The Novel Synthetic Route to $LiCo_yNi_{1-y}O_2$ as a Cathode Material in Lithium Secondary Batteries

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The structure and electrochemical properties of the $Li_xCo_yNi_{1-y}O_2$ (y=0.1, 0.3, 0.5, 0.7, 1.0) system synthesized by solid state reaction with various starting materials have been investigated to optimize the characteristics and synthetic conditions of the $Li_xCo_yNi_{1-y}O_2$. The first discharge capacities of $Li_xCo_yNi_{1-y}O_2$ are 60 mAh/g-180 mAh/g with synthetic conditions. Among them, the $Li_xNi_{0.7}Co_{0.3}O_2$, which was prepared with LiOH, NiO, and Co_3O_4 at 850 °C, had the best electrochemical properties. The first discharge capacity of the compound was 180 mAh/g.

Keywords : Lithium secondary battery, Cathode materials, $LiCo_yNi_{1-y}O_2$.

Introduction

$LiNiO_2$,[1-6] $LiCoO_2$,[7-15] and $LiCo_yNi_{1-y}O_2$[16-20] have been studied intensively as cathode active materials in lithium secondary batteries. From previous studies, $LiNiO_2$ is a nonstoichiometric compound with the formula of $[Li^+_{1-z}Ni^{2+}_z][Ni^{3+}Ni^{2+}_z]O_2$ $(0 \leq z \leq 0.2)$, depending on preparation conditions.[4,5] A small amount of structural disorder due to the displacement of nickel and lithium ions in $LiNiO_2$ strongly affects the electrochemical properties, such as the working voltage and discharge capacity. As the deintercalation reaction proceeds below x = 0.5 in Li_xNiO_2, some structural irreversible rearrangements occur, leading to irreversible electrochemical reactions.[2] $LiCoO_2$ is easily prepared and gives high voltage and good reversibility in Li/$LiMO_2$ cells. Although $LiCoO_2$ does not have structural disorder, $LiCoO_2$ is expensive compare with other cathode materials in lithium batteries and has a higher voltage (4 V) than $LiNiO_2$ (3.5-4.0 V), consequently the oxidation of the nonaqueous electrolyte during prolonged cycling occurs.

These considerations have led to the electrochemical studies of the $LiCo_yNi_{1-y}O_2$ series. In the present study, the structure and electrochemical properties of the $Li_xCo_yNi_{1-y}O_2$ (y = 0.1, 0.3, 0.5, 0.7, 1.0) system synthesized by solid state reaction with various starting materials have been investigated to optimize the characteristics and synthetic conditions of the $Li_xCo_yNi_{1-y}O_2$.

Experimental Section

The $Li_xCo_yNi_{1-y}O_2$ compounds were prepared by conventional solid state reactions. The starting materials were LiOH, Li_2CO_3, NiO, $NiCO_3$, Co_3O_4, and $CoCO_3$. The $Li_xCo_yNi_{1-y}O_2$ compounds were prepared by heating a mixture of starting materials (ex. LiOH, NiO, and Co_3O_4) in the appropriate ratio to 700-900 °C for 40 hrs with intermittent grinding in air after preheating at 600 °C for 20 hrs in air.

The X-ray diffraction patterns were recorded using a MAC Science MXP 18 XRF diffractometer with Ni-filtered Cu Kα radiation by step scanning (0.02°) in the 2θ range of 10-100°. Scanning electron microscopy (SEM) was performed with a Hitachi S800 microscope to investigate the morphology of the samples.

To investigate the electrochemical properties of $Li_xCo_yNi_{1-y}O_2$, the electrochemical cell was fabricated as follows. A cathode was prepared with 89% (wt. %) $Li_xCo_yNi_{1-y}O_2$, 10% acetylene black, and 1% Polytetrafluoroethylene (PTFE) binder. The electrolyte was 1 M $LiPF_6$-ethylene carbonate (EC): diethyl carbonate (DEC) (1 : 1) solution. A lithium metal anode was used. Test cells were assembled in a glove box filled with argon gas. The cells were cycled in the voltage range 3.2-4.3 V with constant current density (200 μA/cm^2), using a galvanostatic charge/discharge cycle tester.

