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$LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ Cathode Material for a Li-Ion Cell

Jaephil Cho

Samsung SDI Co., Ltd., Chonan City, Chungchongnam-Do, Korea

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The effects of a partial substitution of Co with Mg in $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ material on its X-ray structure, electrochemical properties, and thermal stability in the charged (delithiated) state have been studied. Results showed that the lattice parameters *a* and *c* as well as the *c*/*a* ratio increased as the *x*-value increased. The DSC exothermic peak of the charged electrode $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ (when $x = 0.04$ or higher) was significantly smaller than that of $LiNi_{0.74}Co_{0.26}O_2$, indicating that the Mg substitution improved its thermal stability. The improvements of both the electrochemical and thermal stability are possibly due to the reduced cation mixing and improvement of layer structure by the expansion of the *c*-axis.

Introduction

Partially substituted $LiNiO_2$ positive-electrode materials have been studied extensively for use in Li-ion cells to replace the presently popular $LiCoO_2$.[1−6] $LiNiO_2$ has a higher capacity and its raw material cost is lower than that of $LiCoO_2$, but it has a few disadvantages, such as thermal instability, which is directly related to Li-ion safety, and multiple crystallographic phase changes during electrochemical cycling, causing structural instability of the $LiNiO_2$.[2] Many previous studies were aimed at improvement of the material by a partial substitution of the Ni with another transition metal or metals. One of the most extensively studied materials is $LiNi_{1-x}Co_xO_2$.[7−12] The substitution of the Ni with Co up to $x = 0.5$ has been reported to improve its thermal and structural instability on cycling, although the substitution reduces the electrochemical capacity slightly. Such improvement is understood to be due to reduced amounts of the hexagonal and monoclinic phase transitions that cause the NiO_2 layer distortion at voltages above 4 V.

A Ga substitution ($LiNi_{0.98}Ga_{0.02}O_2$) was reported to improve the cycle life, showing 95% retention of its initial capacity (190 mAh/g) after 100 cycles between cutoff voltages of 4.3 and 2.5 V, although it also showed a disadvantage of high irreversible capacity of ≈30% of its initial discharge capacity.[6] The substitution of the Ni by a small amount of Nb^{5+}, Ca^{2+}, and In^{3+} cations ($LiNi_{0.99}M_{0.01}O_2$) decreased the lattice distortion on charge (Li extraction). However, their discharge capacities reduced to unattractive values for a practical application of 143, 130, and 120 mAh/g for M = In, Ca, and Nb, respectively, when cycled between 4.2 and 2.6 V. An Al-substituted compound, $LiNi_{0.75}Al_{0.25}O_2$, has also been reported to show a relatively low capacity (≈160 mAh/g) and high irreversible capacity of 50 mAh/g.[5] $LiNi_{0.75}Ti_{0.125}Mg_{0.125}O_2$, which contains both Ti and Mg, showed an attractive initial capacity of 290 mAh/g but at a high charge voltage of 5 V (discharge to 3 V) and with a high irreversible capacity value of 90 mAh/g.[14] The irreversible capacity values of the cathode are preferably smaller than 10−14% for a Li-ion cell with commercially available graphite anode materials. For a new positive-electrode material to be attractive for replacing the presently used $LiCoO_2$, it needs to have good capacity retention upon cycling at relatively high rates of 0.2−1 C in addition to an improved capacity

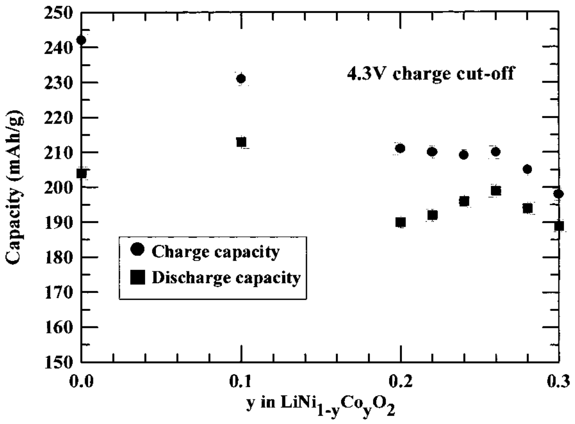

Figure 1. Plot of the initial charge and discharge capacities as a function of y = Co in $LiNi_{1-y}Co_yO_2$.

