



Water Adsorption and Storage Characteristics of Optimized LiCoO₂ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ Composite Cathode Material for Li-Ion Cells

Noh Mijung,^a Youngil Lee,^b and Jaephil Cho^{a,*}

^aDepartment of Applied Chemistry, Kumoh National Institute of Technology, Gumi, Korea

^bDepartment of Chemistry, University of Ulsan, Ulsan, Korea

This study investigated water adsorption and storage characterization of optimized LiCoO₂ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ composite with a weight ratio of 4:1 (LiCoO₂:LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂) in terms of the electrochemical properties and metal dissolution upon storage in air or in an electrolyte at 90°C. LiCoO₂ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ exhibited moisture (LiOH) and carbon (Li₂CO₃) contents of 198 and 627 ppm, respectively, after 7 days storage in air with a relative humidity of 60%. However, the composite sample annealed at 900°C showed moisture content of 100 ppm under the same condition. The simple mixing of LiCoO₂ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ exhibited a twofold higher moisture and carbon content than the same material annealed at 900°C. This enhancement was attributed to the possible formation of a structurally robust phase after annealing. The annealed sample showed no reduction in its initial capacity and capacity retention even after exposure to air, compared with the samples before being exposure to air. The results indicate that LiOH and Li₂CO₃ at amounts < 100 ppm had little influence on the electrochemical properties. Upon 90°C storage at 4.3 V, the concentration of Ni and Co in the electrolyte dissolved from the individual LiCoO₂ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathodes was > 300 ppm but that from the annealed composite was only 70 ppm. Such metals dissolution resulted in local destruction of the LiCoO₂ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ structure, but the composite annealed at 900°C for 2 h was structurally stable.

© 2006 The Electrochemical Society. [DOI: 10.1149/1.2186041] All rights reserved.

Manuscript submitted December 7, 2005; revised manuscript received January 17, 2006. Available electronically April 3, 2006.

The greatest technical hurdle for commercial Li-ion cells, using a 4.2-V cutoff voltage, is the thermal instability of the cell with the cathode making the most significant contribution to the thermal instability.¹⁻⁹ The delithiated cathode violently generates the oxygen from the reaction with the flammable electrolyte, resulting in thermal runaway at elevated temperatures or overcharged states. The LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ ternary mixed phase of LiCoO₂, LiNiO₂, LiMnO₂ has α-NaFeO₂ structure and overcomes the drawbacks of LiCoO₂ and LiNiO₂ (thermal instability) and LiMnO₂ (spinel-like phase transformation through minor atomic arrangements, leading to an eventual deterioration of the electrode performance).^{10,11} In addition, the initial discharge capacity of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ is similar to that of LiCoO₂, showing ~154 mAh/g at 4.3 V. Until now, studies on this cathode have been focused on improving the thermal stability, synthetic method, lithium diffusivity, and structural changes upon lithium extraction.¹²⁻¹⁶ However, its major drawback is the low rate capability and low electrode density compared with LiCoO₂. For example, the electrode density of the LiCoO₂ is 3.8 g/cm³ with a mixture of 10 and 5-μm-sized powders, while that of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ is only 3.4 g/cm³. Therefore, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cannot be used as a major component of the cathode materials and can only be used after physical blending with LiCoO₂.

One of the fundamental problems with LiNi_{1-x-y}Co_xMn_yO₂ is the rapid reaction with air, resulting in the formation of Li₂CO₃ and LiOH on the surface.^{17,18} Several studies have reported that the extraction of Li in the lattice led to cation mixing, and metal ions reside in the Li sites.^{19,20} Liu et al. reported that the deterioration of LiNiO₂ upon storage is attributed to both the formation of the Li₂CO₃ phase and the Ni²⁺ ions in the 3a lithium sites.¹⁹ However, there are no reports on the moisture uptakes of the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ upon exposure to air and structural stability upon storage at 90°C. Normally, cathode powders should have < 100 ppm moisture after storage in air for 7 days with a relative humidity of 20%. The moisture in the powders leads to the evolution of gases at charged states upon storage above 60°C.²¹

This paper reports the effect of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ in the LiCoO₂ cathode on the electrochemical and storage behavior after

storage in air and in an electrolyte at 90°C. The optimized composition with a LiCoO₂-to-LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ weight ratio of 4:1 was selected.

