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Effects of Al doping on the microstructure of LiCoO_2 cathode materials

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Abstract

$\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ ($0 \leq x \leq 0.3$, $R\bar{3}m$) powders by the emulsion drying method and their microstructure studies were carried out in order to understand Al-doping effect on the electrochemical properties. Through X-ray diffraction experiment, we confirmed that Co was well substituted by Al while maintaining the $\alpha\text{-NaFeO}_2$ layer structure type. The substitution of Al was effective on suppressing cobalt dissolution at 4.5 V versus Li/Li^+ and on diminishing changes in a - and c -axes during lithium intercalation. For $x = 0.1$, the open-circuit voltage was slightly higher than that of undoped LiCoO_2 . Chemical diffusion coefficient of lithium in $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ was higher than that of LiCoO_2 because of a smaller variation in the longer c -axis. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ powders; Emulsion drying method; Chemical diffusion coefficient; Cobalt dissolution; Variation in c -axis

1. Introduction

The layered transition metal oxide, LiCoO_2 , is the most attractive cathode material for the rechargeable Li-ion battery, because it has high specific capacity, high operating cell voltage and excellent rechargeability. In intense research for high-energy density cathode materials for use in rechargeable lithium-ion batteries, the layered LiCoO_2 has become one of the most promising electrode materials for commercial products by several companies. Simultaneously, extensive studies have been devoted to improve the performance of this electrode [1–6].

In the region of higher potential than 4.2 V for LiCoO_2 , a capacity fading occurred mainly due to the increase in the amount of cobalt dissolution which was found to correlate with a large anisotropic structural change (large change in c -axis versus small change in a -axis) in LiCoO_2 . The use of aluminum ions as a dopant in transition metal layered structure has a beneficial effect which is able to suppress the anisotropic structural change, because the Al^{3+} ions together with lithium ions kept the interlayer distance [2]. Ten percent of Al-doped LiCoO_2 provided a relatively good discharge capacity and showed that less electrolyte decomposition occurred [3]. According to theoretical studies [4,5], Al substitution for transition metal oxides will lead to higher Li intercalation voltages, as the fixed 3+ valence of Al forces more electron exchange with

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oxygen, as confirmed by Jang et al. [6]. In the present investigation, Al-doped LiCoO_2 oxides were synthesized by the emulsion drying method. Using those powders, electrochemical and corresponding structural studies were performed to evaluate the emulsion dried $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ ($x = 0, 0.1, 0.2$ and 0.3) powders.

2. Experimental

Reagent-grade LiNO_3 , $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al(NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (Kanto) were used as starting materials. $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ ($x = 0, 0.1, 0.2$ and 0.3) powders were prepared by the emulsion drying method, as reported previously [7–9]. The obtained powder precursors were calcined at 900°C for 24 h in a Pt crucible in air, and cooled to room temperature in a tube-furnace (Lindberg, USA). The heat-treated products were ground in an agate mortar, and then used to examine their structure by X-ray diffraction (Rigaku Rint 2000, Japan). The morphologies of the products were observed using a scanning electron microscopy (Hitachi S-2250N, Japan). To analyze the dissolution the amount of cobalt, atomic absorption analyses were carried (AAalyst 300, Perkin-Elmer, USA).

$\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ electrodes were prepared by blending with 5 wt.% of graphite, 3 wt.% of PVDF (poly-vinylidene fluoride) in NMP (*n*-methyl pyrrolidone). The slurry was spread on $1 \times 1 \text{ cm}^{-2}$ nickel ex-met, and then dried on the oven in air. The dried electrodes were pressed to enhance adhesion strength, after that, dried again under vacuum state at 120°C for 72 h. Two- and three-electrode electrochemical cells were adapted for the charge–discharge and the other electrochemical experiments, respectively. The reference and counter electrodes were fabricated from lithium metal, and 1 M LiClO_4 EC (ethylene carbonate)–DEC (dimethylene carbonate) used as an electrolyte. The assemblies of electrochemical cell were done in a glove box filled with high purity Ar gas. A constant current, 0.1 mA cm^{-2} , was applied to working electrode for the charge–discharge experiment. Three-electrode cells were employed to measure open circuit voltage (OCV) and closed circuit voltage (CCV) as a function of Li content. The samples were electro-

chemically reduced by a current of 0.1 mA cm^{-2} . When the potential of the cell reached some cut-off potential, current was not applied any more, then equilibrated for 24 h. However, accurate measurement of equilibrium state is difficult as reported [10]. Therefore, we measured the observable OCV at room temperature. The electrochemical impedance measurements were carried out in the potential range of $4.3\text{--}3.4 \text{ V}_{\text{Li/Li}^+}$, applying 100 kHz to 1 mHz frequency with an ac-amplitude of $10 \text{ mV}_{\text{rms}}$. Transmission electron microscopic (TEM, Hitachi, H-800, Japan) observation was carried out using cycled cathode. Pieces of the cathode were ultrasonically de-agglomerated and dispersed on an amorphous carbon grid supported by a Cu frame for TEM observation. The accelerated voltage of electron beam was 200 kV.