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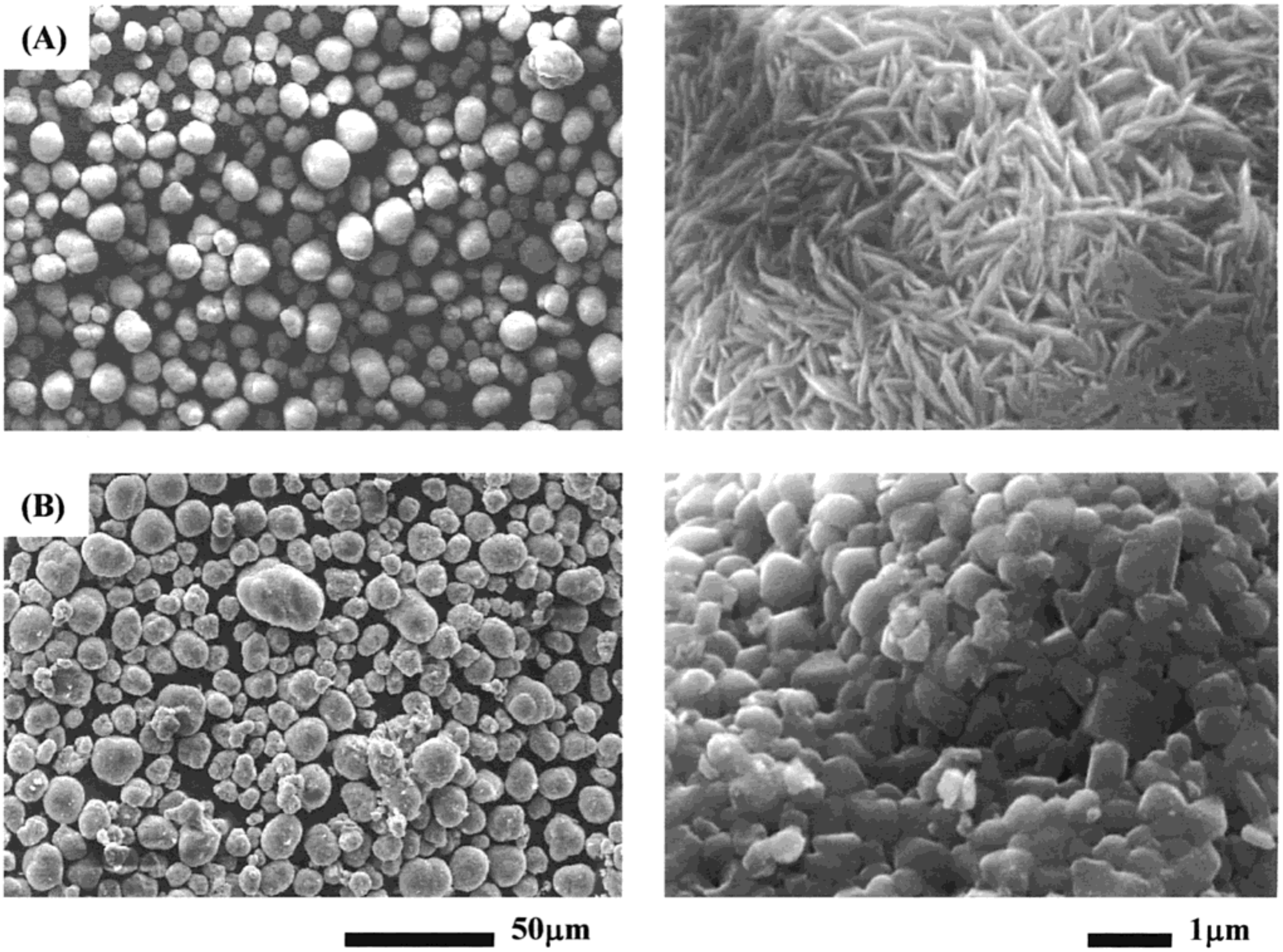

Figure 2. SEM pictures of (A) $Ni_{0.74}Co_{0.26-x}Mg_x(OH)_2$ and (B) $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ prepared by heat treatment at 700 °C.

over that of $LiCoO_2$.[15,16] It was reported that an initial capacity and capacity retention upon cycling is strongly influenced by the degree of cation mixing in the $LiNi_{1-x}Co_xO_2$ material.[2] Cation mixing is the phenomena of Li ions partially occupying 3b sites that are normally occupied by the transition metal ions (Co or Ni) instead of their normal 3*a* sites and vice versa in the space group R_{3-m}. Because the Li ions in the 3b sites are not expected to participate in electrode reactions and to affect the lattice structure, the cation mixing is expected to reduce the capacity and affect the stability and electrochemical reversibility of the positive-electrode material. An actual decrease in initial capacity and improvement of capacity retention upon cycling of the positive-electrode materials was reported as the cation mixing decreased.[2] Results of a differential scanning calorimetry (DSC) study of $LiNi_{1-x}Co_xO_2$ showed that its thermal decomposition temperature (the onset temperature of the exothermic peak) was raised while the peak size shrank as the cation mixing decreased by increasing Co content.[2,9]

In this paper, we have studied the effects of a partial substitution of Co with Mg in $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ (where $x = 0-0.06$) on its X-ray structure in relation to the cation mixing, electrochemical behavior, and thermal stability.

