

Short communication

## Effect of CO<sub>2</sub> on layered Li<sub>1+z</sub>Ni<sub>1-x-y</sub>Co<sub>x</sub>M<sub>y</sub>O<sub>2</sub> (M = Al, Mn) cathode materials for lithium ion batteries

Kenji Shizuka<sup>a,\*</sup>, Chikara Kiyohara<sup>b</sup>, Kouji Shima<sup>c</sup>, Yasuo Takeda<sup>d</sup>

<sup>a</sup> Battery Materials Laboratory, Research and Development Division, Mitsubishi Chemical Group Science and Technology Research Center Inc., 8-3-1, Chuo, Ami, Inashiki, Ibaraki 300-0332, Japan

<sup>b</sup> Mitsubishi Chemical Group Science and Technology Research Center Inc., 1000, Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan

<sup>c</sup> Mitsubishi Chemical Corporation, 1, Bannosu-cho, Sakaide, Kagawa 762-8510, Japan

<sup>d</sup> Department of Chemistry Faculty of Engineering, Mie University, Yamachi, Kurima-Cho, Tsu, Mie 514-8507, Japan

Received 1 August 2006; received in revised form 27 December 2006; accepted 4 January 2007

Available online 16 January 2007

### Abstract

We investigated the effect of CO<sub>2</sub> on layered Li<sub>1+z</sub>Ni<sub>1-x-y</sub>Co<sub>x</sub>M<sub>y</sub>O<sub>2</sub> (M = Al, Mn) cathode materials for lithium ion batteries which were prepared by solid-state reactions. Li<sub>1+z</sub>Ni<sub>(1-x)/2</sub>Co<sub>x</sub>Mn<sub>(1-x)/2</sub>O<sub>2</sub> (Ni/Mn mole ratio = 1) singularly exhibited high storage stability. On the other hand, Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> samples were very unstable due to CO<sub>2</sub> absorption. XPS and XRD measurements showed the reduction of Ni<sup>3+</sup> to Ni<sup>2+</sup> and the formation of Li<sub>2</sub>CO<sub>3</sub> for Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> samples after CO<sub>2</sub> exposure. SEM images also indicated that the surfaces of CO<sub>2</sub>-treated samples were covered with passivation films, which may contain Li<sub>2</sub>CO<sub>3</sub>. The relationship between CO<sub>2</sub>-exposure time and CO<sub>3</sub><sup>2-</sup> content suggests that there are two steps in the carbonation reactions; the first step occurs with the excess Li components, Li<sub>2</sub>O for example, and the second with LiNi<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> itself. It is well consistent with the fact that the discharge capacity was not decreased and the capacity retention was improved until the excess lithium is consumed and then fast deterioration occurred.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Lithium ion battery; Cathode; Li<sub>1+z</sub>Ni<sub>1-x-y</sub>Co<sub>x</sub>M<sub>y</sub>O<sub>2</sub>; CO<sub>2</sub>; Ni valence

### 1. Introduction

Co- and Al-doped layered LiNi<sub>1-x-y</sub>Co<sub>x</sub>Al<sub>y</sub>O<sub>2</sub> has been used as cathode materials in lithium ion batteries. This material is relatively low in cost and excellent in specific capacity and cycle life. However, its surface is strongly basic compared to LiCoO<sub>2</sub>. It is closely related to the chemical instability of LiNiO<sub>2</sub> after contacting with CO<sub>2</sub> and H<sub>2</sub>O in air. Matsumoto et al. [1] reported that almost 8% of Li was converted to Li<sub>2</sub>CO<sub>3</sub> on the surface of LiNi<sub>0.81</sub>Al<sub>0.03</sub>Co<sub>0.16</sub>O<sub>2</sub> after exposure to air for 500 h even at room temperature. Moshtev et al. [2] also investigated the reaction of LiNiO<sub>2</sub> with H<sub>2</sub>O and indicated that LiNiO<sub>2</sub> can be chemically delithiated in H<sub>2</sub>O without electron exchange to form LiOH. Recently, Liu et al. [3] studied the origin of deterioration of LiNiO<sub>2</sub> cathode material during storage in air. They proposed a surface reaction mechanism based on the reduction of Ni and

the evolution of active oxygen species. Yet enough examination has not been carried out for the other LiNiO<sub>2</sub>-based cathode with the different composition. In addition, the CO<sub>2</sub> effect on the electrochemical performance of LiNiO<sub>2</sub>-based cathode material is not clear.