3. Results and discussion

Fig. 1 displays XRD patterns of products obtained by the emulsion drying method as a function of Al content. All samples were calcined at 900°C for 24 h in air. The Miller indices were indexed assuming that these characteristic lines correspond to the $\alpha\text{-NaFeO}_2$ structure. Some groups mentioned the Ni site substitution with Al in LiNiO_2 having the same layer structure as LiCoO_2 [2,11,12]. In those cases [2,11], a single phase was hardly obtained because of the formation of undesired impurity phase. As seen in these XRD patterns, $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ ($x = 0, 0.1, 0.2$ and 0.3) phases were easily synthesized from the emulsion-dried powder precursor. We believe that the solid solubility limitation of our samples prepared by the emulsion drying method is also as high as those reported previously [3,6,13], although there is a possibility to form some second phases such as $\beta\text{-LiAlO}_2$ ($Pna2_1$) and $\gamma\text{-LiAlO}_2$ ($P4_12_12_1$) at a higher temperature of 900°C . The amorphous traces between 15 and 25° in 2θ is due mainly to the polymer sample holder. From this figure, it could be seen that Al was well occupied in the $3a$ cobalt site of $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ ($x = 0.1, 0.2$ and 0.3 , $R\bar{3}m$) while maintaining the $\alpha\text{-NaFeO}_2$ layer structure type.

In order to illustrate the relation between the unit cell and Al content, x , the a - and c -lattice parameters were calculated [14]. Obviously, the a -axis de-

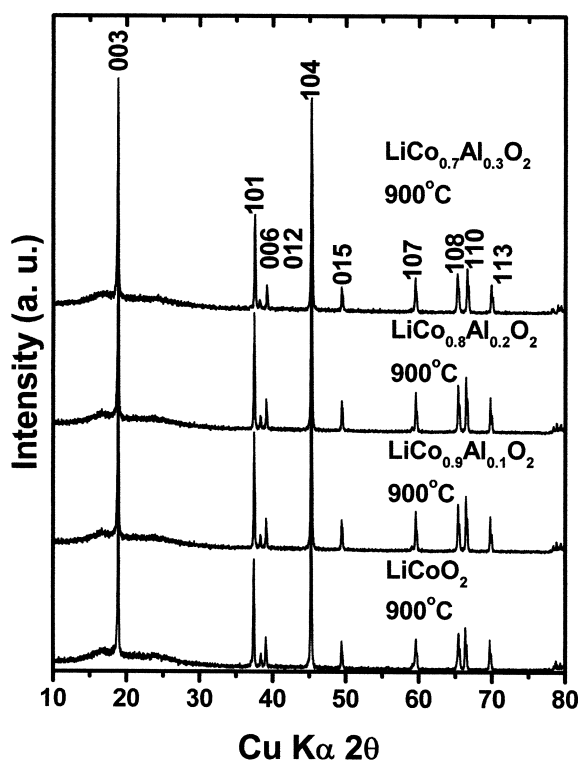


Fig. 1. XRD patterns of $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ ($x=0, 0.1, 0.2$ and 0.3) powders calcined at 900°C for 24 h in air.

creased, while the c -axis increased linearly with increasing Al content, as shown in Fig. 2. This is typical tendency for such a solid solution. The lattice variation can be explained by using the crystal lattice parameters of $\alpha\text{-LiAlO}_2$ ($a = 2.800 \text{ \AA}$, $c = 14.22 \text{ \AA}$, $R\bar{3}m$ [15]) oxide which shows a smaller a -axis and larger c -axis values than those of LiCoO_2 . Because of the formation of the solid solution between LiCoO_2 and $\alpha\text{-LiAlO}_2$ phases, it is reasonable that the a -axis decreases and c -axis increases for $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ ($x = 0.1, 0.2$ and 0.3) compositions, compared to those of undoped LiCoO_2 . The phase separation from $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ to LiCoO_2 and $\alpha\text{-LiAlO}_2$ does not occur due mainly to the homogeneous cations mixing of Li, Co and Al in the initial emulsion state, as we described previously [7]. The variation in measured lattice parameters was in good agreement with those reported previously [6,13].

Fig. 3 shows SEM photographs of $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ ($x = 0, 0.1, 0.2$ and 0.3) powders calcined at 900°C

for 24 h in air. The powders consist of well-crystallized particles with hexagonal form, and the particle size is of almost sub-micron order in diameter. As the doping amount of Al increases, the particle size becomes smaller. Furthermore, the colors of fired powders were changed from blue black into dark brown with increasing doped Al content. Generally, blue black materials have narrower band gap between conduction and valence bands than brown materials. We believe that the LiCoO_2 shows a semiconductor property rather than the Al-doped LiCoO_2 .