Experimental Section

Selection of $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$: The discharge capacities of $LiNi_{1-y}Co_yO_2$ compounds were measured as a function of *y*. A plot of the capacities against *y* showed a maximum at $y = 0.26$ as shown in Figure 1. The composition, $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$, was selected for the present study of the effect of the Mg substitution to take advantage of (a) the capacity maximum point for the cobalt content and (b) other beneficial effects of the $LiNi_{1-y}Co_yO_2$ compound as the Co content increased up to $y = 0.3$. The beneficial effects include improved cycle life, reduced irreversible capacity, and improved thermal stability as the *y*-value increases.[2]

$Ni_{0.74}Co_{0.26-x}Mg_x(OH)_2$ material of spherical particles (≈13 μm in diameter) was prepared by coprecipitation from a solution containing the stoichiometric amounts of nickel and cobalt nitrates and magnesium nitrate by addition of NaOH and NH_4OH solution in a specially designed reactor for spherical particles according to the reactions[4]

$$0.74Ni^{2+}(aq) + (0.26 - x)Co^{2+}(aq) + xMg^{2+}(aq) + xNH_4OH(aq) \rightarrow [Ni_{0.74}Co_{0.26-x}Mg_x(NH_3)_n{}^{2+}](aq) + nH_2O + (x - n)NH_4OH(aq) \quad (1)$$

$$[Ni_{0.74}Co_{0.26-x}Mg_x(NH_3)_n{}^{2+}](aq) + yOH^- + zH_2O \rightarrow Ni_{0.74}Co_{0.26-x}Mg_x(OH)_2(s)\downarrow + zNH_4OH + (n - z)NH_3 \quad (2)$$

The particle size was controlled by reaction time in the reacter. The pH was controlled by NaOH and maintained

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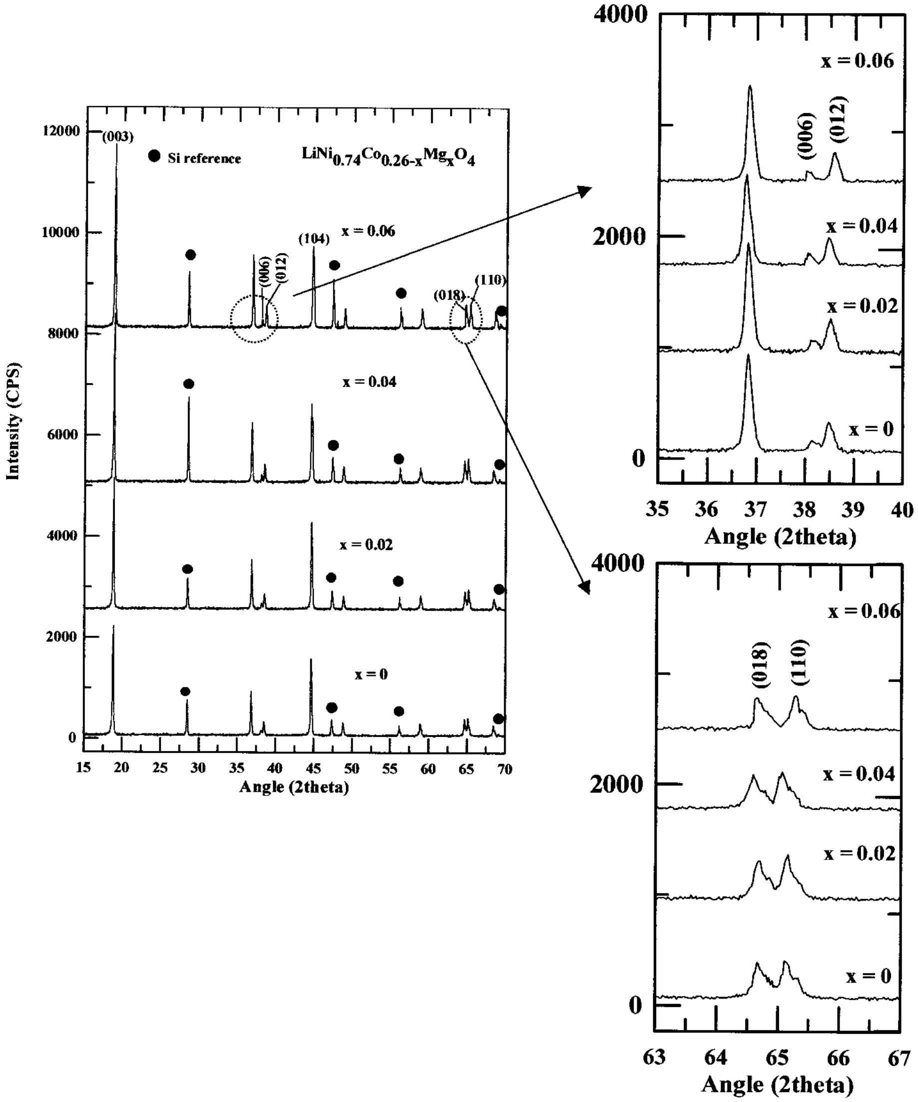