In this study, we investigated the effect of CO<sub>2</sub> on Li<sub>1+z</sub>Ni<sub>1-x-y</sub>Co<sub>x</sub>M<sub>y</sub>O<sub>2</sub> (M = Al, Mn) cathode materials using chemical analysis, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and scanning electron microscopy (SEM). A surface reaction mechanism was proposed to interpret the chemical instability of Li<sub>1+z</sub>Ni<sub>1-x-y</sub>Co<sub>x</sub>M<sub>y</sub>O<sub>2</sub> during storage in air. In this formula, *z* means the excess lithium content. In addition, we also discussed whether the excess lithium exists in the crystal or out of the crystal (on the surface).

### 2. Experimental

Cathode materials in Table 1 were prepared by solid-state reactions with stoichiometric mixing of Ni(OH)<sub>2</sub>, Co(OH)<sub>2</sub>, Mn<sub>3</sub>O<sub>4</sub>, AlOOH and LiOH, followed by calcination for 10 h.

\* Corresponding author. Tel.: +81 29 887 5284; fax: +81 29 887 3308.  
E-mail address: [shizuka.kenji@mp.m-kagaku.co.jp](mailto:shizuka.kenji@mp.m-kagaku.co.jp) (K. Shizuka).

Table 1  
Sample list

Sample	$\text{Li}_{1+z}\text{Ni}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$	$x$	$y$	$z$	Calcination temperature ( $^{\circ}\text{C}$ )	Under
1a	$\text{Li}_{1.02}\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$	0.33	0.33	0.02	950	Air
1b	$\text{Li}_{0.14}\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$	0.33	0.33	0.14	950	Air
2	$\text{Li}_{1.00}\text{Ni}_{0.50}\text{Co}_{0.20}\text{Mn}_{0.30}\text{O}_2$	0.20	0.30	0.00	950	Air
3a	$\text{Li}_{1.040}\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$	0.15	0.05	0.040	740	$\text{O}_2$
3b	$\text{Li}_{1.074}\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$	0.15	0.05	0.074	740	$\text{O}_2$

The storage stability on air and  $\text{CO}_2$  exposure was monitored by  $\text{CO}_3^{2-}$  content and electrochemical performance. Air-exposure tests were carried out at  $30^{\circ}\text{C}$  and 80% RH (relative humidity) for 1 month.  $\text{CO}_2$ -exposure tests were performed for samples 3a and 3b ( $\text{Li}_{1+z}\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ,  $z=0.05$ , 0.10) in 100%- $\text{CO}_2$  or 5%- $\text{CO}_2$  atmosphere at 400 or  $200^{\circ}\text{C}$  for 1, 2, 6, 12 and 24 h.  $\text{CO}_3^{2-}$  content was measured by ion chromatography (Dionex DX-120 with Dionex IonPac ICE-AS1 column).

Electrochemical tests were carried out using the 2032 coin-type cells. Each cathode consisted of 75 wt.% of the active material, 20 wt.% of acetylene black, and 5 wt.% of PTFE. Lithium metal or graphite and 1 M  $\text{LiPF}_6$  EC/DEC (3:7, v/v) were used as the negative electrode and the electrolyte, respectively. The discharge capacity was examined at a current density of  $0.2\text{ mA cm}^{-2}$  between 3.2 and 4.2 V versus  $\text{Li}/\text{Li}^+$  at  $25^{\circ}\text{C}$ . The rate capability before and after the exposure test was monitored as the ratio of the discharge capacities at current densities of 11 and  $0.2\text{ mA cm}^{-2}$  between 3.0 and 4.2 V versus  $\text{Li}/\text{Li}^+$  at  $25^{\circ}\text{C}$ . Charge–discharge cycling tests were carried out galvanostatically at an apparent current density of 1 C in the voltage range between 3.0 and 4.1 V versus carbon at  $60^{\circ}\text{C}$ .

Powder X-ray diffraction (XRD) was carried out to determine the crystal structure by PANalytical PW1700 with  $\text{Cu K}\alpha$  radiation. X-ray photoelectron spectra (XPS) were measured to elucidate the change of Ni valence on the surface by Physical Electronics ESCA-5500MC with  $\text{Al K}\alpha$  radiation. SEM images were obtained to clarify the morphology by Hitachi S-4500.

### 3. Results and discussion

#### 3.1. Storage stability of $\text{Li}_{1+z}\text{Ni}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$

Generally, it is well known that  $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$  cathode materials are not stable upon storage due to their chemical activeness, such as  $\text{CO}_2$  absorption. It is undesirable because it is difficult to handle such materials without deterioration. Therefore, it is important to clarify what is the origin of the storage instability for  $\text{Li}_{1+z}\text{Ni}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$ . In order to examine the storage stability of  $\text{Li}_{1+z}\text{Ni}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$ , we investigated the change of  $\text{CO}_3^{2-}$  content and electrochemical rate performance before and after the air-exposure test.

