid-state reaction method.

The mixture of starting materials in the compositions $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) was mixed and pelletized. This pellet was heat-treated in air at 650 °C for 20 h, and was then ground, mixed, pelletized again and calcined at 750 °C, 800 °C or 850 °C for 20 h. This pellet was cooled at a cooling rate of 50 °C/min, ground, mixed and pelletized again. It was then calcined again at 750 °C, 800 °C or 850 °C for 20 h.

The phase identification of the synthesized samples was carried out by X-ray diffraction (XRD) analysis with Cu Kα radiation using a Rigaku type III/A X-ray diffractometer. The scanning rate was 4°/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) or a field emission scanning electron microscope (FE-SEM).

The electrochemical cells consisted of $LiNi_{1-y}Co_yO_2$ as a positive electrode, Li foil as a negative electrode, and an electrolyte [Purelyte (Samsung Chemicals Ltd.)] prepared by dissolving 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. 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. The cell was assembled in a glove box filled with argon. All of the electrochemical tests were performed at room temperature with a potentiostatic/galvanostatic system. The cells were cycled at a current density of 200 μA/cm^2 between 3.2 and 4.3 V.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of $LiNi_{1-y}Co_yO_2$ ($y = 0.1$. 0.3 and 0.5) powders synthesized at 800 °C for 20 h from $LiOH{\cdot}H_2O$, NiO and Co_3O_4. They are identified as corresponding to the α-$NaFeO_2$ structure of the rhombohedral system (space group; $R\bar{3}m$). The diffraction angles of the peaks corresponding to this structure increase as the content of Co increases. Impurity peaks appear at the diffraction angles $2\theta = 21^\circ$ and 32°. These peaks were identified as those of the Li_2CO_3 phase. As the Co content increases, the intensities of these peaks decrease.

The SEM micrographs of $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) synthesized at 800 °C for 20 h from $LiOH{\cdot}H_2O$, NiO and Co_3O_4 are shown in Fig. 2. The samples consist of large and small particles. Some large particles are agglomerated. As Co content increases, particles get larger.

Fig. 3 presents the SEM micrographs of $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) synthesized at 800 °C for 20 h from Li_2CO_3, NiO and Co_3O_4. The forms of particles are irregular and the particle sizes are not homogeneous. Some particles are agglomerated. These particles are a little larger than those synthesized from $LiOH{\cdot}H_2O$, NiO and Co_3O_4 in Fig. 2.

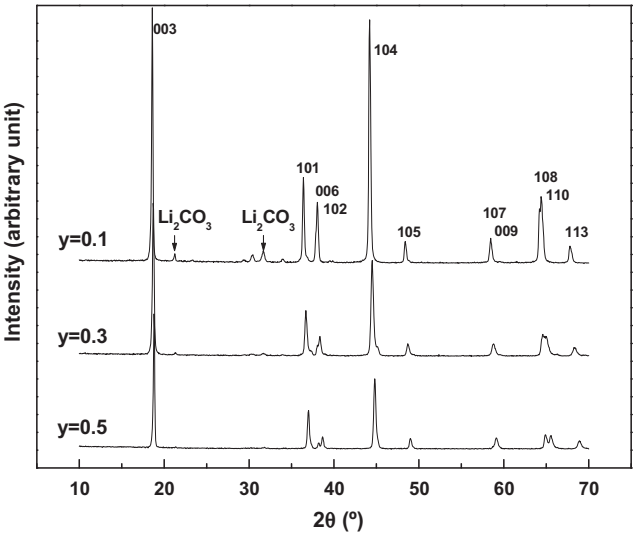

Fig. 1. XRD patterns of $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) powders synthesized at 800 °C for 20 h from $LiOH{\cdot}H_2O$, NiO and Co_3O_4.

The XRD patterns of $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) powders synthesized at 750 °C for 40 h from Li_2CO_3, NiO and Co_3O_4 are exhibited in Fig. 4. They are identified as corresponding to the α-$NaFeO_2$ structure of the rhombohedral system (space group; $R\bar{3}m$). The diffraction angles of the peaks corresponding to this structure increase as the content of Co increases. Li_2CO_3 peaks appear at the diffraction angles $2\theta = 21^\circ$ and 32°. As the Co content increases, the intensities of these peaks decrease.

