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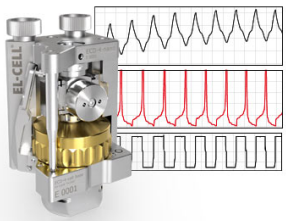

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Electrochemical Properties and Thermal Stability of $Li_aNi_{1-x}Co_xO_2$ Cathode Materials

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Conductive and electrochemical properties as well as thermal stability of $Li_aNi_{1-x}Co_xO_2$ where $x = 0$-0.3 and $a = 1.0$-0.4 have been studied using impedance spectroscopy, galvanostatic intermittent titration technique, cyclic voltammetry, electrochemical cycling, and differential scanning calorimetry (DSC). The electronic conductivity of partially charged material ($a \leq 0.8$) increases substantially when the cobalt content is increased to $x = 0.3$ from 0.2. The mobility, chemical diffusion coefficient, and Li^+ ion diffusion coefficient in the partially charged material are in the neighborhood of 10^{-6} cm^{-2}/V s, 10^{-8} cm^2/s, and 5×10^{-10} cm^2/s, respectively, and are rather insensitive to the values of a and x. Results of electrochemical and DSC studies show that $LiNi_{0.7}Co_{0.3}O_2$ is the best cathode material for a Li cell of all materials studied here in view of the best cycle stability, the smallest irreversible capacity, and the greatest thermal stability with minimal reduction of specific capacity from that of $LiNiO_2$.
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In an effort to improve energy density of Li-ion cells, $LiNiO_2$ has been studied extensively as a cathode material by many investigators[1-12] because its specific capacity is higher than that of $LiCoO_2$, which is presently used in most commercially available Li-ion cells. $LiNiO_2$ shows a specific capacity up to 203 mAh/g (cf. 160 mAh/g for $LiCoO_2$) when cycled between 2.75 and 4.3 V *vs.* Li metal. This potential (4.3V *vs.* Li metal) corresponds approximately to a 4.2 V charging voltage for a practical Li-ion cell, because the potential of an incompletely charged carbon anode in the cell at the end of charge is approximately 0.1 V *vs.* Li. [1,2]

$LiNiO_2$, however, also has a few disadvantages compared to $LiCoO_2$ as a cathode material. Its major disadvantages are (*i*) it is less stable structurally upon cycling,[12] (*ii*) it is more difficult to synthesize in consistent quality,[13] and (*iii*) it has greater safety problems due to its more exothermic decomposition when liberating oxygen compared to $LiCoO_2$. [5,6] Because of these difficulties, a Li-ion cell in which $LiNiO_2$ is used as the cathode material is not yet available commercially. Recently, $LiNi_{1-x}M_xO_2$ where M is one of the transition or alkaline earth metals, has been studied extensively in an effort to solve these problems by stabilizing the structure of $LiNiO_2$. [3-11] Of these substituted compounds, $LiNi_{1-x}Co_xO_2$ has been identified as one of the most attractive materials.[10-16]

In an electrochemical study of $LiNi_{1-x}Co_xO_2$ ($x = 0.2$ and 0.3) in a $LiNi_{1-x}Co_xO_2$/Li cell which was cycled between 4 and 2.7 V at low currents (0.07-0.4 mA/cm^2), Delmas *et al.* reported that $LiNi_{0.7}Co_{0.3}O_2$ showed better capacity retention than $LiNi_{0.8}Co_{0.2}O_2$ as a result of enhanced layering characteristics as the Co content increased.[15,16] In contrast, Ohzuku *et al.* reported capacity fading behavior of $LiNi_{1-x}Co_xO_2$ similar to that of $LiNiO_2$ when they were cycled between 4.2 and 2.5 V at a current density of 0.17 mA/cm^2, [17] Also, Li *et al.* reported capacity fading behavior of $LiNi_{0.85}Co_{1.5}O_2$ similar to that of $LiNi_{0.67}Co_{0.33}O_2$ when they were cycled between 4.25 and 3 V at a current density of 0.5 mA/cm^2, [10] indicating that the capacity fading behavior of $LiNi_{1-x}Co_xO_2$ during cycling is not affected significantly by the Co content (x value). Because these results apparently conflict with each other, it is desirable to understand the effect of the Co content on the capacity fading behavior for possible benefits in practical cells.

Commercially available Li-ion cells containing $LiCoO_2$ as the cathode material are typically charged to two different cutoff voltages, *i.e.*, 4.1 and 4.2 V, which corresponds to approximately 4.2 and 4.3 V *vs.* Li, respectively.[18,19] $LiCoO_2$ is structurally stable at both voltages.[20,21] However, the effect of cutoff voltage on cycling performance of $LiNi_{1-x}Co_xO_2$ is largely unknown, although these voltages are likely to affect the stability in view of the potential-dependent crystallographic phase transitions of $LiNiO_2$. [22] It has been reported that $LiNiO_2$ exhibits a series of phase transitions during cycling, and such phase transitions are a cause of deterioration of its structural stability, resulting in capacity fading.[13] Although the addition of Co to $LiNiO_2$ has been shown to improve structural stability during cycling,[10] information on the electrochemical properties of the modified material is rather limited. The magnitude of irreversible capacity of the cathode material is also important to know to achieve good Li-ion cell performance. However, information on the composition-dependent irreversible capacity of $LiNi_{1-x}Co_xO_2$ and its dependence on cutoff voltages are not available in the open literature to our knowledge. The thermal stability of the cathode material of a Li-ion cell is of great interest in connection with cell safety.[5,6,24] It has been reported that $LiNi_{1-x}Co_xO_2$ where $x > 0$ is more stable than $LiNiO_2$. [5]