Fig. 1 shows the  $\text{CO}_3^{2-}$  content before and after the exposure test for  $\text{Li}_{1+z}\text{Ni}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$ . The most remarkable point in Fig. 1 is that  $\text{Li}_{1+z}\text{Ni}_{(1-x)/2}\text{Co}_x\text{Mn}_{(1-x)/2}\text{O}_2$  (Ni/Mn mole ratio = 1) samples (1a, 1b) exhibited very low  $\text{CO}_2$  contents. On the other hand,  $\text{Li}_{1+z}\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (3a and 3b) con-

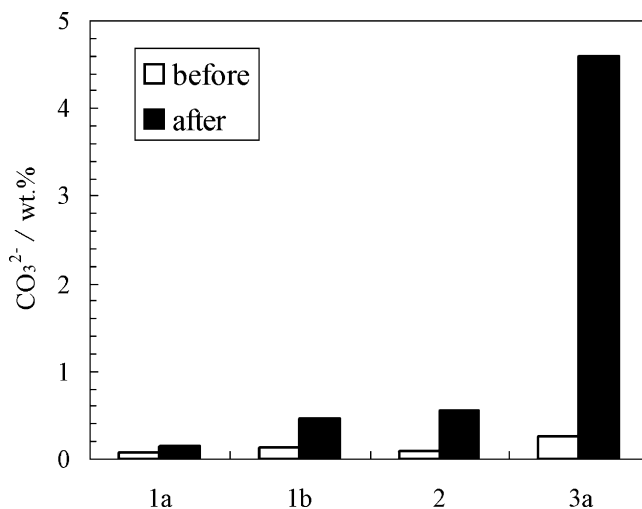


Fig. 1.  $\text{CO}_3^{2-}$  content before and after the exposure test for  $\text{Li}_{1+z}\text{Ni}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$ .

tain more  $\text{CO}_2$  than others. From these results, it is clear that  $\text{Li}_{1+z}\text{Ni}_{(1-x)/2}\text{Co}_x\text{Mn}_{(1-x)/2}\text{O}_2$  series singularly exhibit high storage stability in  $\text{Li}_{1+z}\text{Ni}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$  cathode materials. Fig. 2 shows the rate capability before and after the exposure test. The rate capability deteriorated as the  $\text{CO}_3^{2-}$  content increased in Fig. 1.

From these results, it is clear that the rate capability decreases as the  $\text{CO}_3^{2-}$  content increases and therefore the electrochem-

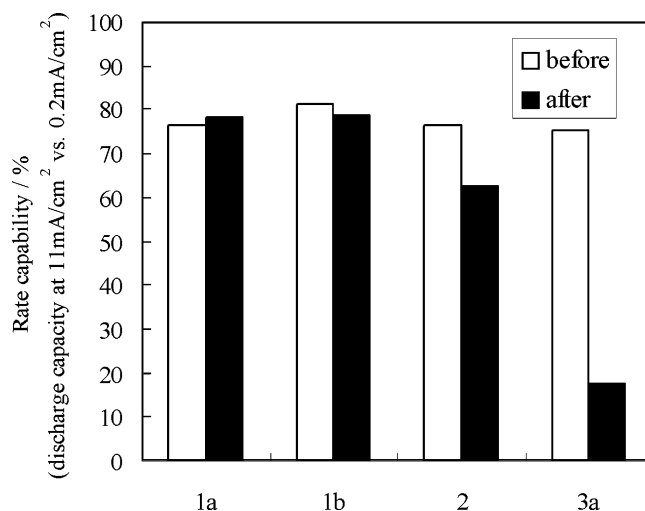


Fig. 2. Rate capability before and after the exposure test for  $\text{Li}_{1+z}\text{Ni}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$ .

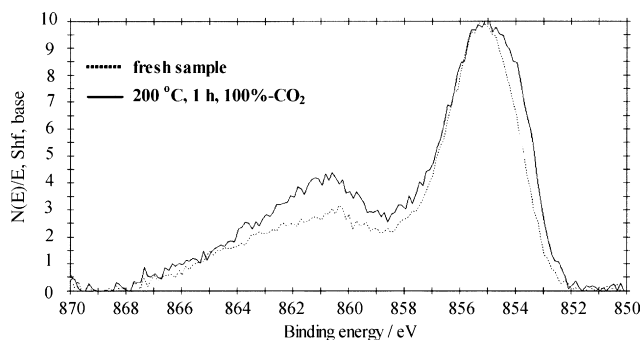


Fig. 3. Ni 2p<sub>3/2</sub> XPS of Li<sub>1+y</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> before and after CO<sub>2</sub> 100%-CO<sub>2</sub> exposure at 200 °C for 1 h.

ical performance of sample 3a suffers severe deterioration by CO<sub>2</sub> in air.