The electrochemical initial discharge behaviors were examined in a range of $3.4\text{--}4.3 \text{ V}_{\text{Li/Li}^+}$ to investigate the dependence on Al doping content. Fig. 4 shows the initial discharge curves as a function of lithium content, δ , for the $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ ($0 \leq x \leq 0.3$) composite electrodes. The amounts of intercalated lithium, δ , were calculated from the weight of active material and the total charge transferred. Firstly, we supposed that the electrochemical reaction into the electrode would occur reversibly. The electrode potential of $\text{Li}_\delta\text{Co}_{1-x}\text{Al}_x\text{O}_2$, E , is given by following [16,17]:

$$E = E^0 + k\delta - \frac{RT}{F} \ln \frac{\delta}{1-\delta}, \quad \delta_{\min} \leq \delta \leq \delta_{\max} \quad (1)$$

where E^0 is the standard electrode potential, the parameter k represents the interaction energy between the intercalated lithium ions in the oxide lattice ($k > 0$, attractive interaction; $k < 0$, repulsive interaction), R is the gas constant, T is the absolute temperature, and F is the Faraday constant. For $x=0$, voltage plateau regions were observed around $4.15, 4.05$ and $3.9 \text{ V}_{\text{Li/Li}^+}$. The narrow plateaus observed in 4.15 and $4.05 \text{ V}_{\text{Li/Li}^+}$ resulted from phase transition between ordered and disordered lithium ion arrangements in CoO_2 framework [18]. The plateau around $3.9 \text{ V}_{\text{Li/Li}^+}$ was due to the first-order phase transition, resulting in decrease in the c -axis in hexagonal unit cell [18]. The amount of reversibly intercalated lithium was approximately $\text{Li/Co} = 0.57$, corresponding to the discharge capacity as high as 156 mAh/g . For the Al containing electrodes in Fig. 4, however, only monotonously decreasing discharge curves, which suggest a single-phase reaction, were observed. This could be explained by the Eq. (1), that is, the existence of strong repulsive

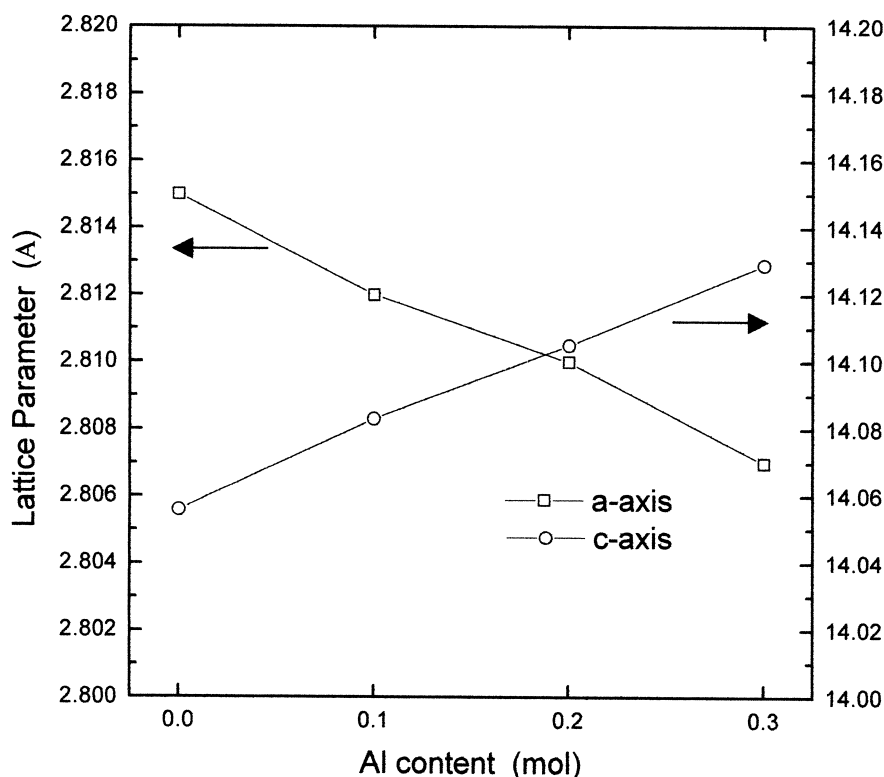


Fig. 2. The variation in the measured lattice parameter of $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ ($x=0, 0.1, 0.2$ and 0.3) powders calcined at 900°C for 24 h in air: ($\square$) a -axis; ($\circ$) c -axis.

interaction ($k < 0$) between the lithium ions in the oxide lattice results in potential decreasing behaviors in discharge. Provided that the repulsive interaction was very small in the Al doped electrodes, these electrodes would show the discharge curve similar to LiCoO_2 electrode. For $x=0.1$, the amounts of reversibly intercalated lithium into the electrodes was $\text{Li}/\text{Co}=0.40$ (110 mAh/g), and this obtained value was very close to the values previously reported by Nazri et al. [3]. For the case of $x=0.3$, the initial discharge capacity was approximate 60 mAh/g — oxide. That is, the amount of the intercalated lithium decreased with increasing Al content [6,13], even though the Al-doped materials have smaller particle size than that of LiCoO_2 .

In order to follow a change in the crystal structure of $\text{Li}_x\text{Co}_{1-x}\text{Al}_x\text{O}_2$ ($x=0$ and 0.1) electrodes during discharge, XRD studies were carried out as a function of intercalated lithium, δ . As $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ showed a relatively poor electrochemical discharge

capacity in the first discharge, this sample was excluded in this experiment. As seen in the XRD patterns in Fig. 5a,b, the layer structure was maintained during discharge in both samples. The (003) Bragg angle of both samples moved gradually toward higher angle direction with progressing intercalation reaction. Spontaneously, the (110) diffraction peaks shifted to lower 2θ position [6]. Moreover, it was found that the broadness of the (108) peaks of $\text{Li}_x\text{Co}_{0.9}\text{Al}_{0.1}\text{O}_2$ is larger than that of Li_xCoO_2 . As seen in Fig. 5b, we confirmed that the (108) peak was getting broader and slightly shifted to the lower angle during discharge process, implying increase in the a -axis and decreasing in the c -axis.