Among other required properties of Li-ion cell cathode materials are good electrochemical reversibility, stability upon cycling, high chemical diffusion coefficient of Li^+ ions, and high electronic conductivity. The Li^+ ion chemical diffusion coefficient and electronic conductivity play important roles in governing the performance of cathode materials. Tukamoto *et al.*[25] reported that the overall conductivity of $LiCoO_2$ is in the order of 10^{-3} cm^{-1} Ω^{-1} at room temperature and is dominated by electronic conductivity. Molenda *et al.*[26] studied the electronic conductivity of Li_aCoO_2 as a function of a. The conductivity of Li_aCoO_2 increased very rapidly as the a value decreased from unity, *e.g.*, 10^{-3} cm^{-1} Ω^{-1} when $a = 1$, 1 cm^{-1} Ω^{-1} when $a = 0.8$, and 10^2 cm^{-1} Ω^{-1} when $a = 0.17$. The Li^+ ion chemical diffusion coefficient of in Li_aCoO_2 has been investigated by various authors. Using the galvanostatic intermittant titration technique (GITT), Mizushima *et al.*[27] and Kikkawa *et al.*[28] obtained a value in the vicinity of 5×10^{-9} cm^2/s in the a range of 0.2-0.8, whereas Thomas *et al.*[29] reported a value higher by an order of magnitude (5×10^{-8} cm^2/s) using an impedance spectroscopic technique. The Li^+ ion chemical diffusion coefficient in Li_aNiO_2 was reported by Bruce *et al.*[30] using an impedance spectroscopic technique as $D = 2 \times 10^{-7}$ cm^2/s in the a range of 0.2-0.7.

In the present paper we report the results of a comprehensive study of conductive and electrochemical properties as well as thermal stability of $Li_aNi_{1-x}Co_xO_2$ compounds as a function of the Co content ($x = 0$-0.3), degree of Li^+-ion extraction (a value), and the charge cutoff voltages during cycling.

Experimental

Material preparation.—$LiNi_{1-x}Co_xO_2$ ($x = 0$, 0.1, 0.2, and 0.3) powder samples were prepared by mixing appropriate amounts of $LiOH{\cdot}H_2O$ and $Ni_{1-x}Co_x(OH)_2$ (Li/(Li + Ni + Co) = 1.01) followed by heating the mixture at 700°C for 13 h under dry air atmos-

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phere. This synthetic method provided the following advantages over previously reported methods[9,10]: (*i*) reduced sintering temperature (700°C), (*ii*) air atmosphere instead of oxygen, and (*iii*) reduced soak time (13 h) at 700°C. Analyses of Li content a in $Li_aNi_{1-x}Co_xO_2$ compounds were carried out using inductively coupled plasma-mass spectroscopy (ICP-MS) (Himadachi, Japan). The Li content in the present sample was $a = 0.998$.

Electrical conductivity measurements.—A powder sample of $LiNi_{1-x}Co_xO_2$ of about 0.5 g was pressed into pellets (without using a binder or additive) 10 mm diam and 2 mm thick followed by heating at 700°C for 4 h. For preparation of partially extracted ($Li_aNi_{1-x}Co_xO_2$ with $a = 0.8$, 0.6, and 0.4), samples, the Li^+ ion was extracted electrochemically from the $LiNi_{1-x}Co_xO_2$ pellet in a coin-type $LiNi_{1-x}Co_xO_2$/Li cell. An empirical relationship between equilibrium potential and degree of Li^+ ion extraction from $LiNi_{1-x}Co_xO_2$, which was similar to one previously used,[8] was used to determine the value of a. The coin cell was charged using a potentiostat/galvanostat (EG&G Princeton Applied Research 273A) at 300 $\mu A/cm^2$ to a predetermined voltage followed by further charging at this voltage for 30 h until the current dropped to 10 $\mu A/cm^2$. The predetermined voltage values were 3.7, 3.8, and 4 V for a values of 0.8, 0.6, and 0.4, respectively. After charging, the coin cells were disassembled to remove the $LiNi_{1-x}Co_xO_2$ pellets followed by rinsing them with dimethyl carbonate (DMC) to remove $LiPF_6$ salt from the pellets. The pellets were then vacuum-dried at 80°C. Gold was sputtered on each face of the pellet sample for ac impedance measurements, which were carried out using a potentiostat/galvanostat (EG&G 273A).

Preparation of cathodes and test cells.—Cathodes for battery test cells were made of the cathode material, super P carbon black (3M, Belgium) and polyvinylidene fluoride (PVdF) binder (Kureha Company) in a weight ratio of 92:4:4. Electrodes were prepared by coating a cathode slurry onto an Al foil followed by drying at 130°C for 20 min. The slurry was prepared by thoroughly mixing a *N*-methyl-2-pyrrolidone(NMP) solution of PVdF (water content below 0.01%), carbon black, and the powder cathode material. Coin-type battery test cells (size 2016) prepared in a helium-filled glove box contained a cathode, a Li metal anode, a microporous polyethylene separator, and an electrolyte consisting of a 1 M solution of $LiPF_6$ in 1:1 (by volume) mixture of ethylene carbonate (EC) and DMC. Each test cathode contained approximately 30 mg of $LiNi_{1-x}Co_xO_2$ material. Test cells were aged at room temperature for 24 h after the addition of electrolyte before electrochemical testing.