Figure 3. XRD spectra of $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ compounds with $x = 0-0.06$ with expanded views of the spectra in sections of 35°−40° and 63°−67°.

at 10. A longer reaction time in the solution resulted in a larger particle size. $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ was prepared by mixing stoichiometric amounts of 1.02:1 in LiOH and $Ni_{0.74}Co_{0.26-x}Mg_x(OH)_2$, followed by heat treatment at 700 °C for 13 h in a steam of dried air. Excess amount of Li is used to compensate for the loss of Li during firing. Particle shapes of the $Ni_{0.74}Co_{0.26-x}Mg_x(OH)_2$ and $Ni_{0.74}Co_{0.26-x}Mg_xO_2$ powders and their expanded views of a single particle are shown in Figure 2A,B, respectively. The hydroxide particles were made of needle-shaped grains (0.1−0.2 μm in diameter) (Figure 2A), which were transformed into rock-shaped grains of substantially large size (0.5 μm) after heat treatment at 700 °C (Figure 2B). The shape of the particles, however, remained approximately the same (spherical) after the heat treatment. The powder morphology of the $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ was studied with a Philips XL30 scanning electron microscope (SEM).

The procedure of coin-type test cells (2016 size) for Li/$LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ half cells (where $x = 0-0.04$) and C/$LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ Li-ion cells was described previously.[2] The anode electrode consisted of mesophase pitch carbon fiber (MCF) and polyvinylidene fluoride (PVDF) binder in a weight ratio of 90:10 in *N*-methyl-2-pyrrolidone (NMP). The weight ratio of MCF to $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ in Li-ion test cells was 1.1. The electrolyte was 1 M $LiPF_6$ solution of ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 vol %). Cycling tests were carried out at various charge and discharge rates of constant current with two different charge cutoff voltages of 4.2 and 4.3 V using a Toyo multichannel cycler (the current accuracy was 0.5% or better). The initial open-circuit voltages of the samples ranged between 2.7 and 2.75 V. The cycle life test regime of the half cells consisted of 1−2 cycles at a 0.1 C rate for both charging and discharging, 3 cycles at a 0.2 C rate, 5−10 cycles at a 0.5 C rate, and finally at a 1 C rate for the total of 100 cycles between the cutoff voltages. Cycle life tests of the Li-ion cells were carried out between cutoff voltages of 4.3 and 2.75 V by running 5 cycles at 0.2 C followed by additional cycles at a 1 C rate for a total of 100 cycles. Samples for X-ray diffraction (XRD) patterns of the cycled electrodes (20, 40, and 80 cycles) were prepared as follows: Cycling was stopped at the end of discharge at 2.75 V and held at this potential for 30 h. The cells were then carefully dissembled in an argon-filled glovebox to recover the cycled cathode. The sample was subsequently washed with dimethyl carbonate (DMC) to remove $LiPF_6$ followed by drying in a vacuum oven at 80 °C overnight.

Cathode samples for DSC were prepared as follows: cells were initially charged to 4.2 and 4.3 V at a 0.1 C rate (1 C = 180 mA/g), holding them at the cutoff voltage for 40 h. These were then dissembled in a glovebox to remove the charged cathode samples. All sample electrodes contained 30−35% of electrolyte by the weight of dry cathode. Approximately 10 mg of the cathode containing the electrolyte was hermetically sealed in an aluminum DSC sample pan. Active material only

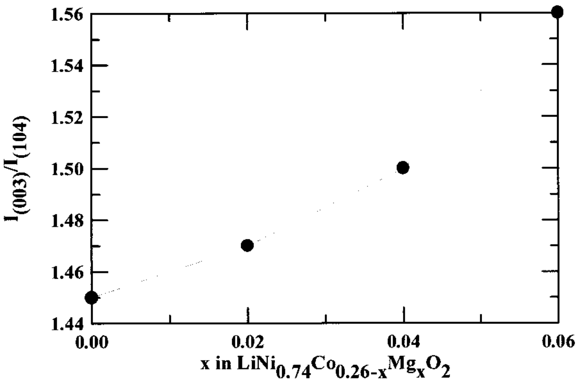

Figure 4. Plot of the the intensity ratios of (003)/(104) as a function of the Mg content (x) in $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$.

was used for the calculation of heat flow. The heating rate of the DSC experiment was 3 °C/min. A Philips PW 1840 X-ray diffractometer was used for the X-ray analyses.