### 3.2. XPS of Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> before and after CO<sub>2</sub> treatment

It is interesting that the CO<sub>2</sub> absorptivity is very high for Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>, and very low for Li<sub>1+z</sub>Ni<sub>(1-x)/2</sub>Co<sub>x</sub>Mn<sub>(1-x)/2</sub>O<sub>2</sub>. We expected that it should be caused by difference of Ni valence in Li<sub>1+z</sub>Ni<sub>1-x-y</sub>Co<sub>x</sub>Mn<sub>y</sub>O<sub>2</sub>. The oxidation states of Ni, Co and Mn are 2+, 3+, and 4+, respectively, in LiNi<sub>(1-x)/2</sub>Co<sub>x</sub>Mn<sub>(1-x)/2</sub>O<sub>2</sub> series [4–8]. It is supposed that unstable Ni<sup>3+</sup> is responsible for CO<sub>2</sub> absorption.

Fig. 3 shows the Ni 2p<sub>3/2</sub> XPS of Li<sub>1+y</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> before and after CO<sub>2</sub> exposure (in 100%-CO<sub>2</sub> at 200 °C for 1 h). While the main peak of the fresh sample is at 855.0 eV, that of the CO<sub>2</sub>-treated sample has a shoulder at 854.5 eV, which shows that more Ni<sup>2+</sup> exists on the surface. It indicates that the reduction of Ni<sup>3+</sup> to Ni<sup>2+</sup> occurred by the reaction with CO<sub>2</sub>.

### 3.3. XRD of Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> before and after CO<sub>2</sub> treatment

In order to examine the reaction with CO<sub>2</sub>, XRD measurements were carried out. Fig. 4 shows the XRD patterns for Li<sub>1.040</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> before and after CO<sub>2</sub> exposure (in

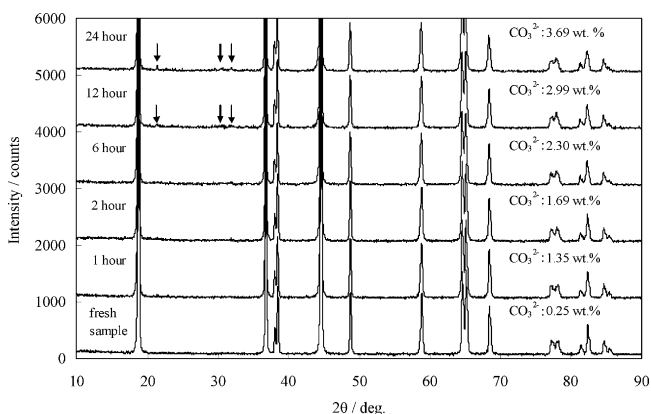


Fig. 4. XRD patterns for Li<sub>1.040</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> before and after 100%-CO<sub>2</sub> exposure at 400 °C.

100%-CO<sub>2</sub> at 400 °C for 1–24 h). Li<sub>2</sub>CO<sub>3</sub> is formed when the CO<sub>3</sub><sup>2-</sup> content is more than ca. 3 wt.% and increases with the CO<sub>3</sub><sup>2-</sup> content as indicated by arrows in Fig. 4.

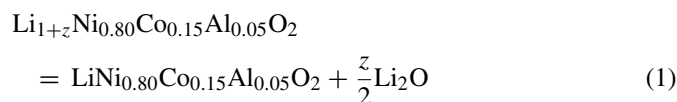
### 3.4. SEM of Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> before and after CO<sub>2</sub> treatment

Fig. 5 shows the SEM images of the surface and CO<sub>2</sub>-treated samples with CO<sub>2</sub> at 400 °C. The difference is obvious; while the fresh sample looks very smooth, those of the CO<sub>2</sub>-treated samples are covered with passivation films, which may be Li<sub>2</sub>CO<sub>3</sub>. The covered area increases gradually as the exposure time increases.

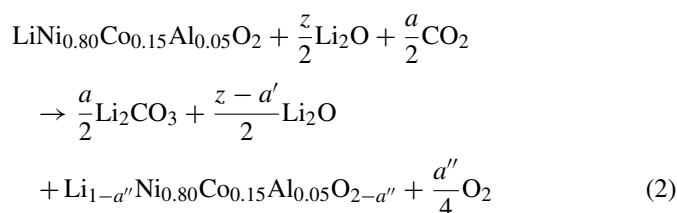
### 3.5. CO<sub>3</sub><sup>2-</sup> content of Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> before and after CO<sub>2</sub> treatment

In order to examine how the carbonation reaction progresses, we investigated the relationship between CO<sub>2</sub>-exposure time and CO<sub>3</sub><sup>2-</sup> content for Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> cathode materials.