Experimental

The coprecipitated Ni_{1/3}Co_{1/3}Mn_{1/3}(OH)₂ powder was prepared by dissolving metal nitrates in water and adjusting the pH to ~11 using NaOH and NH₄OH in the reactor with a rotating mixer with a speed of ~1000 rpm at 50°C. The reaction was stopped after 4-h reaction in order to obtain a particle size < 4 μm. The detailed experimental procedures are described elsewhere.⁴ Ni_{1/3}Co_{1/3}Mn_{1/3}(OH)₂ powder and LiOH·H₂O at a molar ratio of 1:1.05 was thoroughly mixed and fired at 480 and 900°C for 4 and 15 h, respectively. The Li content of the as-prepared sample was 1.01, as confirmed by inductively coupled plasma-mass spectroscopy (ICP-MS) analysis. LiCoO₂ powder was prepared from sintering the mixture of stoichiometric amounts of Li₂CO₃ and Co₃O₄ at 1000°C for 4 h. The moisture (OH⁻) in the sample was determined using a Karl-Fisher moisture titrator at 250°C (prior to measuring, the sample was vacuum-dried at 150°C for 2 h to remove the H₂O molecules adsorbed on the sample). Therefore, the measured moisture was from OH⁻ in LiOH. The carbon content was measured using a CHS element analyzer at 1000°C in an oxygen atmosphere. LiCoO₂ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ with various weight ratios were homogenized in an absolute ethanol and vacuum-dried and annealed at 150 and 900°C for 10 and 2 h, respectively. All the as-prepared samples were kept in a dry holder with a humidity < 10% before the air-exposure test at a relative humidity of 60 and 20%. The electrochemical properties were tested in a coin-type 2016R cell with lithium metal as the anode, and the cathode consisted of the following active materials: Super P carbon black: /poly(vinylidene difluoride) binder with a weight ratio of 94:3:3. The electrolyte for the coin-type half-cells (2016 type) was 1 M LiPF₆ with ethylene carbonate/diethylene carbonate/ethyl methyl carbonate (EC/DEC/EMC = 30:30:40 vol %) (Cheil Industries, Korea). The HF content in the electrolyte was ~10 ppm. The capacity and capacity retention were measured between 3 and 4.3 V at various rates between 0.1 and 1 C (150 mA/g). For the 90°C storage test, the sample electrodes before and after charging to 4.3 V were kept in vials containing 5 g of the electrolytes in a glove box for 1 and 7 days. The amount of metal ions (M = Co, Mn, and Ni) dissolved

* Electrochemical Society Active Member.

^z E-mail: jphoto@kumoh.ac.kr

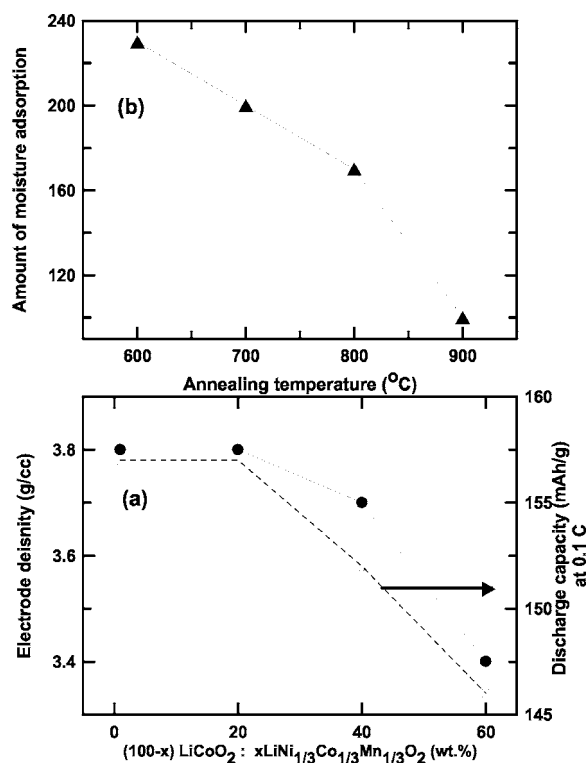


Figure 1. Plots of (a) electrode density as a function of x in $(1-x)$ LiCoO_2 : $x\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (wt %) and (b) the amount of moisture adsorption as a function of annealing temperature of x in (a).

from the samples was measured by ICP-MS, and the electrolytes were obtained from the cycled cells using a centrifugal separation method.

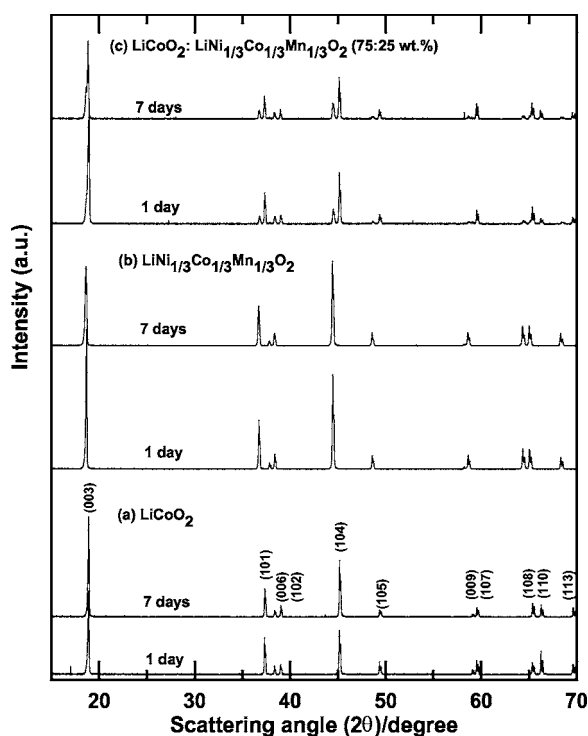


Figure 2. XRD diffraction of (a) LiCoO_2 , (b) $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and (c) LiCoO_2 : $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (75:25 wt %) annealed at 900°C for 2 h after 1 and 7 days air exposure in a relative humidity of 60%.