Fig. 5 presents the variations of intensity ratio of 0 0 3 and 1 0 4 peaks, $I_{0\,0\,3}/I_{1\,0\,4}$, with y in $LiNi_{1-y}Co_yO_2$ synthesized at 800 °C for 20 h or 40 h using NiO, Co_3O_4, and $LiOH{\cdot}H_2O$ or Li_2CO_3 as starting materials. The intensity ratio, $I_{0\,0\,3}/I_{1\,0\,4}$, increases as the Co content increases. The 0 0 3 peak originates from the diffraction of only the $R\bar{3}m$ α-$NaFeO_2$ structure, while the 1 0 4 peak originates from the diffractions of both the $R\bar{3}m$ α-$NaFeO_2$ and $Fm\bar{3}m$ NaCl structures. Therefore, it is possible to calculate the fraction of each phase from the intensity ratio of the 0 0 3 and 1 0 4 peaks. Morales et al. [18] reported that the intensity ratio, $I_{0\,0\,3}/I_{1\,0\,4}$, of the completely stoichiometric composition $LiNiO_2$ is about 1.3. The $LiNi_{0.7}Co_{0.3}O_2$ specimen synthesized for 40 h from $LiOH{\cdot}H_2O$, NiO and Co_3O_4, and the $LiNi_{0.5}Co_{0.5}O_2$ synthesized for 20 h and $LiNi_{0.7}Co_{0.3}O_2$ synthesized for 40 h from Li_2CO_3, NiO and Co_3O_4 have $I_{0\,0\,3}/I_{1\,0\,4}$ values which are nearly 1.3. Ohzuku et al. [30] investigated the factors affecting the electrochemical reactivity of $LiNiO_2$. They reported that as the intensity ratio of the 0 0 3 and 1 0 4 peaks increases, the degree of displacement of the nickel and lithium ions decreases. The disordered region prevents the extension and reduction of the interlayer distance between the NiO_2 sheets, making sliding between the basal planes impossible. Consequently, the nickel ions in the lithium

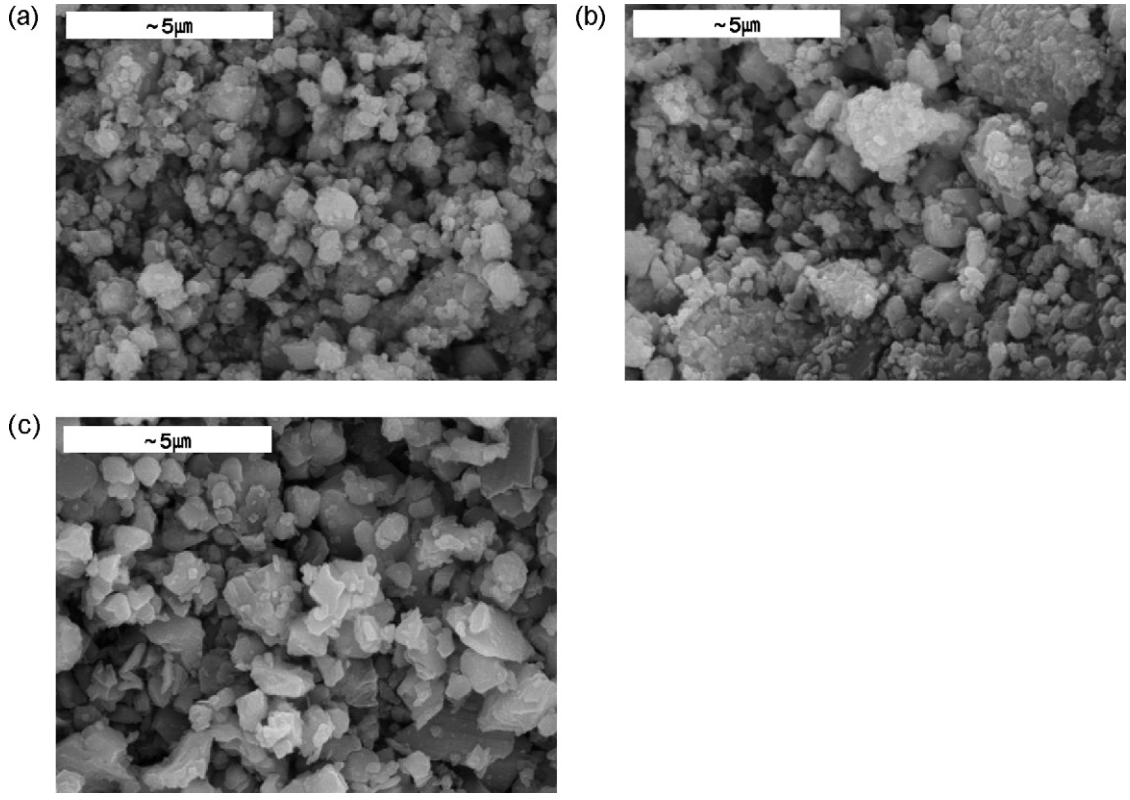

Fig. 2. SEM micrographs of $LiNi_{1-y}Co_yO_2$ synthesized at 800 °C for 20 h from $LiOH{\cdot}H_2O$, NiO and Co_3O_4: (a) $y = 0.1$, (b) $y = 0.3$ and (c) $y = 0.5$.