From Fig. 5, the a - and c -lattice parameters were calculated assuming a hexagonal lattice, as illustrated in Fig. 6. Both electrodes exhibited quite similar tendencies in the variation of the a - and c -axes. Jang et al. [6] reported that the a -axis was shrunken and the c -axis was expanded as the extracted amount of

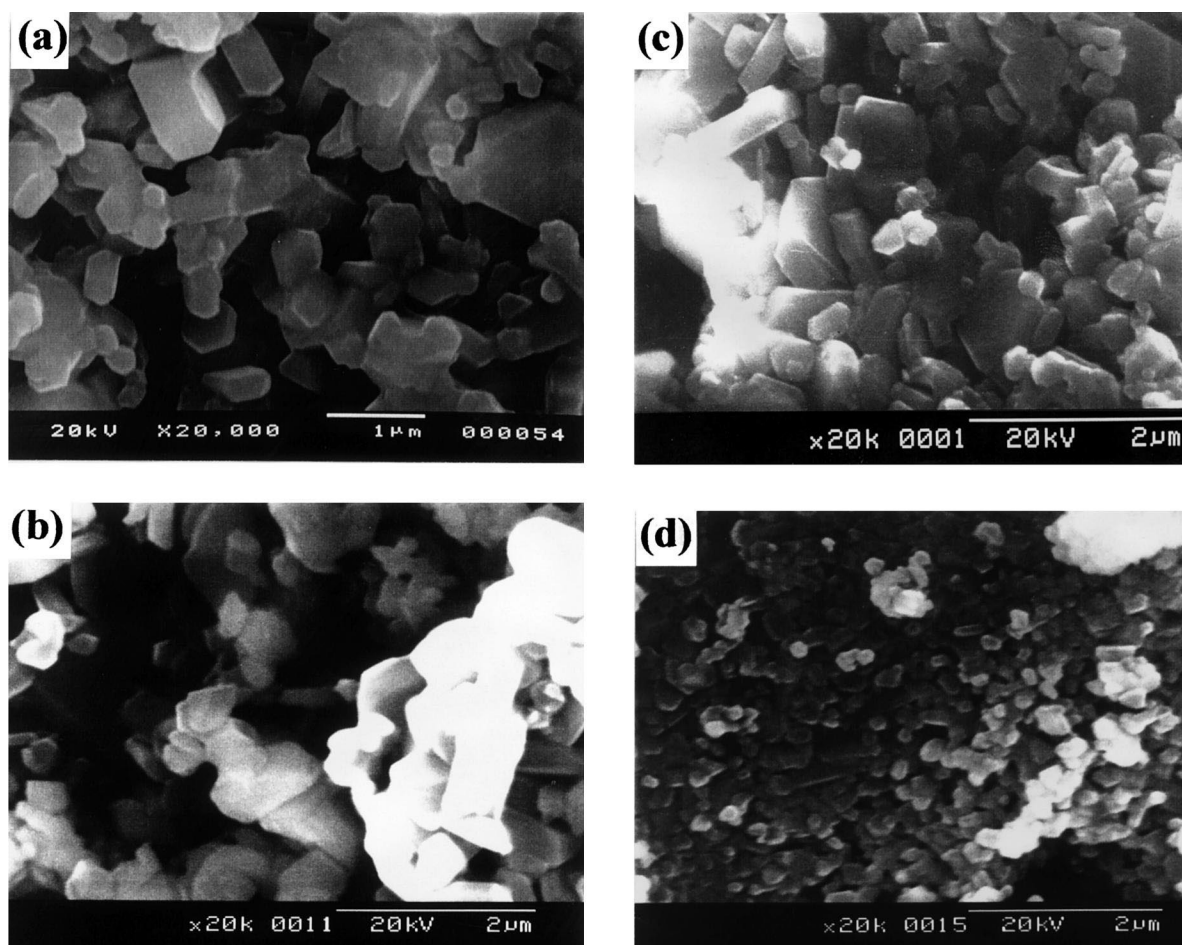


Fig. 3. SEM micrographs of (a) LiCoO_2 , (b) $\text{LiCo}_{0.9}\text{Al}_{0.1}\text{O}_2$, (c) $\text{LiCo}_{0.8}\text{Al}_{0.2}\text{O}_2$, and (d) $\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$ powders calcined at 900°C for 24 h in air.

lithium in cathode increased. Reversibly, the a -axis increased, while the c -axis decreased with increasing the intercalated amount of lithium, δ , in our results. The variations in the a -axis are similar in both electrodes. An interesting point to turn our attention is the variation in the c -axis with δ . The variation in the c -axis of undoped Li_6CoO_2 from 14.20 to 14.05 Å is significantly larger than that of the doped $\text{Li}_6\text{Co}_{0.9}\text{Al}_{0.1}\text{O}_2$ electrode from 14.26 to 14.20 Å. It was thought that the Al-doped sample is more stable than undoped one, according to the standard Gibbs-free energies of the formation at 298 K, i.e. Al_2O_3 (-376.77 kJ/mol), CoO (-51.0 kJ/mol) [19]. Hence, it is reasonable to think that the bonding of

Al–O is much stronger than that of Co–O. This means that the expansion or contraction of the interlayers with incorporating lithium ions may be restricted by the Al substitution.

