# Synthesis and Characterization of $LiAI_{1/4}Ni_{3/4}O_2$ (R3m) for Lithium-Ion (Shuttlecock) Batteries

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# ABSTRACT

The synthesis and characterization of LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> were carried out in order to improve the electrochemical properties of LiNiO<sub>2</sub> for lithium ion batteries. Single phase of LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> (R3m; a = 2.86 Å and c = 14.24 Å in hexagonal setting) was obtained by heating a reaction mixture of LiNO<sub>3</sub>, NiCO<sub>3</sub>, and Al(OH)<sub>3</sub> at 750°C under an oxygen stream for 20 h and examined in nonaqueous lithium cells. LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> was oxidized to  $\Box_{3/4}Li_{1/4}Al_{1/4}Ni_{3/4}O_2$  in the voltage range of 3.5-4.8 V. X-ray diffraction examinations of Li<sub>1-x</sub>Al<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> indicated that the reaction

proceeded in a single phase over the entire range. The rechargeable capacity was observed to be about 150 mAh  $\cdot$  g<sup>-1</sup> based on the sample weight. DSC measurements on fully charged LiNiO<sub>2</sub> and LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> at 4.8 V were also done and the effects of substitution of aluminum for nickel in LiNiO<sub>2</sub> upon the electrochemical properties were discussed in terms of capacity, failure, and safety coupled with overcharge.

Lithium nickelate is one of the most attractive materials for lithium ion (shuttlecock) batteries.<sup>1-6</sup> The reaction mechanism of LiNiO<sub>2</sub> is already known to be a topotactic reaction consisting of three single-phase reactions for 0 < x < 0.75 in  $Li_{1-x}$ NiO<sub>2</sub> (a rhombohedral phase for  $0 < x \ 0.25,$  a monoclinic phase for 0.25 < x < 0.55, and a rhombohedral phase for 0.55 < x < 0.75) and a two-phase reaction for  $0.75 < x < 1.^2$  During the oxidation of LiNiO<sub>2</sub> the interlayer distance between NiO<sub>2</sub> sheets expands almost continuously from ca. 4.73 Å to ca. 4.80 Å as x approaches 0.5 where it levels off until x exceeds 0.75. Rechargeability in this single-phase region is excellent.<sup>2,4,6</sup> However, further oxidation induces ca. 0.3 Å shrinkage in the interlayer distance, so that the rechargeability in the two-phase region for 0.75 < x < 1 is not expected to be good. The shrinkage is associated with the formation of nickel dioxide ( $\overline{R3m}$ ; a = 2.81 Å and c = 13.47 Å in hexagonal setting) which is formed above 4.2 V against a lithium electrode.<sup>2</sup> This is a main reason it is necessary to set the charge-end voltage slightly below 4.2 V (typically 4.1 V) when a cycle life more than one thousand is needed.<sup>4,6</sup> Several efforts have been done to extend a cycle life, such as the addition (or substitution) of manganese,7 aluminum,8-10 or boron<sup>10</sup> into lithium nickelate, and the effects of the addition of these species upon cycleability were described.<sup>7-10</sup> Safety is another key factor to help decide among candidate materials for lithium-ion batteries.<sup>11-13</sup> LiNiO<sub>2</sub> is stable even when it is heated with an organic electrolyte. However, nickel dioxide electrochemically formed from LiNiO<sub>2</sub> is quite active toward organic electrolyte oxidation and this reaction is exothermic, so that overcharge protection is necessary to prevent possible thermal runaway in operating lithium-ion batteries based on LiNiO<sub>2</sub>.

In order to cope with these problems resulting from the formation of nickel dioxide we modified LiNiO<sub>2</sub> by replacing Ni<sup>3+</sup> ions with Al<sup>3+</sup> ions while retaining the high voltage characteristic of LiNiO<sub>2</sub>. The target material,  $LiAl_{1/4}Ni_{3/2}$  $4O_2$ , is a solid solution of LiNiO<sub>2</sub> (R3m; a = 2.88 Å and c =14.19 Å in hexagonal setting) and  $\alpha$ -LiAlO<sub>2</sub> (R3m; a =2.80 Å and c = 14.23 Å). We expect the following topotactic reaction

$$\text{LiAl}_{1/4}\text{Ni}_{3/4}\text{O}_2 \rightarrow \Box_{3/4}\text{Li}_{1/4}\text{Al}_{1/4}\text{Ni}_{3/4}\text{O}_2 + (3/4)\text{Li}^+ + (3/4)e^-$$

where  $\Box$  denotes the vacant octahedral sites in a cubicclose packed oxygen array. The fully charged species is  $\Box_{3/4}Li_{1/4}Al_{1/4}Ni_{3/4}O_2$  which is expected to be an insulator having ca. 4.8 Å of interlayer distance<sup>2</sup> if Ni<sup>4+</sup> ions are in

<sup>e</sup> Electrochemical Society Active Member. <sup>c</sup> Electrochemical Society Student Member.

their low spin states ( $t_2^6g \cdot e_g^0$  in  $O_h$  symmetry) and also be resistive against an electrolyte oxidation.