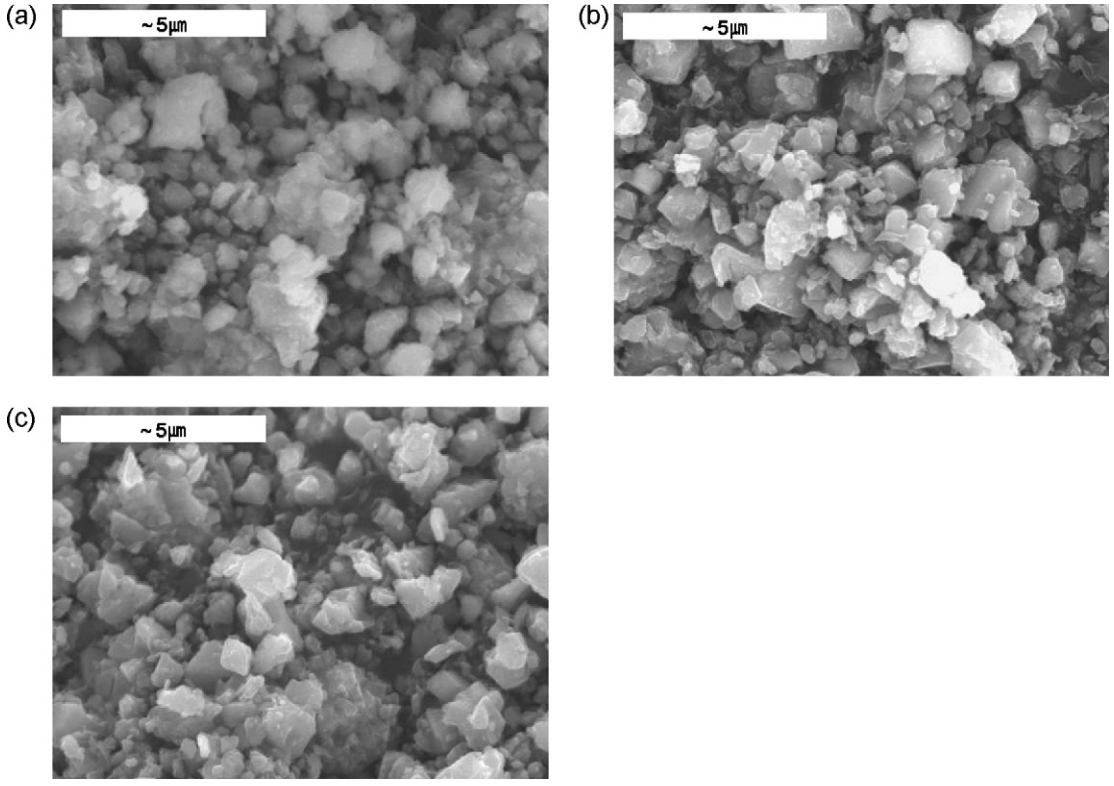

Fig. 3. SEM micrographs of $LiNi_{1-y}Co_yO_2$ synthesized at 800 °C for 20 h from Li_2CO_3, NiO and Co_3O_4: (a) $y = 0.1$, (b) $y = 0.3$ and (c) $y = 0.5$.

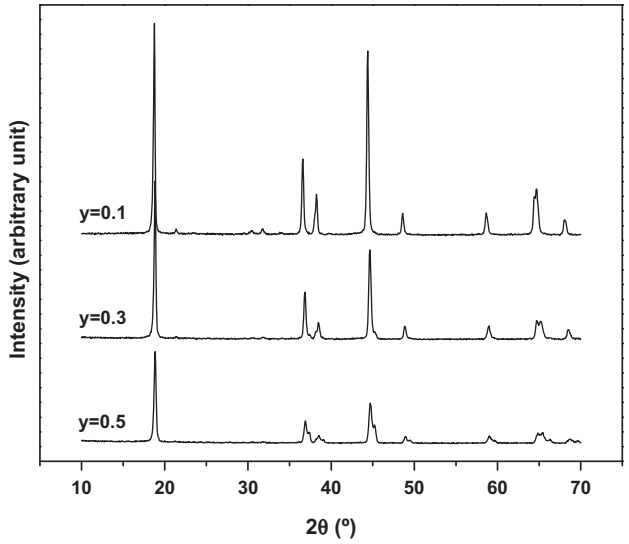

Fig. 4. XRD patterns of $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) powders synthesized at 750 °C for 40 h from Li_2CO_3, NiO and Co_3O_4.