Results and Discussion

XRD Studies. XRD spectra of $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ compounds with various values of x from 0 to 0.06 are shown in Figure 3. The spectra are characteristic of a hexagonal α-$NaFeO_2$ structure in which the oxygen ions are in a closed-packed face-centered cubic array with distortion along the *c*-direction.[3] Single peaks in the hexagonal structure split into (006)/(012) and (018)/(110) pairs with distortion along the *c*-direction.[2,14] The splitting of the peaks into (006)/(012) and (018)/(110) pairs are evident in the present spectra. The degree of the splitting of the peak pairs appears to be increased very slightly as the content of Mg (value of x) increased. However, the extent of the change is so minor that it is not evident when the x-value is up to 0.04 but it is evident when the x-value is 0.06, as shown in Figure 3. The spectra also show an increase of the peak ratio of (003)/(104) as the value of x increases, as shown clearly in Figure 4. Analyses of the lattice parameters from these spectra show that both lattice constants, a and c, as well as the c/a ratio increase as the value of x increases as shown in Figure 5, indicating that the layered characteristics of the compound is enhanced.

The structural parameters were refined using structural models with two different cationic distributions: (i) Co ions located at both the 3a and 3b sites and Ni and Mg ions at the 3b sites; (ii) Ni and Mg ions distributed at both the 3a and 3b sites and Co ions at the 3b sites. The site occupations of each element for both 3a and 3b sites were refined using the constraint that the total occupancy at each site was unity. The structural model (i), however, led to a negative site occupation for the cobalt ions at the 3a sites. This indicates that the cobalt ions are situated only at the 3b sites and the slightly disordered arrangement at the 3a sites is mainly caused by the nickel ions. Hence, the enhancements of the peak ratio of (003)/(104), the c/a ratio, and the splitting of the (006)/(012) and (018)/(110) peak pairs, as x increases in $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$, are all related to the reduction of the cation mixing, as shown in Table 1. The present results appear to indicate that the degree of cation mixing is clearly reduced as the content of Mg increased.

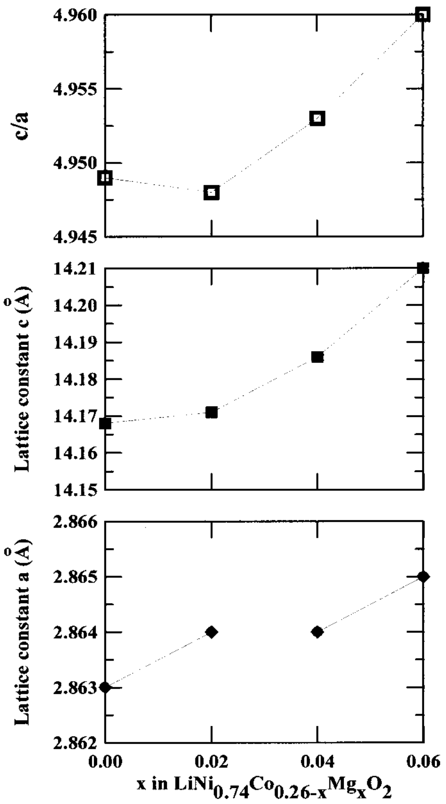

Figure 5. Plots of the c/a ratios and lattice constants a and c as a function of the Mg content (x) in $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$.

Table 1. Rietveld Refinement Results for $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ Powders ($0 \le x \le 0.06$)

sample	$x = 0$	$x = 0.02$	$x = 0.04$	$x = 0.06$
goodness-of-fit parameters				
reduced χ^2	2.234	2.221	2.453	2.221
total R_{wp}[a]	8.23	8.21	8.85	8.21
fractional occupancies				
Li on 3a sites	0.9711	0.9812	0.9891	0.9922
Ni on 3a sites	0.0289	0.0187	0.0108	0.0077
Mg on 3a sites		0.0001	0.0001	0.0001
Li on 3b sites	0.008	0.006	0.003	0.002
Ni on 3b sites	0.744	0.715	0.716	0.720
Co on 3b sites	0.248	0.260	0.243	0.221
Mg on 3b sites		0.019	0.038	0.057

[a] $R_{wp} = [M/\Sigma(wI_o^2)]^{1/2}$ where the quantity minimized is $M = \Sigma w(I_o - I_c)$, with I_o and I_c being the observed and calculated intensities and w a weight related to the error.