Results and Discussion

The X-ray diffraction patterns for $Li_xCo_yNi_{1-y}O_2$ were indexed hexagonal symmetry with space group $R\bar{3}m$ (Fig. 1). The cell parameters were calculated by indexing the peaks with a hexagonal cell. The a and c parameters, related to the intralayer metal-metal distance and interslab distance, respectively, decreased with increasing cobalt content (y) due to the difference in size between the trivalent cobalt ($r(Co^{3+}) = 0.53$, low spin $(t_{2g}^6e_g^0)$) and nickel ($r(Ni^{3+}) = 0.56$, low spin $(t_{2g}^6e_g^1)$) ions. The c/a ratio, indicating the structural anisotropy of the compounds, increased when Co^{3+} was substituted for nickel ($c/a = 2\sqrt{6}$ for a cubic lattice). This variation indicates that the 2D character increases with the substitution of cobalt ions for nickel ions. The results of a structural analysis on the $Li_xCo_yNi_{1-y}O_2$ are similar regardless of the conditions of synthesis.

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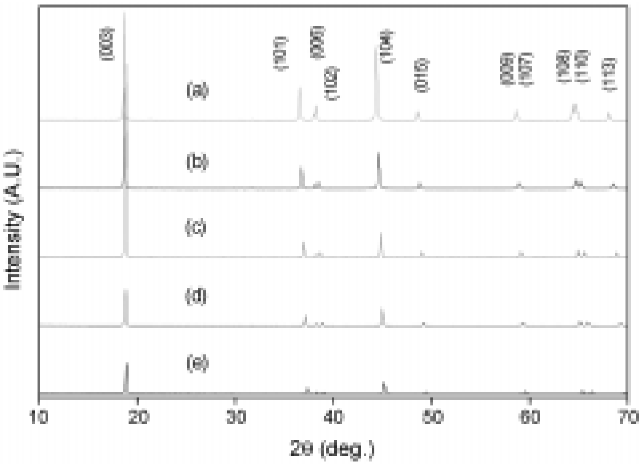

Figure 1. X-ray diffraction patterns of $LiCo_yNi_{1-y}O_2$. (a) $LiNi_{0.9}Co_{0.1}O_2$, (b) $LiNi_{0.7}Co_{0.3}O_2$, (c) $LiNi_{0.5}Co_{0.5}O_2$, (d) $LiNi_{0.3}Co_{0.7}O_2$, (e) $LiCoO_2$.

The SEM images of $Li_xCo_yNi_{1-y}O_2$ synthesized from LiOH, NiO and Co_3O_4 show the particle size decreases with increasing cobalt concentration (y) (Fig. 2). The compounds heat treated at 850 °C have good crystallinity and larger particles. The $LiCo_{0.3}Ni_{0.7}O_2$ heat treated at 850 °C shows well developed layered structure (Fig. 2 (e)).

According to the SEM results of $Li_xCo_yNi_{1-y}O_2$ with various starting materials, the SEM of the compound prepared from lithium carbonate, nickel carbonate and cobalt oxide shows that the spherical particles are aggregated and the particle size increases slightly with increasing cobalt content. The particle size of the compounds prepared from NiO decreases with increasing cobalt content. On the contrary, the particle size of the compounds prepared from $NiCO_3$ increases with cobalt substitution. The particles formed from nickel carbonate and cobalt oxide are aggregated but others have polyhedral shapes. The compounds heat treated at 850 °C have larger particles and better crystallinity than those treated at 800 °C.