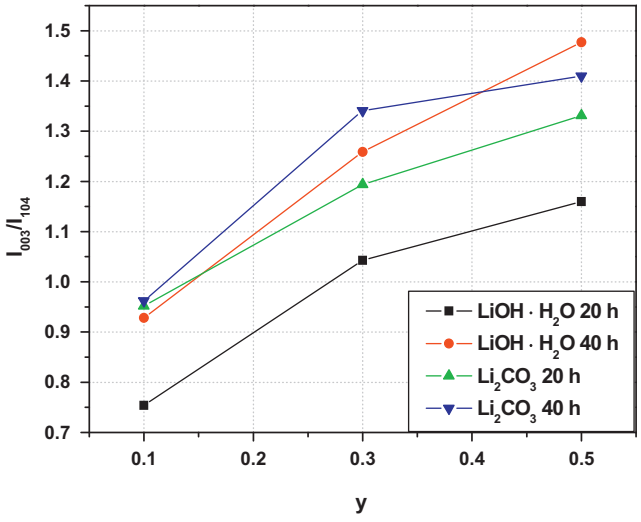

Fig. 5. Variations of intensity ratio of 0 0 3 and 1 0 4 peaks, $I_{0\,0\,3}/I_{1\,0\,4}$, with y in $LiNi_{1-y}Co_yO_2$ synthesized at 800 °C for 20 h or 40 h from NiO, Co_3O_4, and $LiOH{\cdot}H_2O$ or Li_2CO_3.

sheet including the near neighbors are inactive for the electrochemical reaction. Fig. 5 shows that the intensity ratio, $I_{0\,0\,3}/I_{1\,0\,4}$, increases as the Co content increases. This shows that the degree of displacement of the nickel and lithium ions decreases as the Co content increases.

Ohzuku et al. [30] also reported that electroactive $LiNiO_2$ showed a clear split of the (1 0 8) and (1 1 0) lines, which appear in their XRD patterns at the diffraction angle near $2\theta = 65°$ around. Fig. 1 shows that the splitting of the (1 0 8) and (1 1 0) lines becomes clearer as the Co content increases.

Dahn et al. [5] defined the intensity ratio, R, as the relative intensity of the (1 0 2, 0 0 6) peak near $2\theta = 38°$ as compared with that of the (1 0 1) peak near $2\theta = 36.5°$. Their results showed that the intensity ratio, R, increases as the unit cell volume increases. They also showed that the intensity ratio, R,

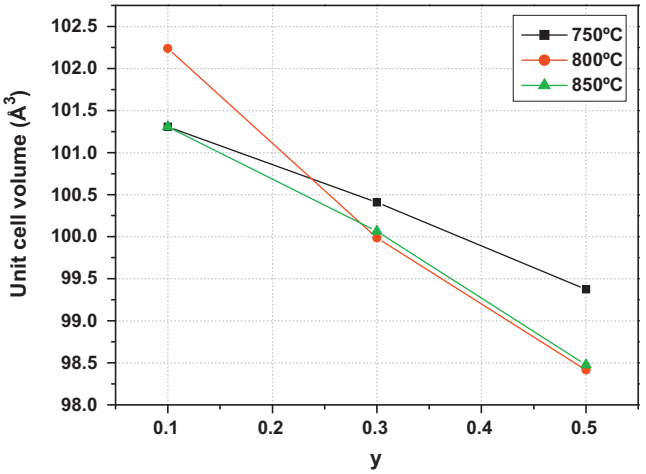

Fig. 6. Variations of unit cell volume with y in $LiNi_{1-y}Co_yO_2$ synthesized at 750, 800 and 850 °C for 40 h from $LiOH{\cdot}H_2O$, NiO and Co_3O_4.

increases rapidly as x decreases in $Li_xNi_{2-x}O_2$. This suggests that, as the unit cell volume increases, x decreases in $Li_xNi_{2-x}O_2$. $Li_xNi_{2-x}O_2$ can be expressed as $(Li_xNi_{1-x})NiO_2$. A decrease in x in $Li_xNi_{2-x}O_2$ corresponds to an increase in the degree of displacement of the nickel and lithium ions.