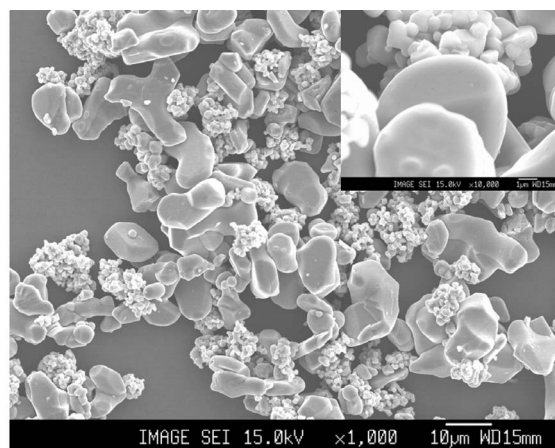


Figure 3. SEM image of the LiCoO_2 : $x\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (4:1 wt %) annealed at 900°C for 2 h.

Powder X-ray diffraction (XRD) measurements were carried out using a M18XHF-SRA diffractometer (MAC Science Co.) with a Cu-target tube was used for XRD measurement with a graphite monochromator. The X-ray photoelectron spectra (XPS) were recorded with a Physical Electronics Quantum 2000 ESCA spectrometer with a Mg K α anode (1253.6 eV) as the X-ray source operated at 24.1 W in a vacuum of $<10^{-8}$ Torr. The binding energy was corrected to the C 1s peak at 284.5 eV.

Results and Discussion

Figure 1 shows the changes in discharge capacities and cathode electrode density of the composite cathodes with $(100-x)\text{LiCoO}_2$: $x\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ after pressing. The highest electrode density and capacities were obtained in the composite with $x = 20$ wt %. In addition, the moisture content of the composite ($x = 20$ wt %) was measured after annealing between 600 and 900°C for 2 h followed by air exposure for 7 days at a relative humidity of 60%. The smallest value was obtained from the sample

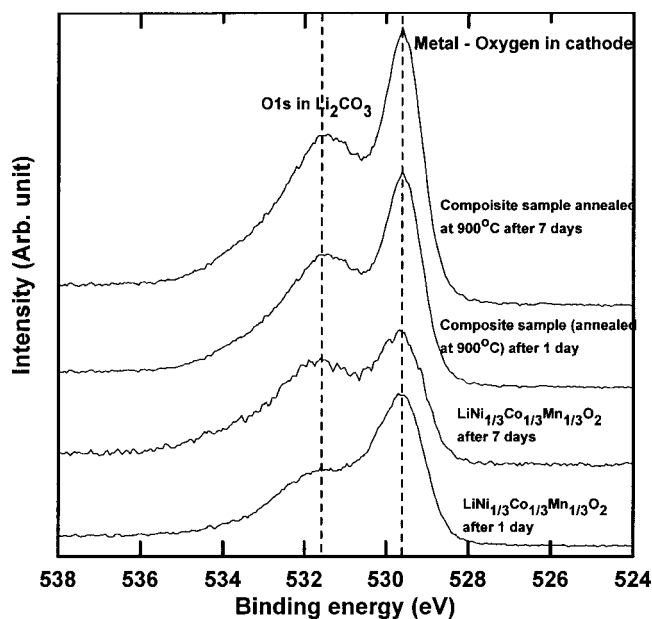


Figure 4. XPS O 1s peak in the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and annealed the composite after 1 day and 7 days air exposure.

Table I. The moisture and carbon content in LiCoO₂, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, annealed at 900°C, and the composite samples (before annealing and after annealing for 2 h at 900°C) after 1 day and exposure to air for 7 days. The composite sample consists of LiCoO₂:LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ at a weight ratio of 4:1. The relative humidity was 60 and 20%. The data is recorded in parts per million.

	1 day	7 days (20%)	7 days (60%)	1 day	7 days (60%)
LiCoO ₂	60	158	198	120	336
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	50	558	627	160	304
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂ (900°C for 2 h)	174	192	648	154	329
Blended sample (before annealing)	95	201	225	140	247
Blended sample (after annealing)	65	88	100	87	100

annealed at 900°C. Accordingly, we select the optimal composite as a 4:1 weight ratio of LiCoO₂ to LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂.

Figure 2 shows the XRD patterns of LiCoO₂ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and the optimized composite materials after 1 and 7 days exposure in a relative humidity of 60%. The patterns were indexed to the hexagonal-type structural group ($R\bar{3}m$). The lattice constants a and c for the LiCoO₂ material were 2.8146(2) and 14.0461(8) Å, respectively. [lattice constants of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ are $a = 2.8612(4)$ and $c = 14.2290(2)$]. In addition, the composite cathode annealed at 900°C, as a (LiCoO₂:LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂) weight ratio of 4:1, shows both phases, and the a and c values of the LiCoO₂ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ were found to be 2.8148(5), 14.0462(5) Å and 2.8558(6), 14.2155(4) Å, respectively. The changes in lattice constants after annealing at 900°C suggests interdiffusion between the LiCoO₂ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (e.g., LiCo_{1-x}M_xO₂ (M is Ni and Mn) and LiCo_{1/3+x}Ni_{1/3}Mn_{1/3}O₂). Figure 3 shows the scanning electron micrograph (SEM) of the composite cathode after annealing at 900°C, and the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ fine powders appear to partially coat the LiCoO₂.