Furthermore, Amatucci et al. have reported that the variation in c -axis is related to the dissolution of cobalt, and most cobalt dissolution occurred over 4.2 V [20]. To analyze the dissolution amount of cobalt from $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ ($0 \leq x \leq 0.3$) composite electrodes, those electrodes were electrochemically oxidized up to 4.5 $V_{\text{Li/Li}^+}$, and then, aged approximate 200 h at room temperature. The amount of dissolved cobalt in the used electrolyte was determined by atomic absorption spectroscopy, as summarized in

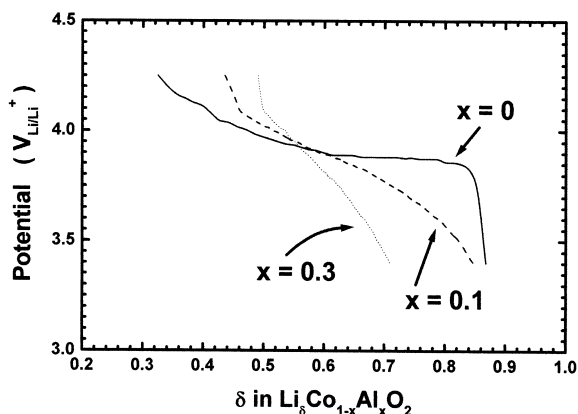


Fig. 4. The initial discharge curves of $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ ($x=0, 0.1$, and 0.3) powders calcined at 900°C as a function of lithium content, δ , and Al content, x .

Table 1. Clearly, as doped Al amount increased in the $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ electrodes, the dissolved amount of cobalt in the electrolyte considerably decreased. From this fact, we confirmed that dissolution of

cobalt was restrained by the Al substitution in $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$, leading to a limited c -axis variation.

A more direct route to deduce the diffusion coefficient shown in Fig. 7a can be obtained from the f_t at which a transition occurs from semi-infinite to finite diffusion behavior lengths as shown in typical impedance spectra (Fig. 7b) [21–25]. The value of the chemical diffusion coefficients, D_{Li^+} , in the $\text{Li}_{\delta}\text{Co}_{1-x}\text{Al}_x\text{O}_2$ composite electrode was calculated by the following equation [23];

$$f_t \approx \tilde{D}/l^2 \quad (2)$$

where l is the radius of a particle. The average radius of oxide particle, l , was determined to be about $0.3 \mu\text{m}$ by the SEM pictures in Fig. 3. Thomas et al. [23] proved that the l value obtained from SEM is much more reliable than the measured value of active surface area. Although lithium exists as lithium ion in the $\text{Li}_{\delta}\text{Co}_{1-x}\text{Al}_x\text{O}_2$, the effect of