Fig. 6-(1) shows the relationship between 100%-CO<sub>2</sub> exposure time and CO<sub>3</sub><sup>2-</sup> content at 400 °C for Li<sub>1.040</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>. The present condition yielded 1.35 wt.% (1 h) to 3.69 wt.% (24 h) of CO<sub>3</sub><sup>2-</sup>. In the case of Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>, the excess 0.040Li in the fresh sample presumably exists as 0.020Li<sub>2</sub>O:



It is generally difficult to distinguish the excess lithium in the crystal from that on the surface. For Li<sub>1+z</sub>Ni<sub>1-x-y</sub>Co<sub>x</sub>Mn<sub>y</sub>O<sub>2</sub> materials, we consider that the most of the excess lithium is incorporated into the crystal, because the lattice parameter linearly changes as the excess lithium content changes [9]. On the other hand, we expect that the excess lithium is not in the crystal but on the surface for Li<sub>1+z</sub>Ni<sub>1-x-y</sub>Co<sub>x</sub>Al<sub>y</sub>O<sub>2</sub> materials, because the lattice parameter is almost the same ( $a = 2.862 \text{ \AA}$ ,  $c = 14.17 \text{ \AA}$  for both of the samples 3a ( $z = 0.040$ ) and 3b ( $z = 0.074$ )). Strictly speaking, the component of excess lithium should be described separately as in the right side of Eq. (1). However, for the sake of convenience, in this paper we consistently describe it as in the left side. And the following reaction may occur between Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> and CO<sub>2</sub>:



where  $a' + a'' = a$ ,  $0 \leq a' \leq z$ ,  $0 \leq a'' \leq 1$ .

Formula (2) means that there are two kinds of Li in Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> that react with CO<sub>2</sub>: one is the excess  $z$ Li on the surface of the active material, and the other is the Li in the active material itself. The extracted lithium content