Table I shows carbon and moisture content of the powders upon open air storage at different relative moisture levels after 7 days. These contents are indicative of the amounts of LiOH and Li₂CO₃ that formed on the particle surface.¹⁷ In the case of LiCoO₂, the moisture content increased from 60 to 158 and 198 ppm after 7 days storage in air at a relative humidity of 20 and 60%, respectively. The moisture content of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ increased rapidly from 158 ppm to 558 and 627 ppm at a relative humidity of 20 and 60%, respectively. However, its moisture content after 7 days was 3 times higher than LiCoO₂. When the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ powder was annealed at 900°C for 2 h, the moisture content decreased rapidly to 192 ppm at 20% humidity. In contrast, the moisture content increased rapidly to 648 ppm after 7 days at 60% humidity. The moisture content of the composite without annealing was 225 ppm after

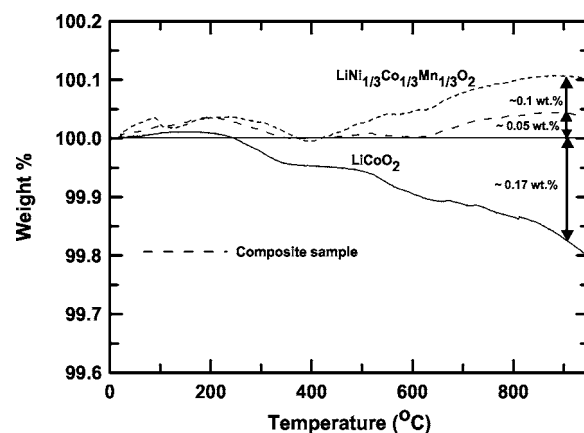
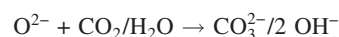


Figure 5. TGA of the LiCoO₂, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, and the composite between 100 and 900°C. The heating rate was 5°C/min.

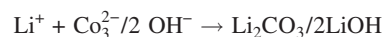
7 days storage at 60% humidity. Surprisingly, the moisture content of the annealed composite sample was 100 ppm, which was half that of the sample without annealing under identical conditions to one before annealing. The trends of the carbon content in the Li₂CO₃ of the samples were similar to those for the moisture.

Table II shows the Rietveld analysis results of the LiCoO₂, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, and the optimized composite (annealed at 900°C) after 1 and 7 days air exposure at 60% humidity (Fig. 1). In contrast to LiCoO₂, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ showed the cation mixing, which corresponded to 9% (metal atoms in Li sites) after air exposure at a relative humidity of 60%. Increased cation mixing in the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ was also observed in higher (104) peak intensity than (003) peak intensity after air exposure. The annealed composite showed no change in the amount of metal atoms in the lithium 3a sites after 7 days. According to Liu et al., the slow and spontaneous reduction of Ni³⁺ to Ni²⁺ occurs in LiNiO₂ during storage, and a weakening of the Ni–O bond causes the formation of surface active oxygen O²⁻.¹⁹

This oxygen undergoes reactions with CO₂/H₂O in air according to the following reaction



LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ contains stable Ni²⁺, which cannot react with CO₂/H₂O. However, when the H₂O on the particle surface absorbs absorbed CO₂ from air, it becomes slightly acidic, attacking the cathode surface of the Li ions according to the following equation



Consequently, Li₂CO₃ formation is expected to cause cation mixing in the sample, which is well supported by Rietveld analysis and water adsorption data. Further evidence for the increasing fraction of Li₂CO₃ in the sample was observed by XPS of the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and the annealed composite samples before

Table II. Rietveld analysis results of the LiCoO₂ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ after exposure to air for 1 and 7 days in a relative humidity of 60%.

	a (Å)	c (Å)	$R_p/R_{wp}/R_B$	Metal amount at 3a sites
LiCoO ₂	2.8146(2)	14.0461(8)	10.5/11.4/2.4	0
LiCoO ₂ (after 7 days)	2.8145(6)	14.0461(3)	10.7/10.5/1.9	0
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	2.8612(4)	14.2290(2)	11.3/11.2/2.1	0.01
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂ (after 7 days)	2.8623(3)	14.2331(6)	12.4/10.6/2.5	0.09
LiCoO ₂ in composite	2.8148(5)	14.0462(5)	14.5/13.3/3.2	0
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂ in composite	2.8558(6)	14.2155(4)	15.2/12.5/2.9	0.01
LiCoO ₂ in composite (after 7 days)	2.8144(5)	14.0461(5)	15.6/11.3/4.2	0
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂ in composite (after 7 days)	2.8555(6)	14.2154(4)	14.2/13.5/3.9	0.01