The electrochemical behavior of the $Li//Li_xCo_yNi_{1-y}O_2$ cell was examined under constant current density (200 $\mu A/cm^2$). The first charge/discharge curves of $Li_xCo_yNi_{1-y}O_2$ prepared with Li_2CO_3, NiO, and $CoCO_3$ are shown in Figure 3. The compounds have large irreversible loss and polarization. The first discharge capacities are 95-140 mAh/g (Fig. 4(i)). The discharge capacity decreases greatly during the prolonged cycles.

The differences in the intercalation rate (x) of $Li_xCo_yNi_{1-y}O_2$ prepared from LiOH, NiO, and Co_3O_4 in the first cycle are ~$0.03e^-$ to ~$0.1e^-$. The voltage differences between

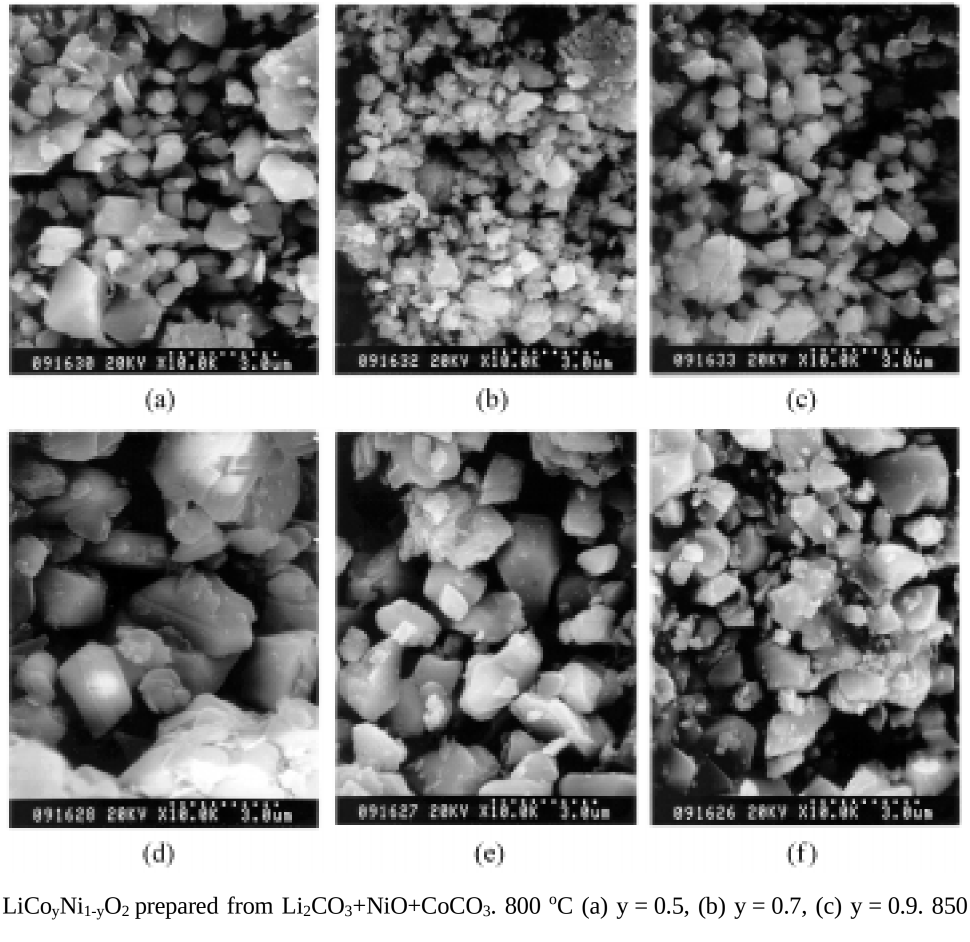

Figure 2. SEM of $LiCo_yNi_{1-y}O_2$ prepared from Li_2CO_3+NiO+$CoCO_3$. 800 °C (a) y = 0.5, (b) y = 0.7, (c) y = 0.9. 850 °C (d) y = 0.5, (e) y = 0.7, (f) y = 0.9