Table 2. Measured Values of Charge, Discharge, and Irreversible Capacities of $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ Material at the Charge Cutoff Voltages of 4.2 and 4.3 V vs Li (with Discharge Voltage, 2.75 V)

	$x = 0.00$	$x = 0.02$	$x = 0.04$	$x = 0.06$
charge capacity, mAh/g				
@ 4.2 V	200	196	192	190
@ 4.3 V	210	206	207	204
discharge capacity, mAh/g				
@ 4.2 V	187	182	172	158
@ 4.3 V	199	193	186	173
irreversible capacity, mAh/g				
@ 4.2 V	13	14	20	32
@ 4.3 V	11	13	21	31

Electrochemical Properties of $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ Electrodes. The charge, discharge, and irreversible capacities of $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ (where $x = 0-0.06$) are summarized in Table 2. Both charge and discharge capacities decreased slightly while the

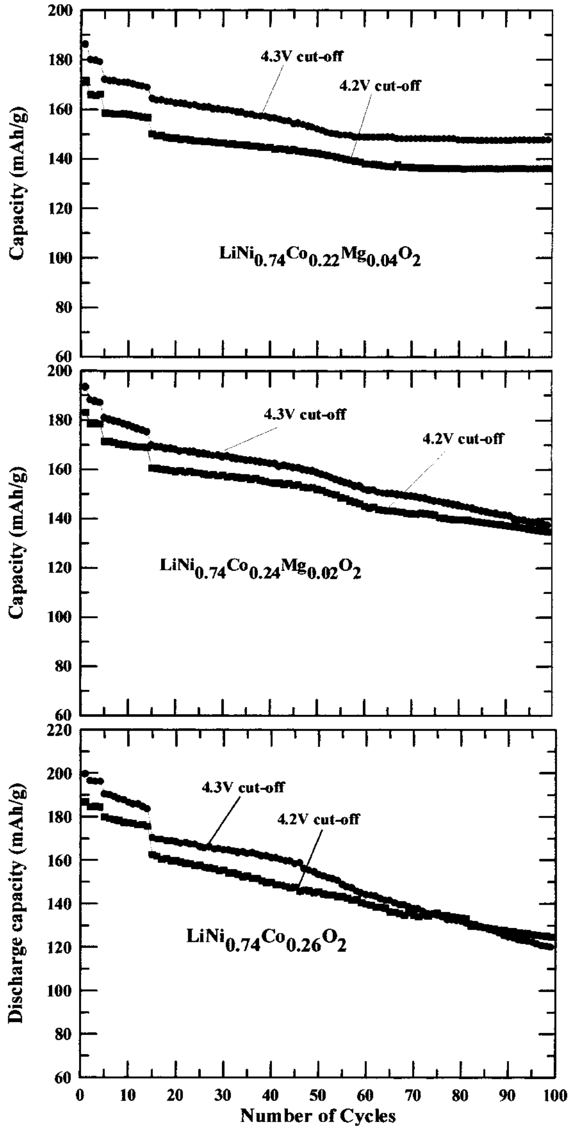

Figure 6. Plots of the discharge capacity of $Ni_{0.74}Co_{0.26-x}Mg_xO_2$ compounds with $x = 0$, 0.02, and 0.04 in a $Li/LiNi_{0.74}Co_{0.26}O_2$ half-cell cycled between 4.3 and 2.75 V as a function of the cycle number. The cells were initially cycled once at charge and discharge rates of 0.1 C, followed by 3 to 5 times at the 0.2 C rate, 10 times at the 0.5 C rate, and finally at the 1 C rate for the total of 100 cycles.

irreversible capacity increased as the content of Mg increased. The decrease of charge and discharge capacities and the increase of irreversible capacity might be due to the decrease in concentration of the active Ni^{3+} or Co^{3+} ions sites for the Li^+ ion intercalation as the Mg content increases.[17] A plausible mechanism of the charge compensation is that Mg^{2+} substitutes either onto Ni^{3+} or onto Co^{3+} sites as follows,

$$2M^{3+} + Mg_M^{2+} \rightarrow 2M^{4+} + V_M \qquad (3)$$

where M = Co or Ni. Capacity changes upon cycling of $Li/LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ half-cells are plotted against the number of cycles (Figure 6). The capacity retention upon cycling at both charge cutoff voltages of 4.2 and 4.3 V improved markedly as the Mg content increased up to $x = 0.04$. ($LiNi_{0.74}Co_{0.20}Mg_{0.06}O_2$ was not tested because its relative capacity was too low to be attractive as shown in Table 2.) $LiNi_{0.74}Co_{0.22}Mg_{0.04}O_2$ showed improved capacity retention of ≈91% of its initial value after 85 cycles at a rate of 1 C as compared with ≈72% for $LiNi_{0.74}Co_{0.26}O_2$, as shown in Figure 6. A similar improvement in the capacity retention of $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ over $LiNi_{0.74}Co_{0.26}O_2$ is also observed with Li-ion cells as shown in Figure 7. The capacity retention of $LiNi_{0.74}Co_{0.22}Mg_{0.04}O_2$ after 94 cycles at a 1 C rate was ≈92% while that of $LiNi_{0.74}Co_{0.26}O_2$ was ≈79%.