Table III. Charge and discharge capacities of the LiCoO_2 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and composite sample with/without annealing at 900°C after 1 (*) and 7 days air exposure in a relative humidity of 60%.^a

	Charge capacity*	Discharge capacity*	Reversible capacity ratio (%)	Discharge capacity after 7 days
LiCoO_2	165	157	95	147
$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$	168	152	90	140
$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (annealed at 900°C)	166	141	85	125
Blended sample without annealing	162	154	95	145
Blended sample after annealing	163	157	96	155

^a A unit of capacity is mAh/g, which was measured between 4.3 and 3 V at a rate of 0.1 C (15 mA/g).

and after air exposure for 7 days (Fig. 4). The O 1s peak intensity of Li_2CO_3 at 531.5 eV in the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ increased as compared to that of the metal–oxygen peak at 529.5 eV after 7 days. However, relative peak intensity appears to be constant in the composite sample even after 7 days exposure.

Table III shows the charge and discharge capacities of LiCoO_2 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and the optimized composite samples along with first cycle efficiencies. The first discharge capacity and reversible capacity ratio of the LiCoO_2 are apparently better than $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. The composite cathode showed a discharge capacity of 154 mAh/g, which is similar to the result of the simple calculation of each discharge capacity value. The annealed composite shows the 156-mAh/g and a 2% enhanced initial efficiency ratio compared with that before annealing. The $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ annealed at 900°C shows a rapid capacity drop to 141 mAh/g. Figure 5 shows the thermogravimetric analysis (TGA) curves of the LiCoO_2 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and the composite samples between room temperature and 900°C . The weight loss or gain of each cathode at 900°C corresponds to $\text{LiCoO}_{1.99}$, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2.006}$, and the composite sample with an oxygen stoichiometry of 2.003.

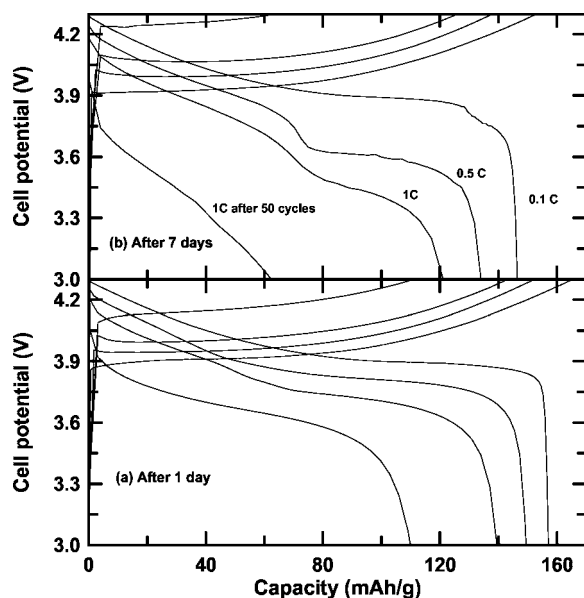


Figure 6. Voltage profiles of the air-exposed LiCoO_2 after (a) 1 day and (b) 7 days in a relative humidity of 60% with a variation in the C rate of 0.1, 0.5, and 1 C after 50 cycles at the rate of 1 C between 3 and 4.3 V.

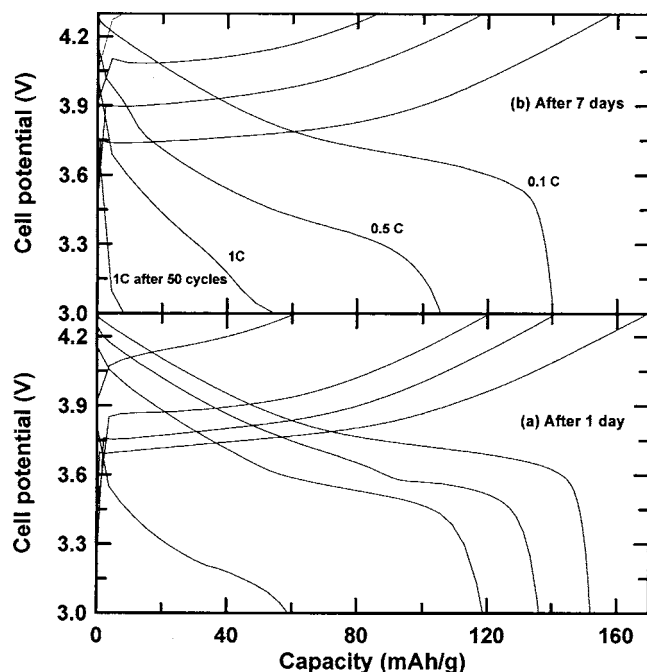


Figure 7. Voltage profiles of the air-exposed $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ after (a) 1 day and (b) 7 days in a relative humidity of 60% with a variation in the C rate at 0.1, 0.5, and 1 C and after 50 cycles at a rate of 1 C between 3 and 4.3 V.

Based on the capacity data, a very small (0.006 mol) oxygen-rich stoichiometry in the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ resulted in a deterioration in capacity, even though a very slight oxygen-rich stoichiometry in the composite did not affect the capacity.