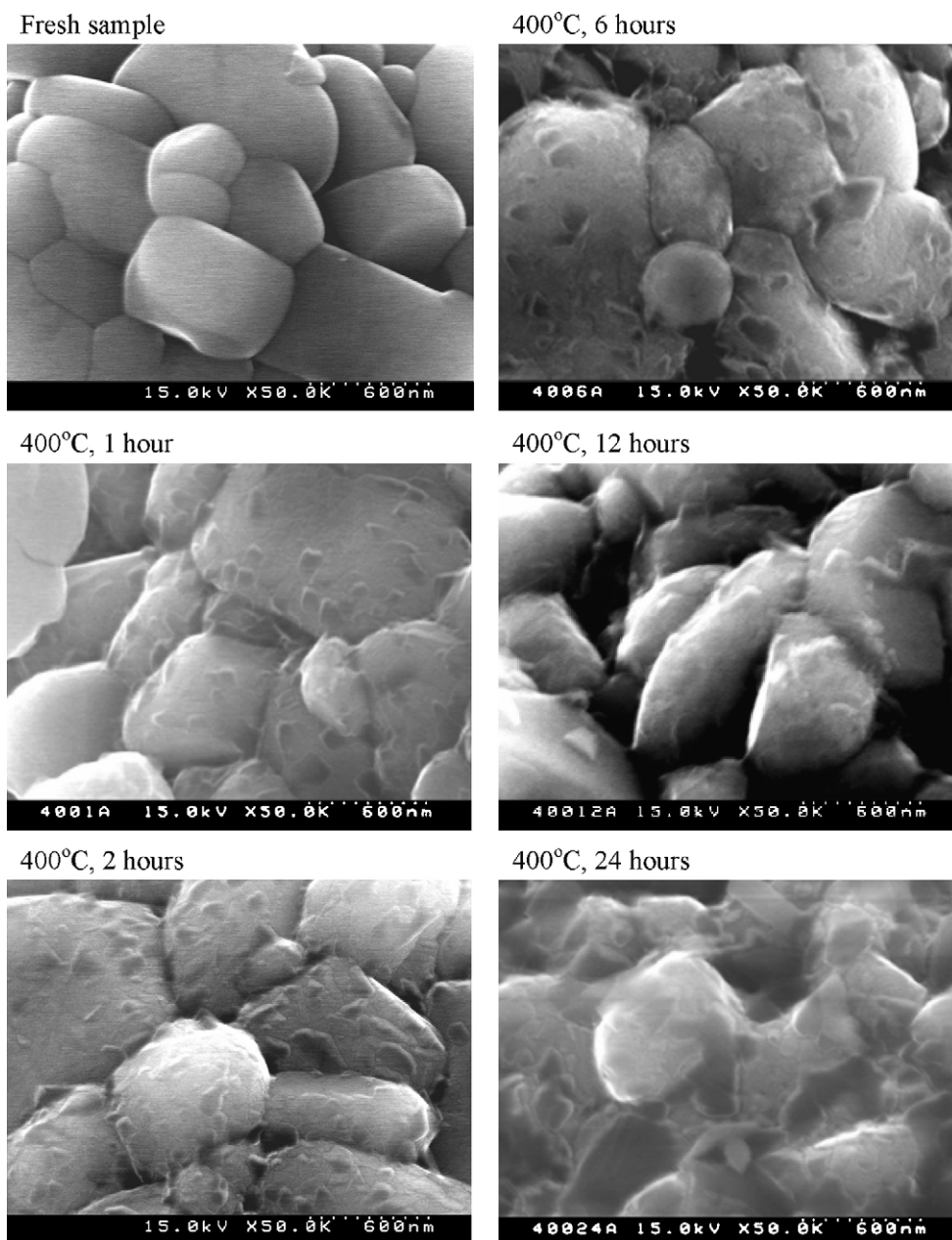


Fig. 5. SEM images for  $\text{Li}_{1.040}\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  before and after 100%- $\text{CO}_2$  exposure at 400 °C.

$a$  in Eq. (2) was calculated from the  $\text{CO}_3^{2-}$  content obtained by chemical analysis. To convert Li delithiation content from  $\text{Li}_{1+z}\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , the following equation was used:

$$a = \frac{2cM_w}{m_w(100 - c)} \quad (3)$$

where  $c$  is the  $\text{CO}_3^{2-}$  content (wt.%), and  $M_w$  and  $m_w$  is the molecular weights ( $\text{g mol}^{-1}$ ) of  $\text{Li}_{1+z}\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  and  $\text{CO}_3^{2-}$  ion, respectively. Table 2 shows the  $c$  and  $a$  values as functions of the 100%- $\text{CO}_2$  exposure time for sample 3a.

Fig. 6-(2) shows the relationship between 5%- $\text{CO}_2$  exposure time and  $\text{CO}_3^{2-}$  content for  $\text{Li}_{1+z}\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  ( $z=0.040, 0.074$ ) at 400 °C. The  $\text{CO}_3^{2-}$  content increased from 0.78 wt.% (1 h) to 1.39 wt.% (24 h) for sample 3a and from

Table 2  
 $\text{CO}_3^{2-}$  content  $c$  (wt.%) and extracted Li content  $a$  value as functions of the  $\text{CO}_2$  exposure time for samples 3a and 3b

Sample	$\text{CO}_2$ gas (%)		$\text{CO}_2$ -exposure time (h)					
			0	1	2	6	12	24
3a	100	$c$	0.25	1.35	1.69	2.30	2.99	3.69
		$a$	0.008	0.044	0.055	0.076	0.099	0.123
3a	5	$c$	0.25	0.78	0.89	1.23	1.34	1.39
		$a$	0.008	0.025	0.029	0.040	0.044	0.045
3b	5	$c$	0.26	1.63	1.77	1.82	2.19	2.48
		$a$	0.008	0.053	0.058	0.060	0.072	0.082

$M_w = 96.36 \text{ g mol}^{-1}$  (sample 3a),  $96.60 \text{ g mol}^{-1}$  (sample 3b),  $m_w = 60.01 \text{ g mol}^{-1}$ .