The variations of unit cell volume with y in $LiNi_{1-y}Co_yO_2$ (from starting materials $LiOH{\cdot}H_2O$, NiO and Co_3O_4) synthesized at 750, 800 and 850 °C for 40 h are shown in Fig. 6. The variations of unit cell volume with y in $LiNi_{1-y}Co_yO_2$ (from starting materials Li_2CO_3, NiO and Co_3O_4) synthesized at 750, 800 and 850 °C for 40 h are presented in Fig. 7. As the value of y increases, the unit cell volume decreases. This shows that as the Co content increases, the degree of displacement of the nickel and lithium ions decreases.

Fig. 8 presents the FE-SEM micrographs of $LiNi_{1-y}Co_yO_2$ ($y = 0.3$ and $y = 0.5$) synthesized at 800 °C for 40 h using $LiOH{\cdot}H_2O$, NiO and Co_3O_4 as starting materials. The samples in the shape of polyhedrons consist of small and large particles. $LiNi_{0.5}Co_{0.5}O_2$ has larger particles than $LiNi_{0.7}Co_{0.3}O_2$.

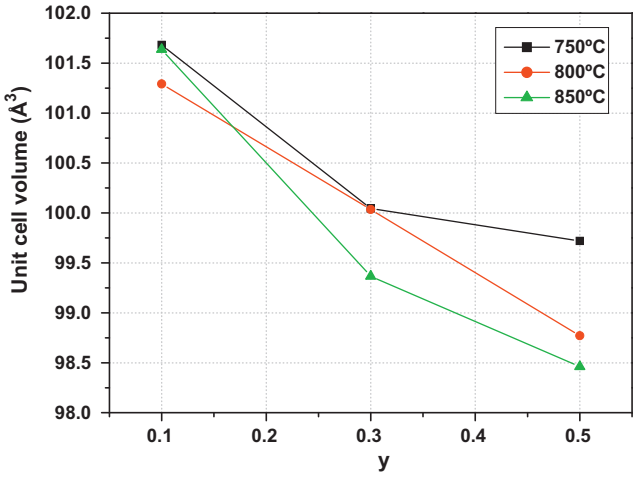

Fig. 7. Variations of unit cell volume with y in $LiNi_{1-y}Co_yO_2$ synthesized at 750, 800 and 850 °C for 40 h from Li_2CO_3, NiO and Co_3O_4.

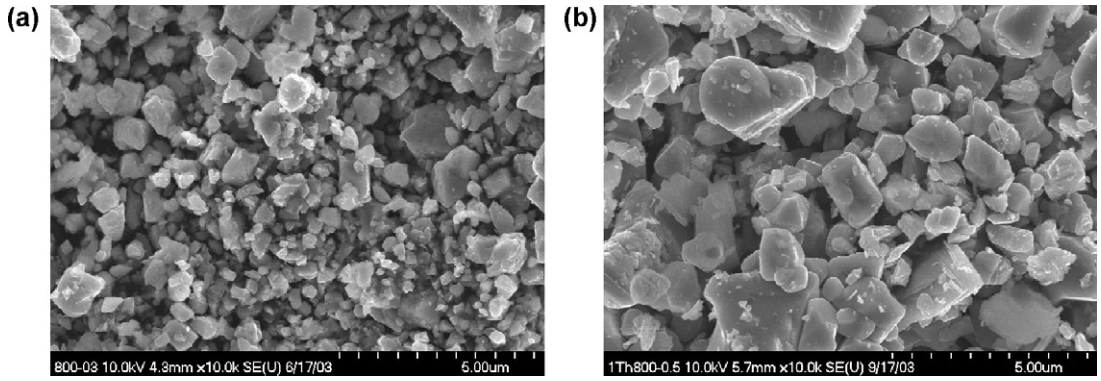

Fig. 8. FE-SEM micrographs of $LiNi_{1-y}Co_yO_2$ synthesized at 800 °C for 40 h from $LiOH{\cdot}H_2O$, NiO and Co_3O_4: (a) $y = 0.3$ and (b) $y = 0.5$.