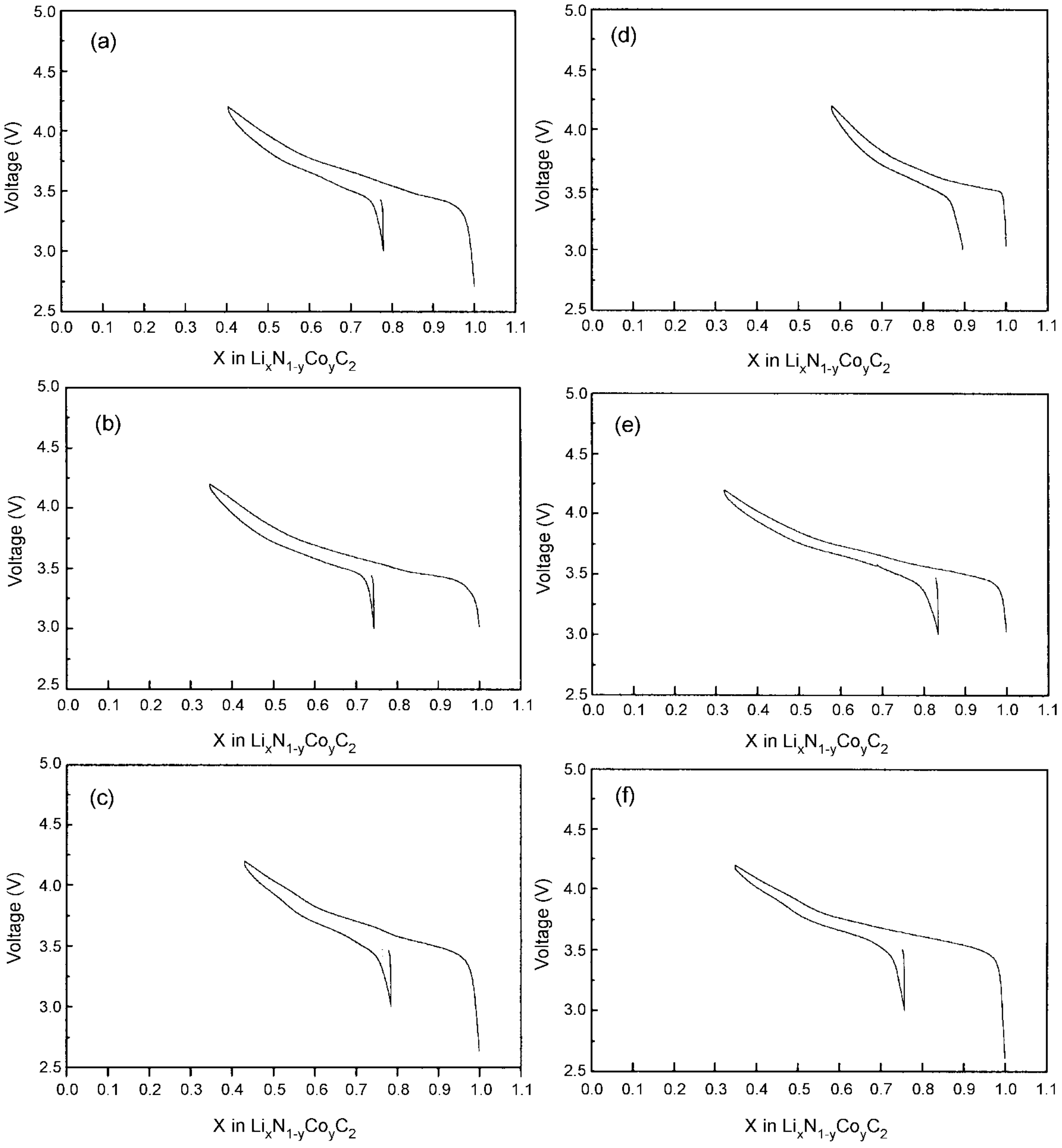

Figure 3. The charge discharge curves of $Li//LiCo_yNi_{1-y}O_2$ prepared from Li_2CO_3+NiO+$CoCO_3$. 800 °C (a) Ni0.5, (b) Ni0.7, (c) Ni0.9. 850 °C (d) Ni0.5, (e) Ni0.7, (f) Ni0.9

charge and discharge for the $Li_xCo_yNi_{1-y}O_2$ are small. These phenomena imply that the compound has small irreversible loss and polarization during the electrochemical reaction. The first discharge capacities are 135-180 mAh/g, which are higher than those of the compounds prepared with other starting materials (Fig. 4(ii)). The discharge capacity variation of the compounds is small compared with others.