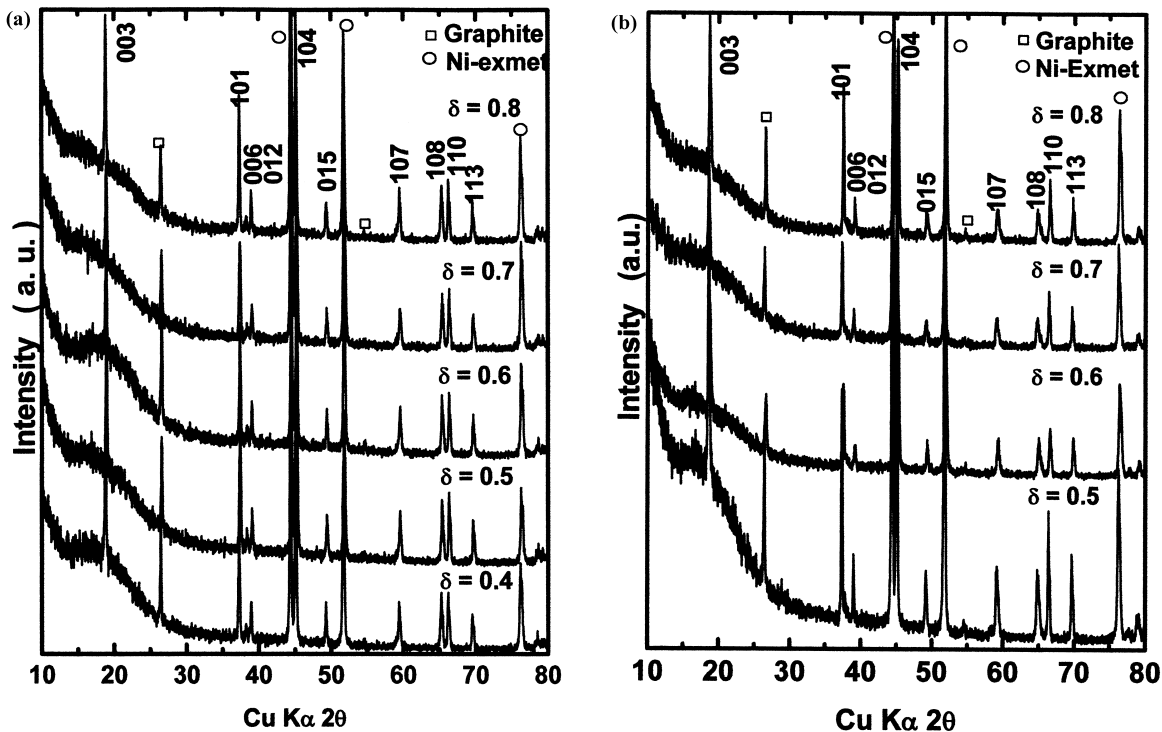


Fig. 5. XRD patterns as a function of Li content in (a) $\text{Li}_{\delta}\text{CoO}_2$ and (b) $\text{Li}_{\delta}\text{Co}_{0.9}\text{Al}_{0.1}\text{O}_2$ prepared by an electrochemical reduction at 0.1 mA cm^{-2} . The materials were obtained by calcination at 900°C for 24 h in air.

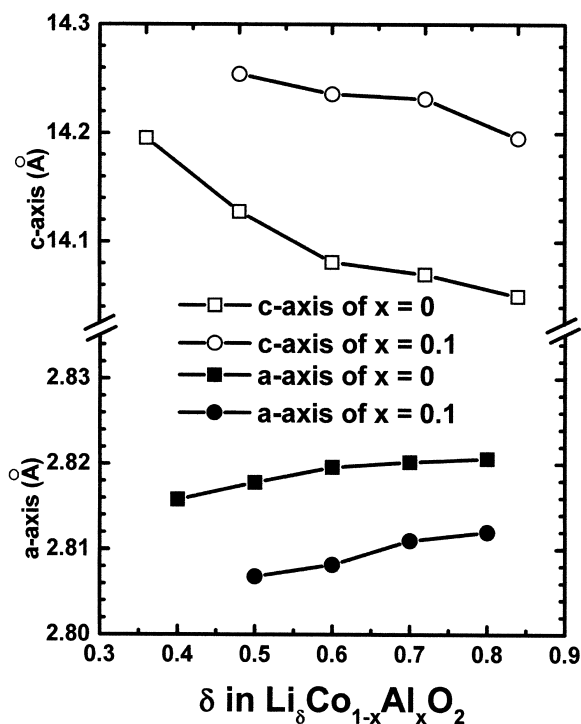


Fig. 6. Variation in the lattice parameters, a and c , in a hexagonal setting, as a function of Li content in $\text{Li}_\delta\text{CoO}_2$ and $\text{Li}_\delta\text{Co}_{0.9}\text{Al}_{0.1}\text{O}_2$ prepared by electrochemical reduction at 0.1 mA cm^{-2} . The material were obtained by calcination at 900°C for 24 h in air.

Table 1

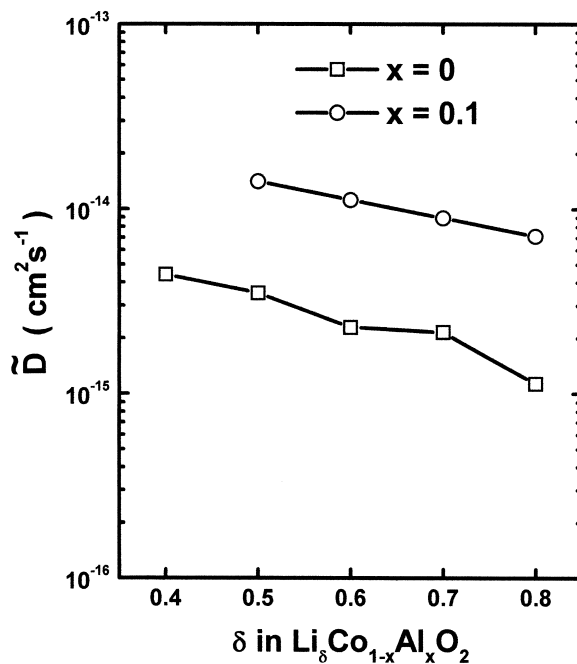
Cobalt dissolution in electrolyte (10 ml in volume) from $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ ($x=0, 0.1, 0.2$ and 0.3) electrodes^a

Composition	Cobalt dissolution amount (ppm)
LiCoO_2	20.1
$\text{LiCo}_{0.9}\text{Al}_{0.1}\text{O}_2$	5.05
$\text{LiCo}_{0.8}\text{Al}_{0.2}\text{O}_2$	4.2
$\text{LiCo}_{0.7}\text{Al}_{0.3}\text{O}_2$	3.6

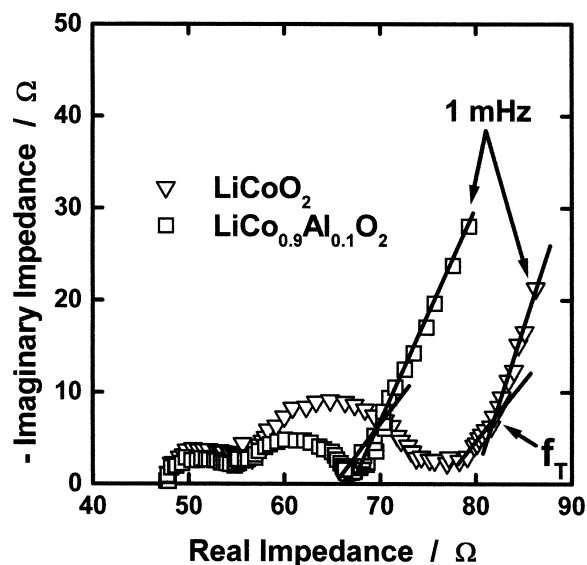
^a The total amount of electrolyte used was 1 ml for the atomic absorption spectroscopic experiment.

electric field and surface morphology of the used electrode was neglected in present measurement.