Table III also compares the discharge capacities of the LiCoO_2 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and the composite after 7 days storage in a relative humidity of 60%, and all the cathodes showed a large capacity decrease except for the annealed composite. For instance,

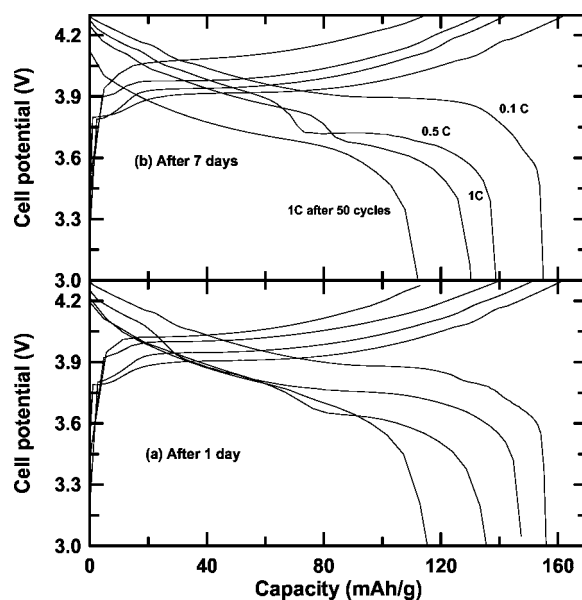


Figure 8. Voltage profiles of the air-exposed, annealed composite after (a) 1 day and (b) 7 days in a relative humidity of 60% with a variation in the C rate at 0.1, 0.5, and 1 C and after 50 cycles at the rate of 1 C between 3 and 4.3 V.

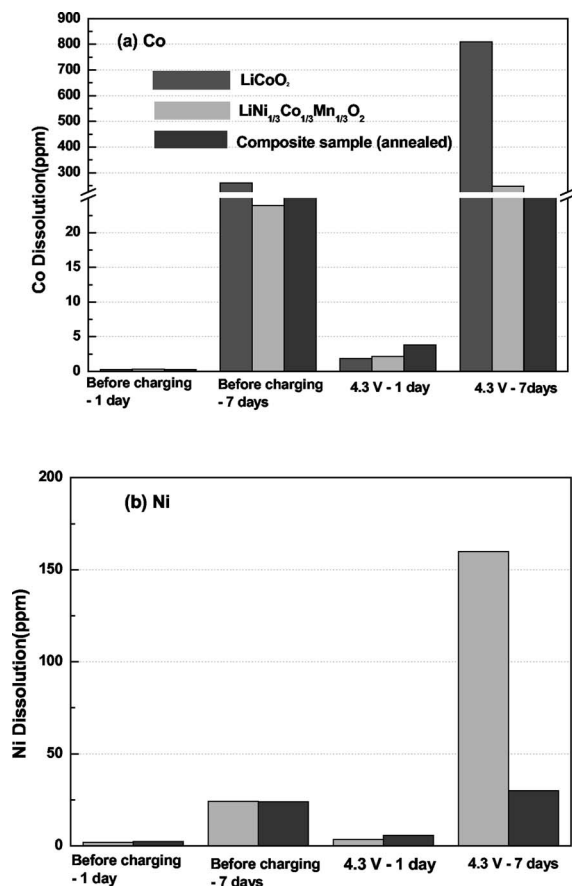


Figure 9. Plots of (a) Co dissolution and (b) Ni dissolution in LiCoO₂, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, and annealed composite electrodes before charging and after charging at 4.3 V at 90°C. All the samples were soaked in the electrolyte.

LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and annealed LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ samples exhibited discharge capacities of 140 and 125 mAh/g after 7 days, respectively. This is coincident with the trends of the moisture and carbon. However, a LiOH and Li₂CO₃ content in the sample < 100 ppm did not affect the capacity. Furthermore, the capacity retention and rate capability of the LiCoO₂, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, and the annealed composite cathodes were compared after air exposure for 7 days at a relative humidity of 60% in Fig. 6-8. The LiCoO₂ and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathodes showed deteriorating capacity with an increasing rate from 0.1 to 1 C, and after 50 cycles. In the case of LiCoO₂, the capacity retention after 50 cycles at 1 C was 71% after 1 day exposure but decreased to 30% after 7 days exposure. A similar result in the rate capability was observed, and discharge capacities at 0.1 and 1-C rates decreased to 147 and 110 mAh/g, respectively, after 7 days from 157 and 122 mAh/g, respectively. The LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cathode showed inferior characteristics to LiCoO₂, for example, 5% capacity retention was observed after 50 cycles at a 1-C rate (150 mA/g) after 7 days storage. Such drastic capacity fading was attributed to LiOH and Li₂CO₃ impurities on the particles acting as insulators, thereby increasing the interfacial resistance. The composite sample annealed at 900°C showed no decrease in either the rate capability or the cycle life after 7 days.