The first discharge capacity of $Li_xCo_yNi_{1-y}O_2$ synthesized with Li_2CO_3, NiO, and Co_3O_4 is 130-160 mAh/g (Fig. 4(iii)). In this case, the discharge capacity variation of $LiCo_{0.1}Ni_{0.9}O_2$ heat treated at 800 °C exceeds the others.

The first discharge capacity of the compounds fabricated with Li_2CO_3, $NiCO_3$, and Co_3O_4 is 70-150 mAh/g (Fig. 4 (iv)). The discharge capacity variation of the compounds is also observed. $LiCo_{0.1}Ni_{0.9}O_2$ heat treated at 850 °C shows the smallest variation with prolonged cycles. The discharge capacity variation of these compounds is smaller than those prepared by other methods, but their capacities are smaller.

The first discharge capacity of $Li_xCo_yNi_{1-y}O_2$ started from Li_2CO_3, $NiCO_3$, and $CoCO_3$ is 60 to 150 mAh/g (Fig. 4(v)). These values are the smallest. In this case, $LiCo_{0.1}Ni_{0.9}O_2$ heat treated at 800 °C has good discharge capacity variation. The discharge capacities of these compounds decrease greatly with the cycles.

The electrochemical properties of $Li_xCo_yNi_{1-y}O_2$ prepared with various starting materials are summarized as follows. The discharge capacity increases with increasing cobalt content, but the irreversible loss and cycle performance become