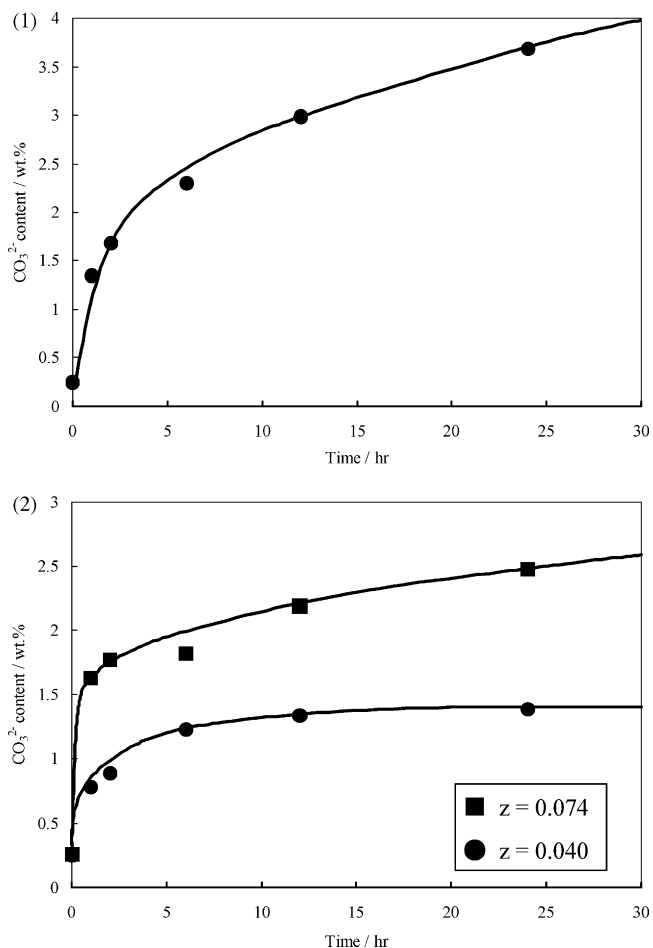


Fig. 6. (1) Relationship between 100%-CO<sub>2</sub> gas exposure time and CO<sub>3</sub><sup>2-</sup> content at 400 °C for Li<sub>1.040</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>; (2) relationship between 5%-CO<sub>2</sub> gas exposure time and CO<sub>3</sub><sup>2-</sup> content for Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (z = 0.040, 0.074).

1.63 wt.% (1 h) to 2.48 wt.% (24 h) for sample 3b. The *c* and *a* values are also shown in Table 2 for the 5%-CO<sub>2</sub> exposure of samples 3a and 3b.

These results show that the carbonation behavior is different between 100%-CO<sub>2</sub> and 5%-CO<sub>2</sub> exposure. In the case of 100%-CO<sub>2</sub>, CO<sub>3</sub><sup>2-</sup> content increases monotonously with the exposure time. On the other hand, in the case of 5%-CO<sub>2</sub>, it is nearly saturated at around 1.5 wt.% (sample 3a) and 2.5 wt.% (sample 3b). These results indicate that the carbonation reaction has two steps. First, the excess lithium on the surface, *z*Li in Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>, reacts with CO<sub>2</sub>:



After all surface lithium ions are consumed, the second slow reaction starts:

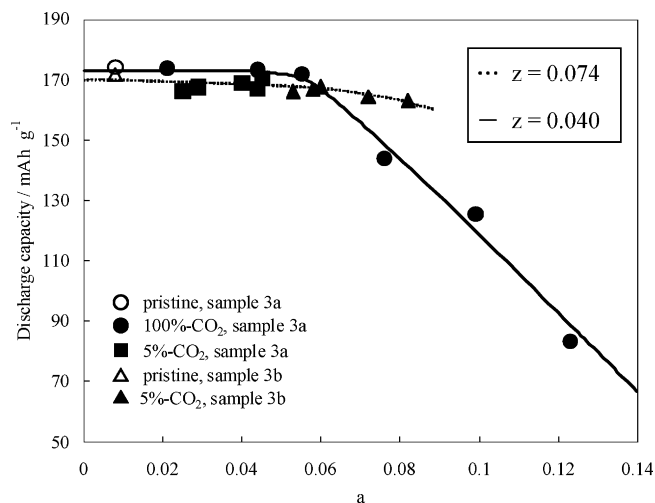
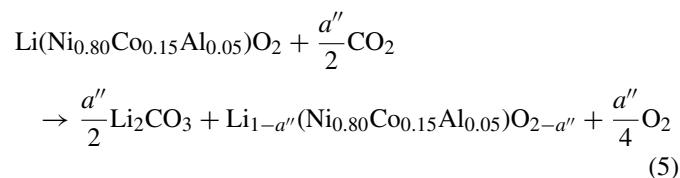


Fig. 7. Relationship between extracted lithium content *a* and discharge capacity for Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>.

The latter reaction is supposed to be too slow to occur in the 5%-CO<sub>2</sub> atmosphere.

### 3.6. Cell performance

Fig. 7 shows the relationship between the extracted lithium content *a* and the discharge capacity for Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>. This result indicates the discharge capacity is not decreased until the excess lithium content, *z*Li in Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>, is consumed by the carbonation, and it deteriorates rapidly as consuming more lithium beyond *z*Li in Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>.

Fig. 8 shows that the relationship between *a* and the capacity retention after the 100th cycle. This result indicates that the capacity retention is maintained, or even improved, until the excess lithium is consumed, and again deteriorated rapidly after that.