The structural stability of the as-prepared and charged cathodes at 90°C was investigated (see Fig. 9). The electrodes before and after charging to 4.3 V were stored in the electrolytes at 90°C for 1 and 7 days, and the amount of metal (Ni, and Co) dissolution was measured using ICP-MS. In the case of LiCoO₂, no Co ions were detected in the electrode before charging. However, after 7 days

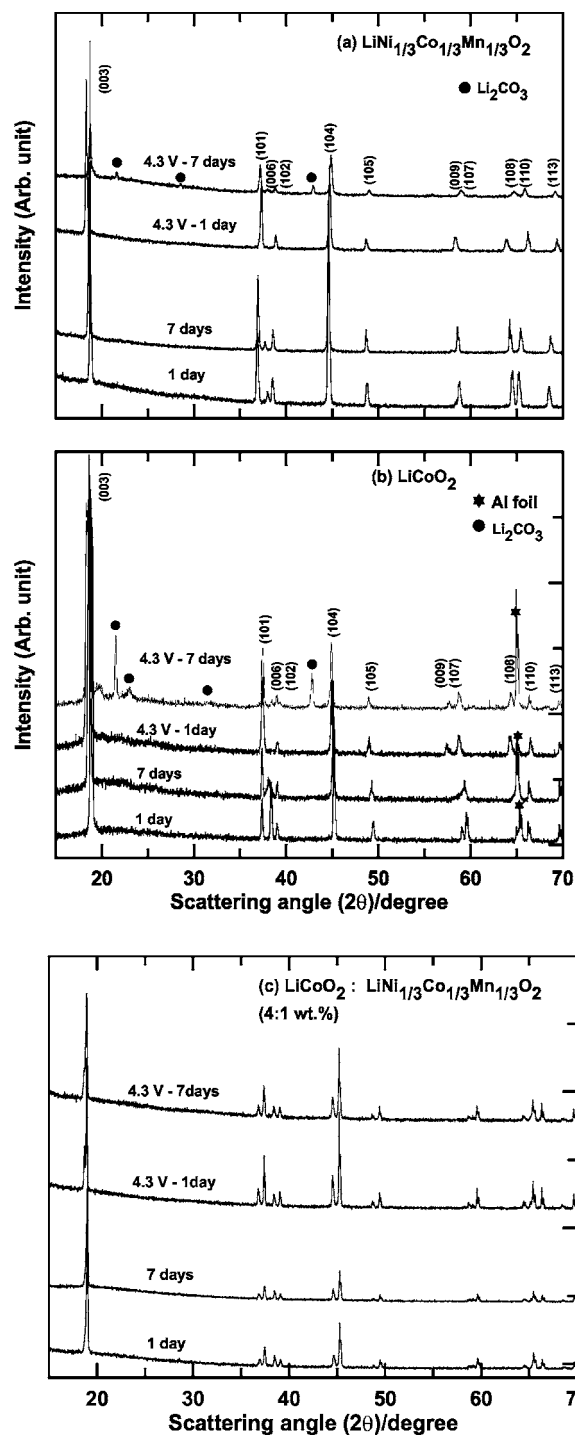
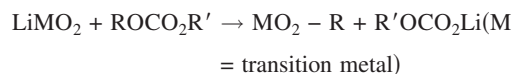


Figure 10. XRD patterns of (a) LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, (b) LiCoO₂, and (c) annealed composite at the same storage conditions in Fig. 9.

storage, 30 ppm Co dissolution was measured. After charging at 4.3 V and holding at this voltage for 7 days, the amount of Co dissolution increased to 810 ppm. In contrast, the level of metal dissolution was smaller in the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ sample than the LiCoO₂, and the amount of Ni and Co in solution after 7 days storage at 4.3 V was 248 and 170 ppm, respectively. The annealed composite shows much lower amount of metal dissolution, with 24 and 25 ppm Co and Ni being detected, respectively. Detectable amounts of LiOH were observed in the cathodes (after 1 day), which is believed to react with LiPF₆, making acidic HF in the electrolytes. HF

can easily dissolve the highly oxidized metal ions. Mn dissolution was not detected because Mn^{4+} ions in the sample did not participate in redox reactions.

Figure 10 shows the XRD patterns of the Li_xCoO_2 , $\text{Li}_x\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and annealed composite stored at different conditions for 1 and 7 days, before charging, and after charging to 4.3 V. The LiCoO_2 cathode electrode stored at 4.3 V for 7 days shows peaks corresponding to Li_2CO_3 , which formed on the particle surface as a result of a reaction between the electrolyte and the particle surface during storage at 90°C. The formation of Li_2CO_3 on the particle surface may result from reactions between the nucleophilic cathode and the highly electrophilic solvents, possibly leading to the formation of lithium alkyl carbonates as follows^{20,22}



Consequently



Evidence of Li_2CO_3 formation is supported by the XRD patterns of Li_xCoO_2 in the sample at 4.3 V after 7 days.