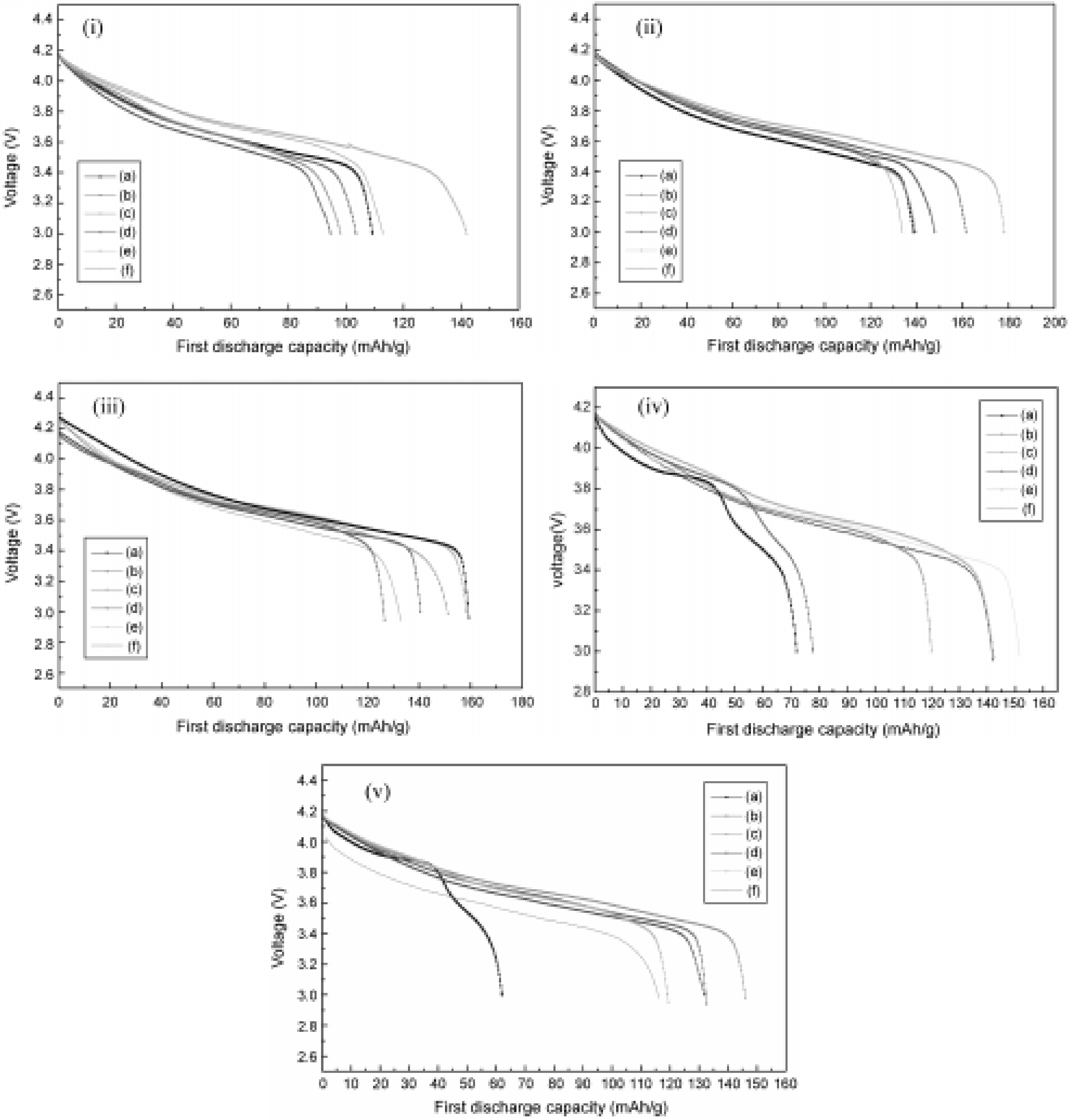

Figure 4. The first discharge capacity of $LiCo_yNi_{1-y}O_2$ prepared with various starting materials. (i) Li_2CO_3 + NiO + $CoCO_3$, (ii) LiOH + NiO + Co_3O_4, (iii) Li_2CO_3 + NiO + Co_3O_4, (iv) Li_2CO_3 + $NiCO_3$ + Co_3O_4, (v) Li_2CO_3 + $NiCO_3$ + $CoCO_3$. 800 °C (a) Ni0.5, (b) Ni0.7, (c) Ni0.9. 850 °C (d) Ni0.5, (e) Ni0.7, (f) Ni0.9

worse. The first discharge capacities of $Li_xCo_yNi_{1-y}O_2$ are 60 mAh/g-180 mAh/g with synthetic conditions. The differences in the intercalation rate of $Li_xCo_yNi_{1-y}O_2$ in the first charge/discharge cycle increase with increasing cobalt content (y). The first discharge capacity of $Li_xCo_yNi_{1-y}O_2$ increases with increasing cobalt concentration. On the contrary, a large decrease in capacities is observed during prolonged cycles when the cobalt ions are substituted for nickel ions. The charge/discharge behavior of the $Li_xCo_yNi_{1-y}O_2$ compounds shows that the best cycling properties are in the Li/ $Li_xCo_{0.3}$-$Ni_{0.7}O_2$ cells. This behavior means that no structural disorder due to the displacement of nickel (and/or cobalt) and lithium ions in the $Li_xCo_{0.3}Ni_{0.7}O_2$ appeared.

Conclusion

The structure and the electrochemical properties of $Li_xCo_yNi_{1-y}O_2$ prepared under various synthesis conditions were investigated. Among them, $Li_xCo_{0.3}Ni_{0.7}O_2$, prepared with LiOH, NiO, and Co_3CO_4 at 850 °C, displayed the best electrochemical properties. The first discharge capacity of the compound was 180 mAh/g.

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