Electrochemical testing.—Cycling tests of the coin-type cells were carried out using charge cutoff voltages of 4.1, 4.2, and 4.3 V at various constant-current charge and discharge rates using a multichannel cycler (Toyo) with current accuracy of 0.5% or better. Cycling tests were carried out initially by charging and discharging cell at the 0.1C rate for one to two cycles, followed by three cycles at the 0.2C rate, five to ten cycles at the 0.5C rate, and finally at the 1C rate for a total of 110 cycles. For GITT measurements, fully charged Li/$LiNi_{1-x}Co_xO_2$ ($x = 0$, 0.1, 0.2, and 0.3) test cells were allowed to reach equilibrium states after each incremental constant-current discharge step by allowing an open-circuit period of 3000 s. Cyclic voltammograms of $LiNi_{1-x}Co_xO_2$ cathodes in the coin cells were recorded at a scan rate of 0.02 mV/s using a potentiostat/galvanostat (EG&G 273A).

Preparation of DSC samples.—Cathode samples for DSC measurements were prepared by charging the coin cells to 4.2 and 4.3 V at the 0.1C rate (1C = 180 mA/g) followed by holding at the respective potential for 20 h. These cells were then dissembled in a glove box to remove the charged cathode which typically contained 30-35 wt % electrolyte, 30 wt % Al foil, 5 wt % combined binder and carbon black, and 30-35 wt % cathode material. Approximately 10 mg of the cathode was cut and hermetically sealed in an Al DSC sample pan. Only the cathode material was used for the calculation of specific heat flow. The heating rate of the DSC experiment was 3°C/min.

Results and Discussion

Structural characterization of $LiNi_{1-x}Co_xO_2$.—X-ray diffraction (XRD) patterns of $LiNi_{1-x}Co_xO_2$ ($x = 0$, 0.1, 0.2 and 0.3) powder samples indicate that they are single phases with a hexagonal-type structure with a space group $R\bar{3}m$, as shown in Fig. 1. In this structure, Co^{3+}, Ni^{3+}, and Li^+ ions occupy at 3b and 3a sites, respectively, on the alternate (111) planes of the rock-salt structure, whereas the oxygen ions form a close-packed face centered cubic (fcc) structure.

The ratio of lattice constants, c/a, increased to 4.948 in $LiNi_{0.7}Co_{0.3}O_2$ from 4.935 in $LiNiO_2$, indicating that lattice expands preferentially in the direction of the c axis. This lattice expansion accompanies increased separation of the 006-012 and 018-110 peak pairs, whereas reduction of the c axis lattice expansion implies conversion of the structure toward a cubic lattice with merging of the peak pairs into single peaks.[14] The increased lattice expansion as indicated by increased separation of the peak pairs is related to the reduction of cation mixing, *i.e.*, a portion of Li ions go into the 3b sites of Ni and Co instead of the normal 3a sites.[5,14] Reduction of (003) peak size was also observed as the x value decreased, as shown in Fig. 1. The cation mixing becomes increasingly more evident as the x value decreased, showing the highest degree of cation mixing with $LiNiO_2$. The possible formation of impurity phases such as LiOH and Li_2CO_3 as a result of cation mixing was suggested earlier.[8] In order to investigate such a possibility, we carried out thermogravimetric analysis of the samples in the temperature range 100-900°C. The measured thermogravimetric analysis (TGA) curves showed no indication of the presence of LiOH or Li_2CO_3 in all samples tested, indicating that these impurity phases may not form at a detectable level, if they form at all. However, the absence of these phases does not necessarily mean that there is no cation mixing.

Electronic conductivity.—The impedance complex-plane plots for $LiaNi_{1-x}Co_xO_2$ exhibited a simple response with a frequency-