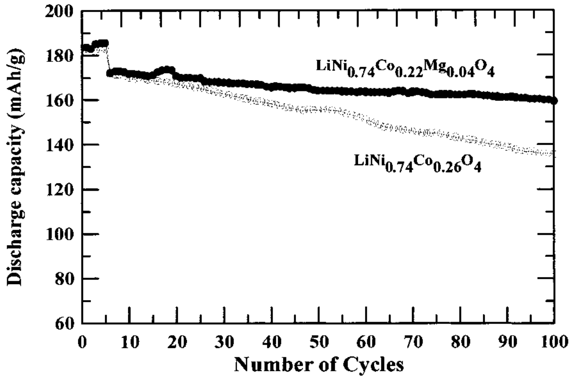

Figure 7. Plots of the discharge capacity of $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ compounds with $x = 0$ and 0.04 in a Li-ion cell ($MCF/LiNi_{0.74}Co_{0.26-x}Mg_xO_2$) cycled between 4.3 and 2.75 V as a function of cycle number. The cells were initially cycled for 5 times at a charge and discharge rate of 0.2 C, followed by the 1 C rate for a total of 100 cycles.

This improvement in the capacity retention might be related to the reduced degree of cation mixing as the content of Mg (value of x) is increased as indicated by the results of the present XRD study because reduction of the cation mixing was reported to improve the stability of $LiNi_{1-x}Co_xO_2$ compounds.[2] Reduced cation mixing in $LiNi_{0.74}Co_{0.22}Mg_{0.04}O_2$ compared with $LiNi_{0.74}Co_{0.26}O_2$ is also indicated by the XRD spectra of these compounds after cycling, as shown in Figure 8. The peak intensity ratio of (003)/(104) of $LiNi_{0.74}Co_{0.26}O_2$ decreased and the splitting of the (018)/(110) pair became less evident with cycling, indicating that the cation mixing may be increased as it is cycled. In contrast, such a trend appears to be the opposite of that for $LiNi_{0.74}Co_{0.22}Mg_{0.04}O_2$, indicating that the cation mixing may be reduced as it is cycled.

Thermal Stability of $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$. Thermal stability of fully charged $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ electrodes at 4.3 V vs Li for 40 h were studied using a DSC technique. The results for x-values of 0, 0.02, 0.04, and 0.06 are shown in Figure 9. The observed exothermic peaks are due to the thermal decomposition of the positive-electrode material releasing oxygen, which is understood as one of the main causes of safety problems of Li-ion cells.[1,14,18] A small Mg doping ($x = 0.02$) appears to increase the overall peak size, as compared to $x = 0$. However, when the x-value was further increased to 0.06, a broad peak with a markedly smaller overall size than the others was observed at a temperature ranging between 190 and 204 °C as shown