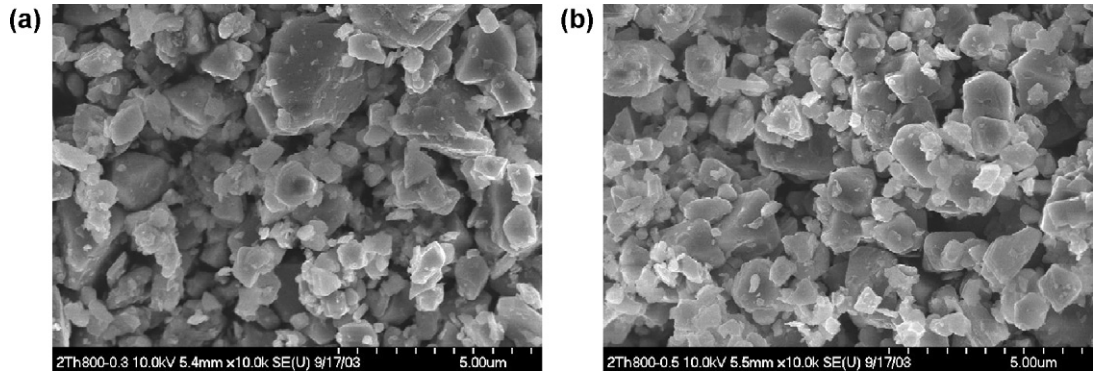

Fig. 9. FE-SEM micrographs of $LiNi_{1-y}Co_yO_2$ synthesized at 800 °C for 40 h from Li_2CO_3, NiO and Co_3O_4: (a) $y = 0.3$ and (b) $y = 0.5$.

The FE-SEM micrographs of $LiNi_{1-y}Co_yO_2$ ($y = 0.3$ and $y = 0.5$) synthesized at 800 °C for 40 h using Li_2CO_3, NiO and Co_3O_4 as starting materials are shown in Fig. 9. The samples in the shape of polyhedrons consist of small and large particles. $LiNi_{0.5}Co_{0.5}O_2$ has larger particles than $LiNi_{0.7}Co_{0.3}O_2$. The particles have quite flat surfaces.

The discharge capacity of $LiNi_{0.9}Co_{0.1}O_2$ was lower than those of $LiNi_{0.7}Co_{0.3}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$. Fig. 10 presents the variations of discharge capacity at 200 μA/cm^2 with the number of cycles for $LiNi_{1-y}Co_yO_2$ ($y = 0.3$ and 0.5) synthesized at 800 °C for 40 h using $LiOH{\cdot}H_2O$, NiO and Co_3O_4 as starting materials. The first discharge capacities of $LiNi_{0.5}Co_{0.5}O_2$ and $LiNi_{0.7}Co_{0.3}O_2$ are 174.3 and 145.5 mAh/g, respectively. The cycling performance of $LiNi_{0.7}Co_{0.3}O_2$ is better than $LiNi_{0.5}Co_{0.5}O_2$. Their discharge capacity fading rates of $LiNi_{0.5}Co_{0.5}O_2$ and $LiNi_{0.7}Co_{0.3}O_2$, which were

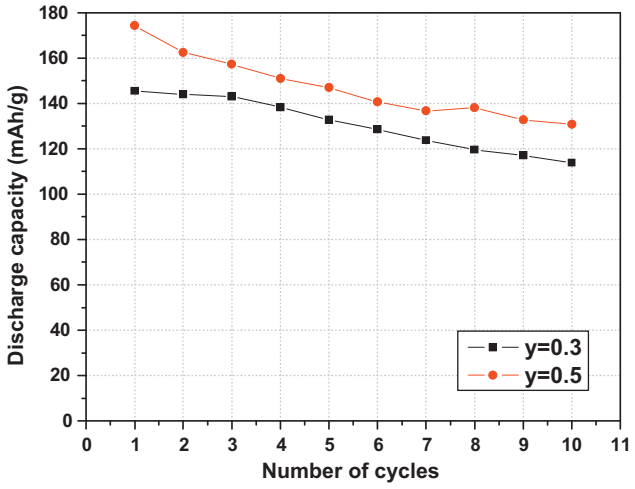

Fig. 10. Variations of discharge capacity at 200 μA/cm^2 with the number of cycles for $LiNi_{1-y}Co_yO_2$ ($y = 0.3$ and 0.5) synthesized at 800 °C for 40 h from $LiOH{\cdot}H_2O$, NiO and Co_3O_4.