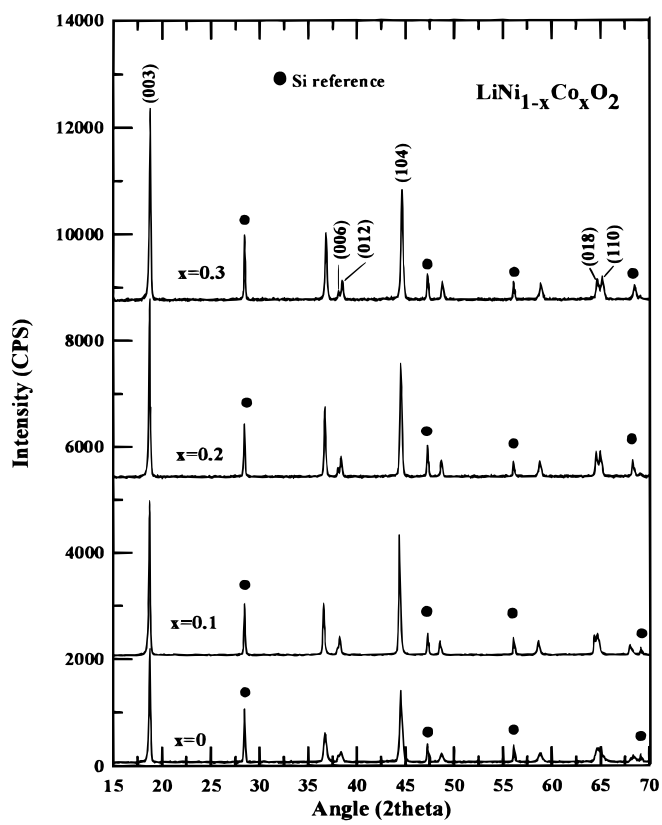

Figure 1. Powder XRD patterns of the $LiNi_{1-x}Co_xO_2$ for $x = 0$, 0.1, 0.2, and 0.3.

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independent impedance in which many data points superimposed at a single point on the real (Z) axis. Because these plots did not show an indication of low-frequency dispersion attributed to charge blocking at the electrode interface, the $Li_aNi_{1-x}Co_xO_2$ electronic conductivity can be obtained directly from the gross resistance of the pellets, analogous to that observed in $LiCoO_2$. [25] The dependence of $Li_aNi_{1-x}Co_xO_2$ electronic conductivity on a value is shown in Fig. 2. The conductivity increased as the a value decreased. The increase, however, was much more gradual than the similar increase reported for Li_aCoO_2. [26] For example, when the a value decreased from 1.0 to 0.8, the $Li_aNi_{1-x}Co_xO_2$ conductivity (x value 0-0.2) increased by a factor of approximately 20 and by a factor of 500 when the x value is 0.3, whereas that of Li_aCoO_2 increased by more than three orders of magnitude.

The present observation is consistent with earlier results on the conductivity of Ni-rich $Li_aNi_{0.8}Co_{0.2}O_2$ and Co-rich $Li_aNi_{0.1}Co_{0.9}O_2$ reported by Saadoune *et al.*[31,32] They reported that in the Ni-rich compound the conduction is dominated by a Ni^{3+}-$O^{2-}Ni^{4+}$ hopping mechanism. Because Ni^{4+} and Co^{3+} ions ($t_{2g}{}^6e_g{}^0$) have a low-spin configuration and are diamagnetic, only the Ni^{3+} ion ($t_{2g}{}^6e_g{}^1$) is expected to participate in the conduction process.[31-33] In the Co-rich compound, Co^{3+} ions may be oxidized to Co^{4+} ions ($t_{2g}{}^5e_g{}^0$) with an incompletely filled t_{2g} orbital before Ni^{3+} ions are fully oxidized to Ni^{4+} ions, leading to t_{2g}-t_{2g} overlapping of cobalt ions. Such orbital overlapping is presumed to be the cause of enhanced conductivity of the Co-rich compounds. In the present observation we speculate that the enhanced conductivity of $LiaNi_{0.7}Co_{0.3}O_2$ over those of $LiaNi_{1-x}Co_xO_2$ (x = 0-0.2) might be because a part of Co^{3+} ions in the former compound (Co-rich) is oxidized to Co^{4+} ions as Li^+ ions are extracted, whereas in the latter compound (Ni-rich) mainly Ni^{3+} ions participate in the oxidation. This speculation may indicate that the transition of the "Ni-rich" to "Co-rich" behavior occurs for Co content (x value) between 0.2 and 0.3.

Chemical and component diffusion coefficients and mobility of Li^+ ion.—The chemical diffusion (D_{Li}) and component diffusion (D_{kLi}) coefficients for Li^+ ion were determined from galvanostatic intermittent titration curves as illustrated in Fig. 3. D_{Li} was calculated from Eq. 1 as a function of Li content (a value) in the cathode materials[34,35]

$$D_{Li} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2\left(\frac{\Delta Es}{\Delta Et}\right)^2 \quad [1]$$

where m_B is the mass of active material, ΔEs the steady-state (or equilibrium) voltage, ΔEt the total change of the transient cell voltage for an applied current I_o for time τ, M_B the molecular weight of active material, S the geometric area of the sample-electrolyte interface, and V_M molar volume of the electrode.

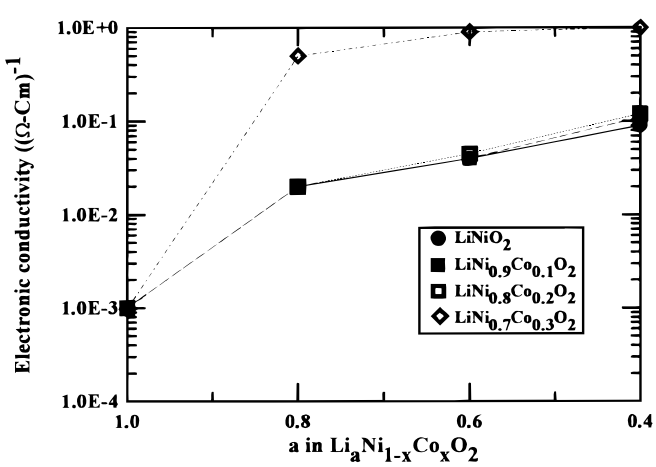

Figure 2. Electronic conductivity of $Li_aNi_{1-x}Co_xO_2$ for x = 0, 0.1, 0.2, and 0.3 as a function of the value of a.