In Fig. 7a, the chemical diffusion coefficients of lithium in $\text{Li}_\delta\text{Co}_{1-x}\text{Al}_x\text{O}_2$ ($x=0.1$) are determined to be of the order of $10^{-14} \text{ cm}^2 \text{ s}^{-1}$ at room temperature. This value is one order magnitude higher than that for LiCoO_2 , proving the suggestion of Jang et al. [6]. The obtained value was smaller than that values



(a)



(b)

Fig. 7. (a) Chemical diffusion coefficient, $\tilde{D}_{\text{Li}^+}$, of lithium ion in $\text{Li}_\delta\text{Co}_{1-x}\text{Al}_x\text{O}_2$ electrode as a function of lithium content at room temperature and (b) typical Nyquist impedance plots of $\text{Li}_\delta\text{CoO}_2$ and $\text{Li}_\delta\text{Co}_{0.9}\text{Al}_{0.1}\text{O}_2$ in 1 M LiClO_4 EC-DEC solution. $\delta=0.5$.

previously reported ($10^{-8} \text{ cm}^2 \text{ s}^{-1}$ [25]). This is probably due to the smaller particle size of the prepared powders by the emulsion drying method. The obtained values decreased with the intercalated lithium content, δ . In the case of these electrodes, it is thought that the number of available site for Li^+ intercalation in the crystal lattice is getting smaller while increasing the intercalated lithium, leading to the decreasing lithium diffusion coefficient with δ . At the same time, the reaction of electrochemical reduction of Co^{4+} to Co^{3+} occurred so that the layer distance would decrease due to the decrease in the coulombic repulsion force between neighbor O–O layers, stabilizing the structure on lithium intercalation and delaying lithium diffusion in the layered structure.

For $x = 0.1$, the Al-doped sample showed higher Li diffusivity. It was due mainly to the enlarged layer distance and the smaller variation in crystal lattice dimension, especially the c -axis, as seen in Fig. 6. In general, Al^{3+} would not attend this redox reaction, so that coulombic repulsion was considerably suppressed by the Al^{3+} doping at the $3a$ cobalt sites. Therefore, we concluded that $\text{LiCo}_{0.9}\text{Al}_{0.1}\text{O}_2$ sample showed higher diffusivity than LiCoO_2 , because of its restricted anisotropic behavior in the c -axis by Al doping.

To understand the structural change after extended cyclings, Fig. 8 shows XRD patterns of LiCoO_2 and $\text{LiCo}_{0.9}\text{Al}_{0.1}\text{O}_2$ electrodes after 50 and 170 cyclings, respectively. Fig. 8 confirms that the layer structure ($R\bar{3}m$) was maintained with cycling. Their lattice parameters were calculated to follow the structural change. Assuming both electrode to be a hexagonal setting, the a -axis of LiCoO_2 was $2.810 \text{ \AA}$, and c -axis was $14.019 \text{ \AA}$ after the 50th discharge ($a = 2.815 \text{ \AA}$, $c = 14.056 \text{ \AA}$ for the as-prepared sample). On the other hand, the Al doping sample showed $a = 2.813 \text{ \AA}$ and $c = 14.086 \text{ \AA}$ after the 170th discharge, which are very close to the values from before cycling ($a = 2.812 \text{ \AA}$, $c = 14.083 \text{ \AA}$). The anisotropic change in the c -axis during extended cycling was inhibited by the addition of electrochemically inactive Al component.

Fig. 9 shows the TEM bright-field image and selected-area diffraction (SAD) pattern of $\text{LiCo}_{0.9}\text{Al}_{0.1}\text{O}_2$ powder after being cycled 170 times at room temperature. Some parts of the particle