Both Co and Ni dissolution into the electrolyte is expected to damage the surface, leading to local destruction of the structure. As shown in Fig. 10, the intensities of the (006) and (102) peaks were reversed and were accompanied by peak broadening. For example, the peak broadening factor (Δk) of the LiCoO_2 cathode after 7 days storage at 4.3 V at 90°C increased to 0.19 from 0.11 (± 0.02) after 1 day. This shows that Co dissolution led to structural defects. A similar behavior was also observed in the $\text{Li}_x\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, even though the rate of Li_2CO_3 formation was somewhat decreased. This is expected to lead to the loss of Ni, Co, and Li ordering in the layered $R\bar{3}m$ structure. This structural change is accompanied by oxygen loss and a lowering of the Ni and Co oxidation states in the surface layer. However, there was no Li_2CO_3 phase in the annealed composite and peak intensity was retained even after 7 days storage at 4.3 V. This suggests that the annealed composite may be turned into a chemically and structurally stable form as a result of both the coating effect and the possible formation of the interdiffused $\text{LiCo}_{1-x}\text{M}_x\text{O}_2$ (M is Ni and Mn) and $\text{LiCo}_{1/3+x}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ phases, as described above.

Conclusion

An optimized composite cathode with a LiCoO_2 to $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ weight ratio of 4:1 showed significantly lower LiOH and Li_2CO_3 levels upon air exposure compared with the individual LiCoO_2 and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. This was attributed to

the formation of stable interdiffused phases. In addition, the rate capability and capacity retention of the composite were much better than LiCoO_2 and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ after exposure to air, and no initial capacity decrease was observed. In particular, the composite sample showed good structural stability at 90°C and it can compensate for the drawbacks associated with the LiCoO_2 cathode.

Acknowledgment

This work was supported by the Division of Advanced Batteries in NGE Program (Project no. 10016439).

Kumoh National Institute of Technology assisted in meeting the publication costs of this article.

References

1. Y. Gao, M. V. Yakovleva, and W. B. Ebner, *Electrochem. Solid-State Lett.*, **1**, 117 (1998).
2. Y. Nishida, K. Nakane, and T. Satoh, *J. Power Sources*, **68**, 561 (1997).
3. J. Cho, *Chem. Mater.*, **13**, 4537 (2001).
4. J. Cho, T.-J. Kim, J. Kim, M. Noh, and B. Park, *J. Electrochem. Soc.*, **151**, A1899 (2004).
5. H. Omand, T. Brousse, C. Marhic, and D. M. Schleich, *J. Electrochem. Soc.*, **151**, A922 (2004).
6. Y. Lee, M. G. Kim, J. Kim, Y. Kim, and J. Cho, *J. Electrochem. Soc.*, **152**, A1824 (2005).
7. H. Arai, M. Tsuda, K. Saito, M. Hayashi, and Y. Sakurai, *Solid State Ionics*, **109**, 295 (1998).
8. M. Yoshio, H. Noguchi, J.-I. Itoh, M. Okada, and T. Mouri, *J. Power Sources*, **90**, 176 (2000).
9. S. H. Park, C. S. Yoon, S. G. Kang, H.-S. Kim, S.-I. Moon, and Y.-K. Sun, *Electrochim. Acta*, **49**, 557 (2004).
10. N. Yabuuchi and T. Ohzuku, *J. Power Sources*, **119**, 171 (2003).
11. J. Choi and A. Manthiram, *Electrochem. Solid-State Lett.*, **8**, C102 (2005).
12. K. M. Shaju, G. V. Subba Rao, and B. V. R. Chowdari, *J. Electrochem. Soc.*, **151**, A1324 (2004).
13. K. M. Shaju, G. V. Subba Rao, and B. V. R. Chowdari, *Electrochim. Acta*, **48**, 145 (2002).
14. S. H. Park, K. S. Park, Y. K. Sun, K. S. Nahm, Y. S. Lee, and M. Yoshio, *Electrochim. Acta*, **46**, 1215 (2001).
15. G.-H. Kim, S. T. Myung, H. J. Bang, J. Prakash, and Y.-K. Sun, *Electrochem. Solid-State Lett.*, **7**, A477 (2004).
16. M. G. Kim, H. J. Shin, J.-H. Kim, S.-H. Park, and Y.-K. Sun, *J. Electrochem. Soc.*, **152**, A1320 (2005).
17. S. W. Song, G. V. Zhuang, and P. N. Ross, Jr., *J. Electrochem. Soc.*, **151**, A1162 (2004).
18. K. Matsumoto, R. Kuzuo, K. Takeya, and A. Yamanaka, *J. Power Sources*, **81-82**, 558 (1999).
19. H. S. Liu, Z. R. Zhang, Z. L. Gong, and Y. Yang, *Electrochem. Solid-State Lett.*, **7**, A190 (2004).
20. D. Aurbach, K. Gamolsky, B. Markosky, G. Salitra, Y. Gofer, U. Heider, R. Oesten, and M. Schmidt, *J. Electrochem. Soc.*, **147**, 1322 (2000).
21. J. Kim, Y. Hong, K. S. Ryu, M. G. Kim, and J. Cho, *Electrochem. Solid-State Lett.*, **9**, A19 (2006).
22. A. M. Andersson, D. P. Abraham, R. Haasch, S. MacLaren, J. Liu, and K. Amine, *J. Electrochem. Soc.*, **149**, A1358 (2002).