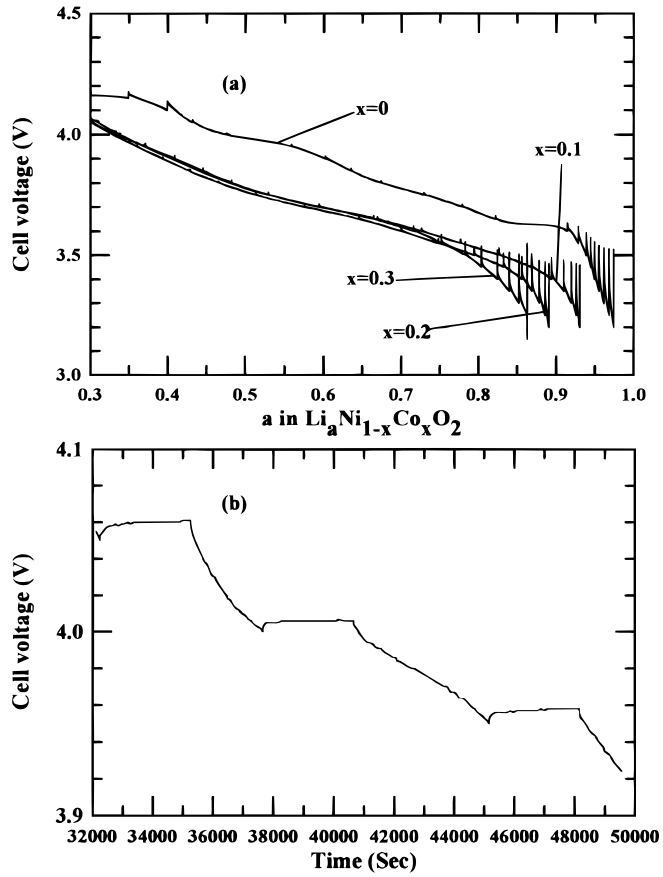

Figure 3. (a) Galvanostatic intermittent discharge curves of $Li_aNi_{1-x}Co_xO_2$ where x = 0, 0.1, 0.2, and 0.3 as a function of the value of a. (b) Intermittent discharge curves allowing the cell to reach equilibrium states by allowing an open-circuit period of 3000 s after each incremental discharge step at 18 mA/g.

The Li^+ ion component diffusion coefficient, which is a measure of the capability of the Li^+ ions to move within the oxide lattice by a random motion without being influenced by a concentration gradient, was calculated from Eq. 2 [34,35]

$$D_{kLi} = D_{Li}\left(\frac{\partial \ln a_{Li}}{\partial \ln c_{Li}}\right)^{-1} = -\frac{4kTm_B V_M I_0}{\pi C_A Z_A q^2 M_B S^2}\frac{\Delta Es}{(\Delta Et)^2} \quad [2]$$

where Z_A is the charge valence of Li, q the elementary charge (1.602×10^{-14} C), T absolute temperature, k the Boltzmann constant, and a_{Li} and c_{Li} activity and concentration of Li in the active material, respectively.

D_{kLi} is related to the electrical mobility of the Li^+ ion (u_{Li}) by the Nernst-Einstein equation[34] from which the mobility was calculated

$$D_{kLi} = kTu_{Li}/q \quad [3]$$

The measured values of Li^+ ion chemical diffusion coefficient in $Li_aNi_{1-x}Co_xO_2$ was approximately 3×10^{-8} cm^2/s when a = 0.3. The value gradually decreased to 1×10^{-8} cm^2/s as the a value increased to 0.8 but was insensitive to Co contents (x values) as shown in Fig. 4. Scattered data points for $LiNiO_2$ are not fully understood but might be related to a phase transition.[36] Values obtained by the GITT technique are lower by an order of magnitude than the reported value of 2×10^{-7} cm^2/s for Li_aNiO_2 where a = 0.2-0.7, as obtained from an impedance measurement.[30] The measured values of Li^+ ion component diffusion coefficient and its mobility are shown in Fig. 5 and 6, respectively. These values are almost inde-

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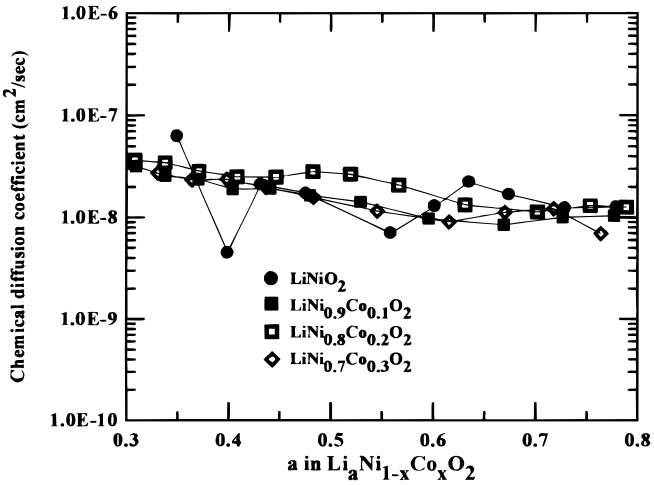

Figure 4. Chemical diffusion coefficient (D_{Li}) of Li^+ ions in $LiaNi_{1-x}Co_xO_2$ for $x = 0$, 0.1, 0.2, and 0.3 as a function of the value of *a*.