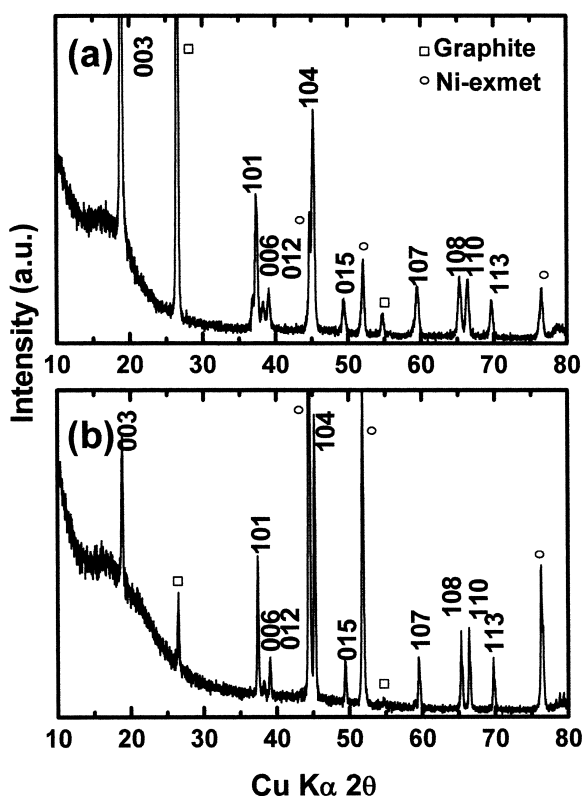


Fig. 8. XRD patterns of (a) 50 times cycled LiCoO_2 and (b) 170 times cycled $\text{LiCo}_{0.9}\text{Al}_{0.1}\text{O}_2$ electrodes at room temperature. The oxide samples were obtained by firing at 900°C for 24 h in air.

showed some signs of damage showing microcracks during cycling, showing severe strain and high dislocation densities in the crystal. Similar results using different synthetic routes have been previously reported [6,26]. We confirmed that the powder prepared by the emulsion drying method was a single crystal particle, which was maintained after extended cycling, because Fig. 9b clearly indicates a single crystal particle in the SAD pattern, exhibiting the appearance of hexagonal spots from the layer structure ($R\bar{3}m$).

4. Conclusion

The emulsion dried $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ ($x = 0, 0.1, 0.2$ and 0.3) solid solution powders were synthesized by the emulsion drying method. We have found some

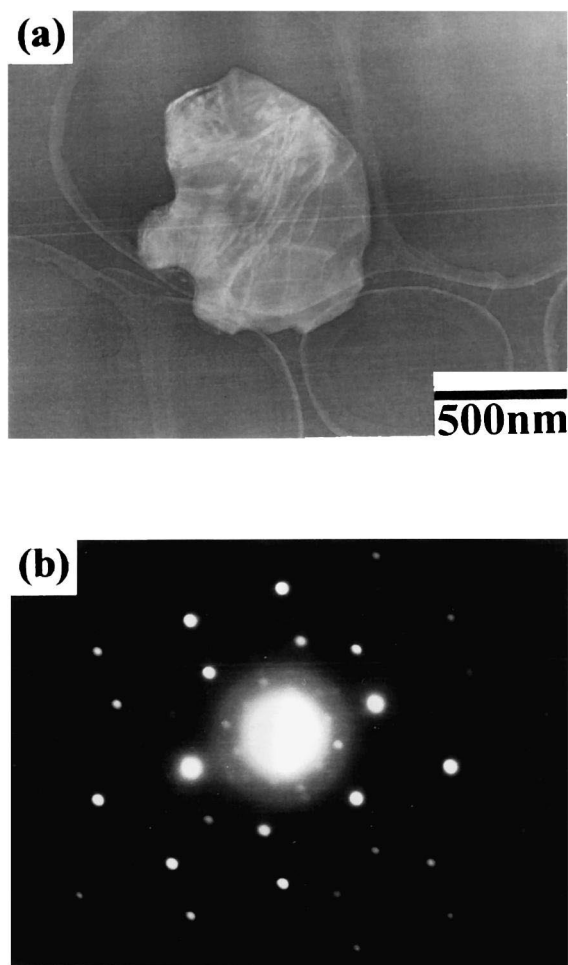


Fig. 9. (a) Bright-field TEM image and (b) selected-area electron diffraction pattern obtained from the $\text{LiCo}_{0.9}\text{Al}_{0.1}\text{O}_2$ electrodes after 170 cyclings at room temperature.

relationships among the discharge capacity, Al content, cobalt dissolution and variation in the c -axis, as illustrated in Fig. 10. According to that, it was concluded that:

1. the initial discharge capacity, variation in the c -axis and cobalt dissolution decreased with increasing Al content, while the open-circuit voltage and chemical diffusion coefficient increased with increasing Al content;
2. the anisotropic change in the c -axis during the extended cyclings was inhibited by the addition of electrochemically inactive Al component;

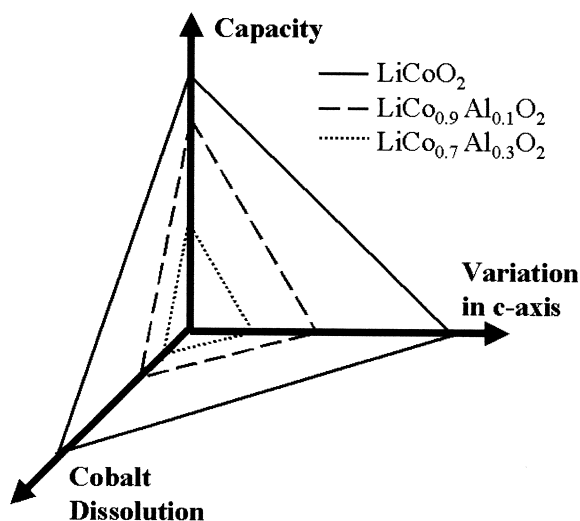


Fig. 10. Schematic diagram for the effect of Al doping on the discharge capacity, cobalt dissolution, and variation in the c -axis.

3. the structural integrity ($R\bar{3}m$) was maintained by a small amount of Al substitution for cobalt site.

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