These results suggest that the second reaction between CO<sub>2</sub> and lithium inside the active material causes the deterioration of

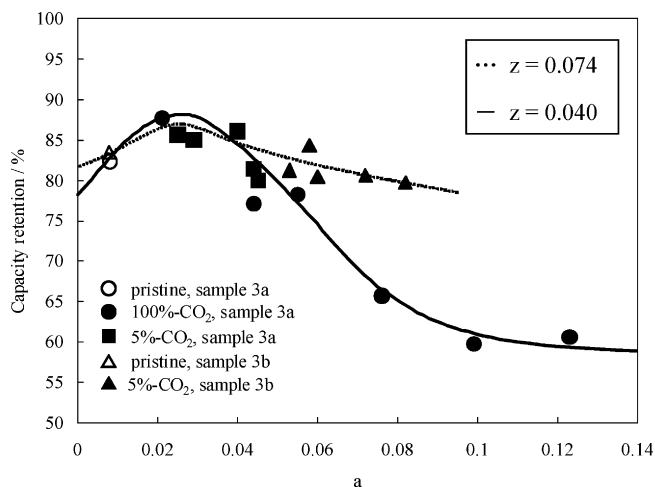


Fig. 8. Relationship between extracted lithium content *a* and capacity retention after the 100th cycle for Li<sub>1+z</sub>Ni<sub>0.80</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>.

the electrochemical performances. In order to avoid deterioration of the electrochemical performances, it is necessary to limit the carbonation reaction only to the excess lithium  $z\text{Li}$  on surface in  $\text{Li}_{1+z}\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ . Carbonation of more lithium may cause loss of efficient lithium and structural disorder of the crystal.

#### 4. Conclusion

In this study, we investigated the effect of  $\text{CO}_2$  on  $\text{Li}_{1+z}\text{Ni}_{1-x-y}\text{Co}_x\text{M}_y\text{O}_2$  ( $\text{M} = \text{Al}, \text{Mn}$ ) cathode materials. In the exposure tests,  $\text{CO}_2$  absorptivity increased as the ratio of  $\text{Ni}^{3+}/\text{Ni}^{2+}$  increased. Especially,  $\text{Li}_{1+z}\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  that consist of almost 100%- $\text{Ni}^{3+}$  rapidly absorbed  $\text{CO}_2$  and the electrochemical performance suffered severe deterioration after the exposure test. Reduction of  $\text{Ni}^{3+}$  to  $\text{Ni}^{2+}$  was observed in the Ni 2p<sub>3/2</sub> XPS after reacting with  $\text{CO}_2$ . The relationship between  $\text{CO}_2$  exposure time and  $\text{CO}_3^{2-}$  content for  $\text{Li}_{1+z}\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  indicated that the first carbonation reaction occurs with excess Li components on the surface and the second with bulk  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ .

The relationship between the extracted lithium content and the electrochemical performance revealed that the discharge capacity was kept and the capacity retention was improved until the excess lithium is consumed, which is followed by rapid deterioration of  $\text{Li}_{1+z}\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ .

#### Acknowledgments

The authors thank Dr. Kaoru Okamoto (Mitsubishi Chemical Group Science and Technology Research Center, Inc.) for fruitful discussion.

Mitsubishi Chemical Group Science and Technology Research Center, Inc., assisted in meeting the publication costs of this article.

#### References

- [1] K. Matsumoto, R. Kuzuo, K. Takeya, A. Yamanaka, J. Power Sources 81–82 (1999) 558.
- [2] R. Moshtev, P. Zlatilova, S. Vasilev, I. Bakolova, A. Kozawa, J. Power Sources 81–82 (1999) 434.
- [3] H.S. Liu, Z.R. Zhang, Z.L. Gong, Y. Yang, Electrochem. Solid-State Lett. 7 (2004) A190.
- [4] Z. Lu, D.D. MacNeil, J.R. Dahn, Electrochem. Solid-State Lett. 4 (2001) 200.
- [5] D.D. MacNeil, Z. Lu, J.R. Dahn, J. Electrochem. Soc. 149 (2002) 1332.
- [6] K.M. Shaju, G.V. Subba Rao, B.V.R. Chowdari, Electrochim. Acta 48 (2002) 145.
- [7] J.-M. Kim, H.-T. Chung, Electrochim. Acta 49 (2004) 937.
- [8] Y. Koyama, I. Tanaka, H. Adachi, Y. Makimura, T. Ohzuku, J. Power Sources 119 (2003) 644.
- [9] K. Shizuka, T. Kobayashi, K. Okahara, K. Okamoto, S. Kanzaki, R. Kanno, J. Power Sources 146 (2005) 589.