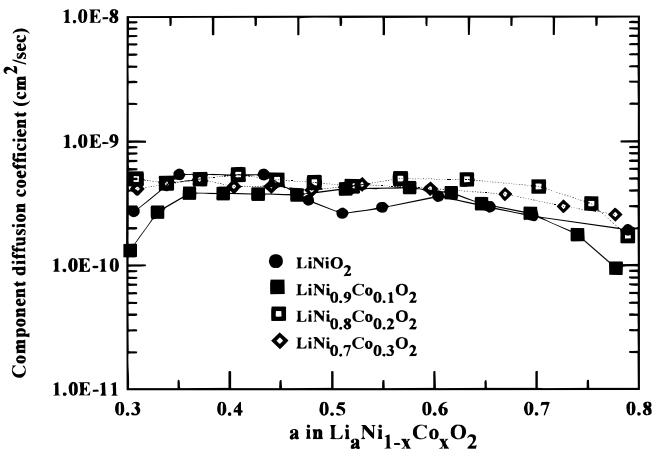

Figure 5. Component diffusion coefficient (D_{kLi}) of Li^+ ions in $Li_aNi_{1-x}Co_xO_2$ for $x = 0$, 0.1, 0.2, and 0.3 as a function of the value of *a*.

pendent of the Li (*a* value) and Co content, although they show a very slight decreasing trend as the *a* value increased from 0.3 to 0.8.

Electrochemical behavior of $LiNi_{1-x}Co_xO_2$ on cycling.—Measured values of initial charge, discharge, and irreversible capacities at various charge cutoff voltages of $LiNi_{1-x}Co_xO_2$ where $x = 0$, 0.1, 0.2, and 0.3 are summarized in Table I. The initial charge capacity values decreased significantly as the cobalt content (value of *x*)

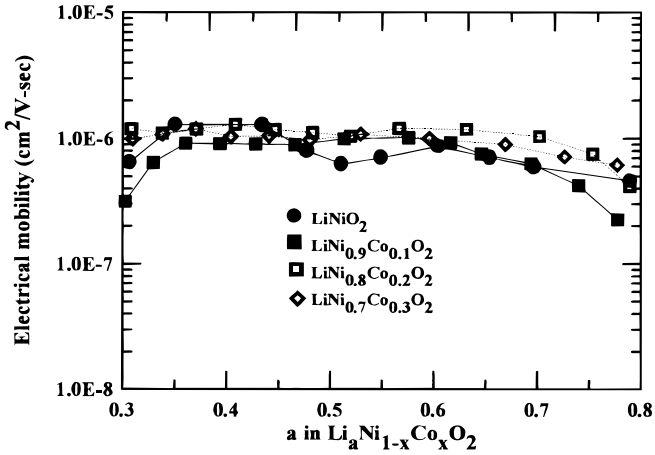

Figure 6. Electrical mobility (u_{Li}) of Li^+ ions in $Li_aNi_{1-x}Co_xO_2$ for $x = 0$, 0.1, 0.2, and 0.3 as a function of the value of *a*.

increased by each step when the charge cutoff voltage was 4.2 and 4.3 V, but the change in the charge capacity was rather insignificant when the cutoff voltage was 4.1 V. The discharge capacity increased when the cobalt content was increased from $x = 0$ to $x = 0.1$ at all cutoff voltages. However, when the *x* value was further increased to 0.2 and 0.3, the discharge capacity values decreased when the charge cutoff voltage was 4.2 and 4.3 V, whereas the values increased when the charge cutoff voltage was 4.1 V. These rather involved patterns of the dependence of capacity values on the composition and the cutoff voltage is due to the presence of a composition-dependent redox couple, "H2+H3," between 4.1 and 4.2 V, as shown by the cyclic voltammograms in Fig. 7. This couple does contribute to the measured capacities when the cutoff voltage is 4.1 V. $LiNiO_2$ shows two electrochemical couples, "M+H2" and "H2+H3." "M+H2" signifies a transition between a monoclinic phase (M) and a hexagonal phase (H2) and "H2+H3" a transition between a hexagonal phase (H2) and another hexagonal phase (H3). [13] The irreversible capacity loss upon cycling was attributed to the deformation of the NiO_2 layer in the $LiNiO_2$ crystal lattice due to the phase transition involving H2 and H3 phases with a shorter *c* axis lattice parameter.[13]

An interesting trend of the irreversible capacity values with the cobalt content in $LiNi_{1-x}Co_xO_2$ was observed. The measured capacity values were in the range 40 ± 2 mAh/g when $x = 0$, 20 ± 2 mAh/g when $x = 0.1$, 21 ± 2 mAh/g when $x = 0.2$, and 10 ± 1 mAh/g when $x = 0.3$, independent of the charge cutoff voltages as shown in Table I. The irreversible capacity value decreased significantly as Co was introduced at the $x = 0.1$ level. An increase of Co content from $x = 0.1$ to $x = 0.2$ did not change the capacity. However, a further increase of the Co content from $x = 0.2$ to $x = 0.3$ changed the capacity significantly. This change is reminiscent of the

Table I. Summary of charge, discharge, and irreversible capacities (mAh/g) of $LiNi_{1-x}Co_xO_2$ where $x = 0$, 0.1, 0.2, and 0.3 at the 0.1C rate with charge cutoff voltages of 4.1, 4.2, and a 4.3 V and a discharge cutoff voltage of 2.75 V.