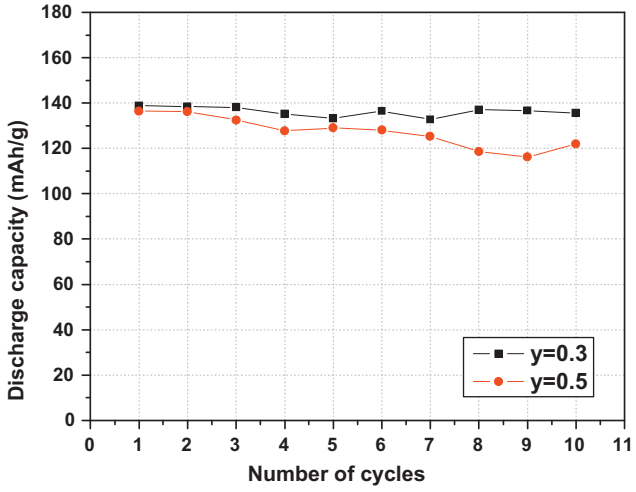

Fig. 11. Variations of discharge capacity at 200 μA/cm^2 with the number of cycles for $LiNi_{1-y}Co_yO_2$ ($y = 0.3$ and 0.5) synthesized at 750 °C for 40 h from Li_2CO_3, NiO and Co_3O_4.

Table 1
Comparison of $LiNi_{i1-y}Co_yO_2$ synthesized from NiO, Co_3O_4, and $LiOH{\cdot}H_2O$ or Li_2CO_3.

	$LiOH{\cdot}H_2O$, NiO and Co_3O_4	Li_2CO_3, NiO and Co_3O_4
Similarities	• α-$NaFeO_2$ structure of the rhombohedral system (space group; $R\bar{3}m$). • Li_2CO_3 peaks were observed at diffraction angles of 21° and 32° in the $LiNi_{0.9}Co_{0.1}O_2$ samples. • Intensities of Li_2CO_3 peaks decreased as the content of Co increased. • Particles grew as the synthesis time increased. • Particles grew as synthesis temperature increased in the same composition. • Particles grew a little larger as the content of Co increased at the same synthesis temperature.	
Differences	• The particle sizes of the samples from $LiOH{\cdot}H_2O$, NiO and Co_3O_4 were relatively bigger than those from Li_2CO_3, NiO and Co_3O_4 at all the temperatures and in all the compositions. • $LiNi_{0.5}Co_{0.5}O_2$ calcined at 800 °C had the largest first discharge capacity and $LiNi_{0.7}Co_{0.3}O_2$ calcined at 800 °C the best cycling performance.	• $LiNi_{0.7}Co_{0.3}O_2$ calcined at 800 °C had the largest first discharge capacity and $LiNi_{0.7}Co_{0.3}O_2$ calcined at 750 °C exhibited the best cycling performance.

obtained from $n = 1$ to $n = 10$, are 4.5 and 3.9 mAh/g/cycle, respectively.

The variations of discharge capacity at 200 μA/cm^2 with the number of cycles for $LiNi_{1-y}Co_yO_2$ ($y = 0.3$ and 0.5) synthesized at 750 °C for 40 h using Li_2CO_3, NiO and Co_3O_4 as starting materials are in Fig. 11. The first discharge capacities of $LiNi_{0.7}Co_{0.3}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$ are 138.8 and 136.5 mAh/g, respectively. The cycling performance of $LiNi_{0.7}Co_{0.3}O_2$ is better than $LiNi_{0.5}Co_{0.5}O_2$. The discharge capacities of $LiNi_{0.7}Co_{0.3}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$ at $n = 10$ are 135.6 and 122.0 mAh/g, respectively. Their discharge capacity fading rates are 0.3 and 2.1 mAh/g/cycle, respectively.

Fig. 12 shows the variations of discharge capacity at 200 μA/cm^2 with the number of cycles for $LiNi_{1-y}Co_yO_2$ ($y = 0.3$ and 0.5) synthesized at 800 °C for 40 h from Li_2CO_3, NiO and Co_3O_4. The first discharge capacities of $LiNi_{0.7}Co_{0.3}O_2$ and $LiNi_{0.5}Co_{0.5}O_2$ are 153.8 and 147.6 mAh/g, respectively. The cycling performance of $LiNi_{0.5}Co_{0.5}O_2$ is better than $LiNi_{0.7}Co_{0.3}O_2$. The discharge capacities of $LiNi_{0.5}Co_{0.5}O_2$ and $LiNi_{0.7}Co_{0.3}O_2$ at $n = 6$ are 141.9 and 122.7 mAh/g, respectively. Their discharge capacity fading rates are 1.3 and 6.3 mAh/g/cycle, respectively.