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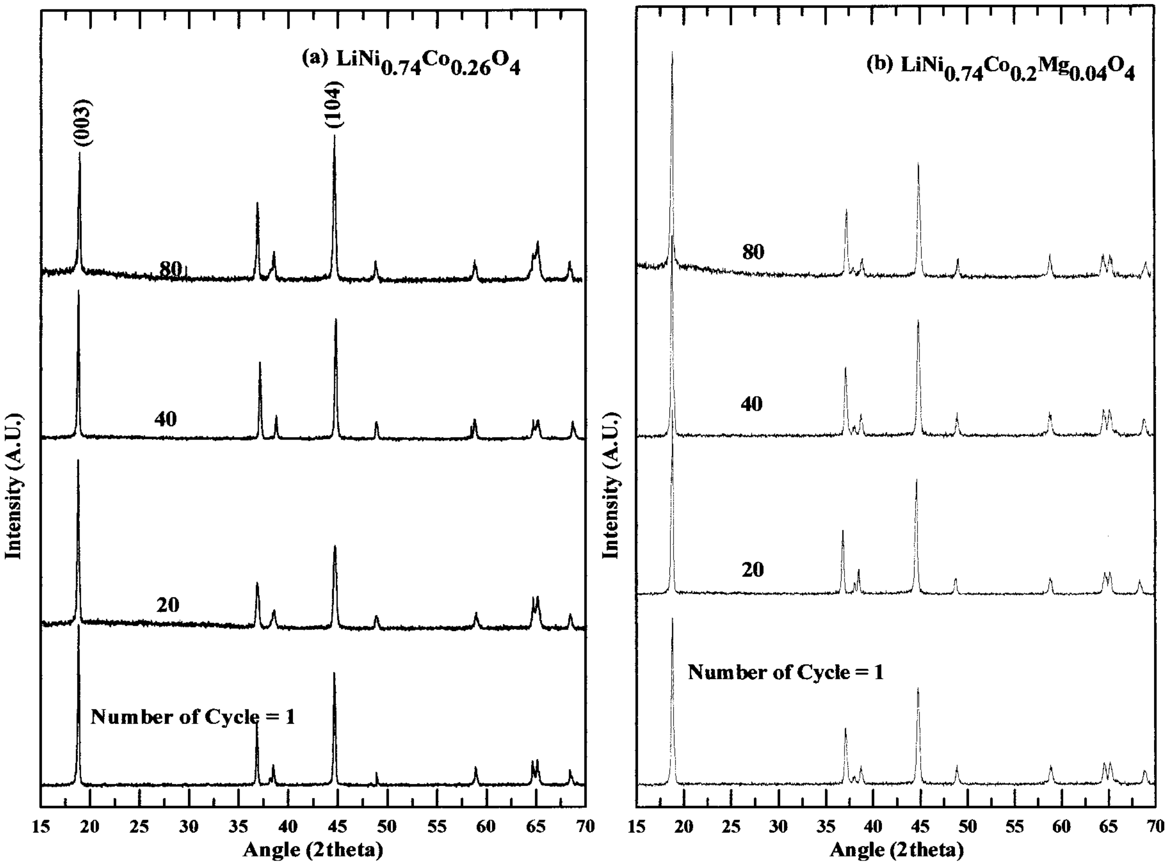

Figure 8. (a) XRD spectra of cycled $LiNi_{0.74}Co_{0.26}O_2$ electrodes between 4.3 and 2.75 V after 1, 20, 40, and 80 cycles. (b) XRD spectra of cycled $LiNi_{0.74}Co_{0.22}Mg_{0.04}O_2$ electrodes between 4.3 and 2.75 V after 1, 20, 40, and 80 cycles.

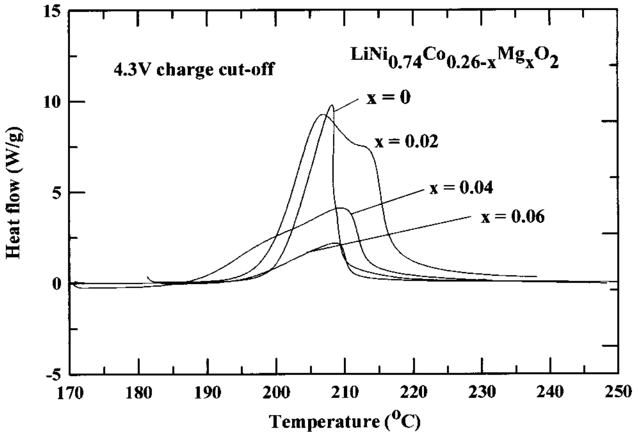

Figure 9. DSC scans of $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ electrodes (where $x = 0$, 0.02, and 0.04) after full charge at 4.3 V vs Li for 40 h. The heating rate for the measurement was 3 °C/min.

in Figure 9. The present DSC results overall appear to indicate that the Mg substitution to $x = 0.04$ or more in the cathode material ($LiNi_{0.74}Co_{0.26-x}Mg_xO_2$) improves its thermally stability noticeably over the that of the nonsubstituted material ($LiNi_{0.74}Co_{0.26}O_2$). The thermal stability behavior may be related to the c/a ratio,[2,9] which decreased slightly when $x = 0.02$ but increased significantly when $x = 0.04$ and 0.06 (Figure 5).

Conclusions

The present results of the XRD study on $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ show the enhancement of the intensity ratio of (003)/(104) peaks, minor widening of (006)/(012) and (018)/(110) peak pairs, and increase of the lattice parameters a and c as well as the c/a ratio as the x-value increased. All these changes appear to point to reduction of the cation mixing as the x-value increases. The capacity retention upon cycling of the $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ material improved as the x-value increases. The DSC exothermic peak of the charged electrode of $LiNi_{0.74}Co_{0.26-x}Mg_xO_2$ (when $x = 0.04$ or higher) was significantly smaller than that of $LiNi_{0.74}Co_{0.26}O_2$, indicating that the Mg substitution improved its thermal stability. The improvements of both the electrochemical and thermal stability are possibly due to the reduced cation mixing and improvement of layer structure by the expansion of the c-axis.

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