	$LiNiO_2$	$LiNi_{0.9}Co_{0.1}O_2$	$LiNi_{0.8}Co_{0.2}O_2$	$LiNi_{0.7}Co_{0.3}O_2$
Charge Capacity (V)				
4.1	186	182	183	175
4.2	219	208	198	189
4.3	242	231	211	198
Discharge Capacity (V)				
4.1	144	161	163	165
4.2	180	187	175	178
4.3	204	213	190	189
Irreversible Capacity (V)				
4.1	42	21	18	10
4.2	39	21	23	11
4.3	38	18	21	9

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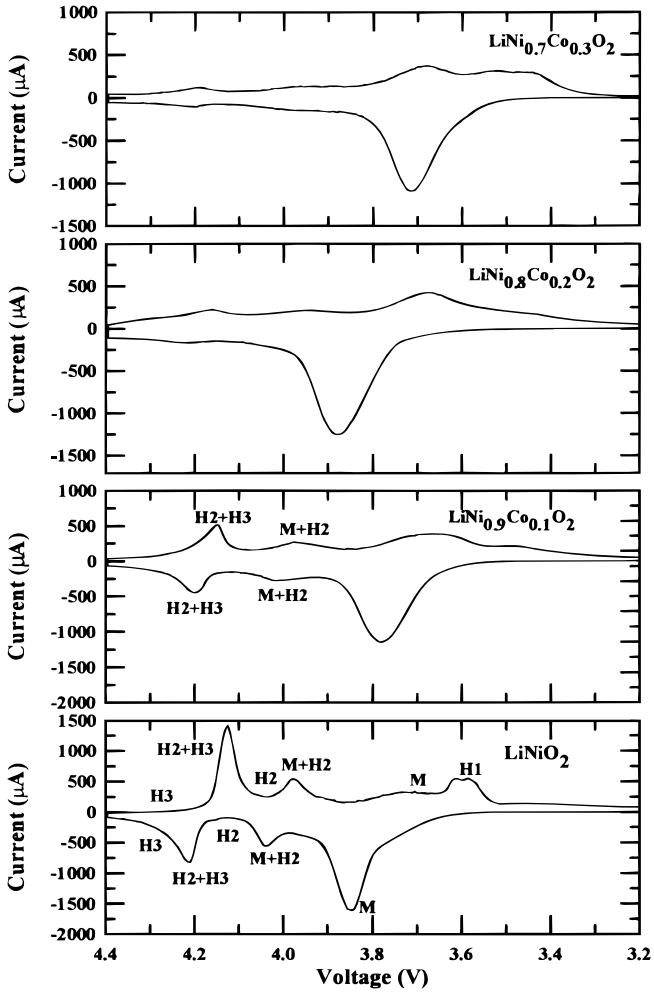

Figure 7. Cyclic voltammograms for the $LiNi_{1-x}Co_xO_2$ for $x = 0$, 0.1, 0.2, and 0.3. The test cell was a coin-type half-cell containing a Li metal reference/counter electrode and a $LiNi_{1-x}Co_xO_2$ cathode. The voltage scan rate was 0.05 mV/s.

electronic conductivity dependence on the x value as discussed previously. Although it appears possible that the reduction of the irreversible capacity as the Co content was increased from $x = 0.2$ to $x = 0.3$ could be related to the partial oxidation of Co^{3+} ion to Co^{4+} during charge, the present results are insufficient to confirm whether or not such a relationship exists.

The electrochemical stability of the cathode material, $LiNi_{1-x}Co_xO_2$, was studied by monitoring the specific capacity changes with cycling at various charge cutoff voltages. Results with a cutoff voltage of 4.3 V for the effects of x values (0, 0.1, 0.2, and 0.3) on the cycle stability are shown in Fig. 8. Results with 4.1 and 4.2 V show a similar overall effect of the x value. The stability (cycle life) is improved markedly in each step of the x value increase from 0 to 0.3, showing the best stability when $x = 0.3$. The present results are in agreement with earlier results by Delmas *et al.*,[15,16] which also showed the best cycling performance of a $LiNi_{1-x}Co_xO_2$/Li ($x = 0$, 0.1, 0.2, and 0.3) cell when $x = 0.3$ with no capacity fading over 50 cycles when cycled between 4 and 3 V. This improvement of the cycle stability as the x value was increased might be due to reduced phase transitions, M+H2 and H2+H3, as indicated by the cyclic voltammograms in Fig. 7 and an earlier study on $LiNiO_2$.[13]

Thermal stability of $LiNi_{1-x}Co_xO_2$.—DSC studies of $LiNi_{1-x}Co_xO_2$ were carried out after charging them at 4.2 and 4.3 V to evaluate the effects of the cobalt content ($x = 0$, 0.1, 0.2, and 0.3) and charge voltages on the thermal stability of the charged material