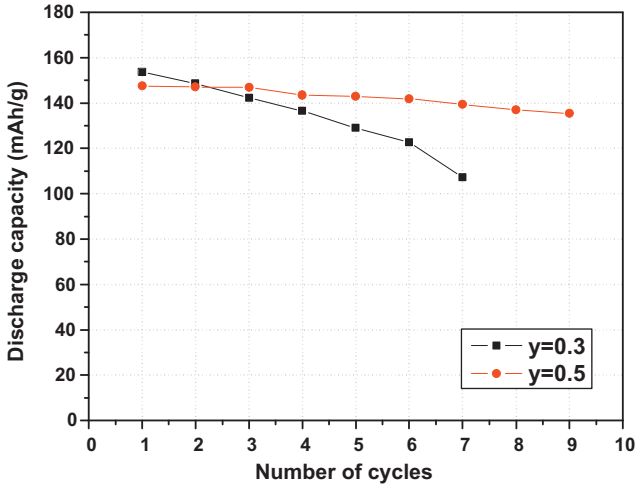

Fig. 12. Variations of discharge capacity at 200 μA/cm^2 with the number of cycles for $LiNi_{1-y}Co_yO_2$ ($y = 0.3$ and 0.5) synthesized at 800 °C for 40 h from Li_2CO_3, NiO and Co_3O_4.

Table 1 compares the physical and electrochemical properties of $LiNi_{1-y}Co_yO_2$ synthesized from NiO, Co_3O_4, and $LiOH{\cdot}H_2O$ or Li_2CO_3. The particle size increases, on the whole, as the synthesis temperature increases and as the Co content increases. The particle sizes of the $LiNi_{1-y}Co_yO_2$ specimens synthesized at all three temperatures from Li_2CO_3, NiO and Co_3O_4 are larger than those of the specimens synthesized from $LiOH{\cdot}H_2O$, NiO and Co_3O_4 for all of the compositions. Among $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) synthesized from $LiOH{\cdot}H_2O$, NiO and Co_3O_4, $LiNi_{0.5}Co_{0.5}O_2$ calcined at 800 °C had the largest first discharge capacity and $LiNi_{0.7}Co_{0.3}O_2$ calcined at 800 °C the best cycling performance. Among $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) synthesized from Li_2CO_3, NiO and Co_3O_4, $LiNi_{0.7}Co_{0.3}O_2$ calcined at 800 °C had the largest first discharge capacity and $LiNi_{0.7}Co_{0.3}O_2$ calcined at 750 °C exhibited the best cycling performance.

Among $LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) synthesized for 40 h from $LiOH{\cdot}H_2O$, NiO and Co_3O_4, and from Li_2CO_3, NiO and Co_3O_4, $LiNi_{0.5}Co_{0.5}O_2$ synthesized from Li_2CO_3, NiO and Co_3O_4 at 800 °C has relatively large first discharge capacity and relatively good cycling performance. This sample is considered the best one with relatively good electrochemical properties.

4. Conclusions

$LiNi_{1-y}Co_yO_2$ ($y = 0.1$, 0.3 and 0.5) were synthesized by the solid-state reaction method at 750 °C, 800 °C and 850 °C from $LiOH{\cdot}H_2O$, NiO and Co_3O_4 and from Li_2CO_3, NiO and Co_3O_4.

$LiNi_{1-y}Co_yO_2$ synthesized from different starting materials had same similarities; they had α-$NaFeO_2$ structure of the rhombohedral system (space group; $R\bar{3}m$). Li_2CO_3 peaks were observed at diffraction angles of 21° and 32° in the $LiNi_{0.9}Co_{0.1}O_2$ samples. The intensities of Li_2CO_3 peaks decreased as the content of Co increased. The particles grew as the synthesis time and temperature increased. They had some differences; the particle sizes of the samples from $LiOH{\cdot}H_2O$, NiO and Co_3O_4 were relatively bigger than those from Li_2CO_3, NiO and Co_3O_4 at all the temperatures and in all the compositions.

Among $LiNi_{1-y}Co_yO_2$ (y = 0.1, 0.3 and 0.5) synthesized for 40 h from $LiOH{\cdot}H_2O$, NiO and Co_3O_4, and from Li_2CO_3, NiO and Co_3O_4, $LiNi_{0.5}Co_{0.5}O_2$ synthesized from Li_2CO_3, NiO and Co_3O_4 at 800 °C has relatively large first discharge capacity and relatively good cycling performance. This sample is considered the best one with relatively good electrochemical properties.

The intensity ratio, $I_{0\,0\,3}/I_{1\,0\,4}$, increases as the Co content increases. The unit cell volumes of the samples synthesized at the same temperature decrease as the Co content increases. These two results indicate that the degree of displacement of the nickel and lithium ions decreases as the Co content increases.

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