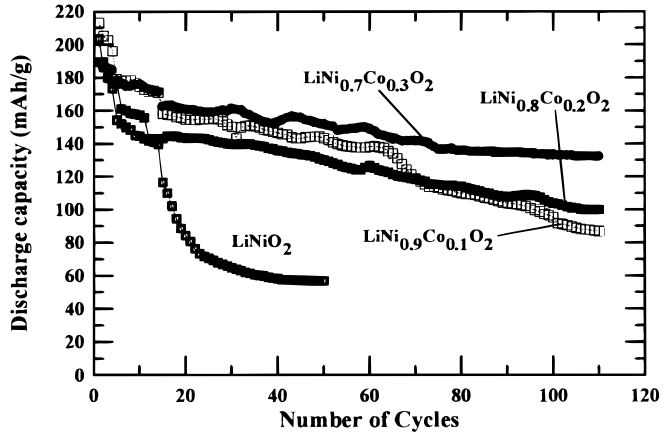

Figure 8. Plots of discharge capacities of $LiNi_{1-x}Co_xO_2$ for $x = 0$, 0.1, 0.2, and 0.3 as a function of the number of cycles with various charge cutoff voltages. The cycle test was carried out initially by charging and discharging at the 0.1C rate for 1-2 cycles, followed by three cycles at the 0.2C rate, 5-10 cycles at the 0.5C rate, and finally at the 1C rate for a total of 110 cycles. Charge and discharge cutoff voltages were 2.75 and 4.3 V, respectively.

in the electrolyte. Results at both charge voltages show clearly that the characteristic exothermic peaks move toward elevated temperature and the peak sizes shrink as the Co content increases, as shown in Fig. 9. These observations are in complete agreement with the results of a similar study on $LiNiO_2$ and $LiNi_{0.8}Co_{0.2}O_2$ after a 40 h float charging at 4.5 V.[5] The results in Fig. 9 also show that the peaks move toward lower temperature and the peak sizes increase as the charge voltage is increased from 4.2 to 4.3 V, indicating that as

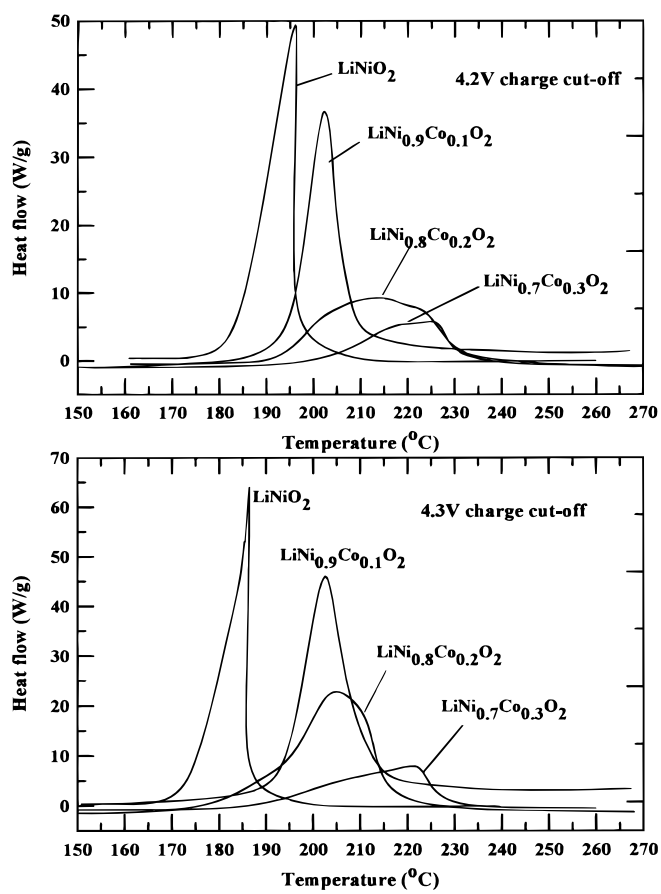

Figure 9. DSC curves of $LiNi_{1-x}Co_xO_2$ electrodes containing electrolyte for $x = 0$, 0.1, 0.2, and 0.3 after charging them at 4.2 and 4.3 V.

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more Li is extracted the less stable the material becomes as generally expected. Although it was anticipated from earlier results,[5] the present results confirm that $LiNi_{0.7}Co_{0.3}O_2$ is the most stable of the materials studied.

Conclusions

The electronic conductivity of $Li_aNi_{1-x}Co_xO_2$, where $x = 0$, 0.1, 0.2, and 0.3, was measured as a function of the value of a. The electronic conductivity of partially charged material ($a < 0.8$) increased substantially when the cobalt content was increased to $x = 0.3$ from 0.2. This conductivity increase might be due to partial oxidation of Co^{3+} to Co^{4+} by Li^+ extraction (charging) when the x value is greater than 0.2, whereas the predominant oxidation is Ni^{3+} to Ni^{4+} when the x value is 0.2 or smaller. The values of mobility, chemical diffusion coefficient, and Li^+ ion component diffusion coefficient in the partially charged material are in the neighborhood of 10^{-6} cm^{-2}/V s, 10^{-6} cm^2/V s, and 5×10^{-10} cm^2/s, respectively, and are rather insensitive to values of a and x. Results of electrochemical and DSC studies show that $LiNi_{0.7}Co_{0.3}O_2$ is the best cathode material for a Li cell among the materials studied in view of the best cycle stability, the smallest irreversible capacity, and the highest thermal stability with a minimal sacrifice in specific capacity.

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