In this paper we report the synthesis and characterization of LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub>, its electrochemical charge and discharge, and the x-ray diffractional measurements for  $Li_{1-x}Al_{1/4}Ni_{3/4}O_2$ . We also report the DSC measurements for the fully charged samples of LiAl1/4Ni3/4O2 and LiNiO2 and discuss the possibility of materials design for advanced batteries.

#### Experimental

 ${\rm LiAl}_{1/4}{\rm Ni}_{3/4}{\rm O}_2$  was prepared by heating a reaction mixture of LiNO<sub>3</sub>, NiCO<sub>3</sub>, and Al(OH)<sub>3</sub> at 750°C under an oxygen stream for 20 h. Preliminary examinations to prepare single phases of  $\alpha$ ,  $\beta$ , and  $\gamma$ -LiAlO<sub>2</sub> were done using combinations of Al<sub>2</sub>O<sub>3</sub> or Al(OH)<sub>3</sub> and LiOH, Li<sub>2</sub>CO<sub>3</sub>, or LiNO<sub>3</sub> at several temperatures in air prior to settle the reaction conditions to prepare  $LiAl_yNi_{1-y}O_2$  as is described in the results section. LiAl<sub>y</sub>Ni<sub>1-y</sub>O<sub>2</sub> was characterized by XRD using an x-ray diffractometer (Type XD-3A, Shimadzu Corp., Japan) with Cu- $K_{\alpha}$  radiation, equipped with a diffracted graphite monochromator.

The experimental conditions used to examine the electrochemical behaviors of LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> were the same as those described previously.2 The cathode mix used was 0.08-0.10 g and consisted of 88 weight percent (w/o) LiAl1/4Ni3/4O2, 6 w/o acetylene black, and 6 w/o Teflon binder, (T-30J, Du Pont-Mitsui Fluorochemicals Co., Ltd., Japan). A constant current of 0.5 mA was applied to the electrode ( $15 \times 20 \text{ mm}^2$ ;  $0.17 \text{ mA} \cdot \text{cm}^{-2}$ ) corresponding to about 5-6 mA  $\cdot$  g<sup>-1</sup> based on the LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> sample weight. The electrolyte was 1 M LiClO<sub>4</sub> dissolved in propylene carbonate (PC) solution containing less than 30 mg · liter<sup>-1</sup> water. In fabricating the cells, all materials except the electrolyte and lithium metal were dried under vacuum at about 60°C at least 2 h before fabrication to avoid possible contamination with water. All procedures in fabricating the cells were done in an argon-filled glove box.

DSC measurements of  ${\rm Li}_{1-x}{\rm Al}_{1/4}{\rm Ni}_{3/4}{\rm O}_2$  and  ${\rm Li}_{1-x}{\rm Ni}{\rm O}_2$ were done using a differential scanning calorimeter (DSC-50, Shimadzu Corp.) combined with a thermal analyzer (TA-50, Shimadzu Corp.).  $Li_{1-x}Al_{1/4}Ni_{3/4}O_2$  and  $Li_{1-x}NiO_2$ were prepared electrochemically using a compressed pellet of  $LiAl_{1/4}Ni_{3/4}O_2$  or  $LiNiO_2$  (forming pressure  $10^3 \text{ kg} \cdot \text{cm}^{-2}$ ; 11.3 mm diam and ca. 0.6 mm thick). The electrochemical oxidation of the pellets was performed galvanostatically at  $0.17 \text{ mA} \cdot \text{cm}^{-2}$  while monitoring the operating voltage. The  $\text{Li}_{1-x}\text{Al}_{1/4}\text{Ni}_{3/4}\text{O}_2$  or  $\text{Li}_{1-x}\text{NiO}_2$  sample containing the electrolyte was sealed in an aluminum cell (5.50 mm diam and ca. 1 mm thick). Twenty milligrams of α-Al<sub>2</sub>O<sub>3</sub> in the alu-

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<sup>4033</sup> 

minum cell was used as a reference. Other sets of experimental conditions are given in the results section.

### Results

Preparation of  $LiAl_yNi_{1-y}O_2$  — A single phase of  $\alpha$ -LiAlO<sub>2</sub> (R3m; a = 2.80 Å, c = 14.23 Å in hexagonal setting) was obtained by heating a reaction mixture of Al(OH)<sub>3</sub> and LiNO<sub>3</sub> (or Li<sub>2</sub>CO<sub>3</sub>) at 650°C for 20 h and then at 750°C for 20 h in air. When we used  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substituting for Al(OH)<sub>3</sub>, single phase of  $\alpha$ -LiAlO<sub>2</sub> was hardly obtained. Any combination with LiOH did not give a single phase of  $\alpha$ -LiAlO<sub>2</sub>.  $\beta$ -LiAlO<sub>2</sub> (Pna2<sub>1</sub>; a = 5.28 Å, b = 6.31 Å, c = 4.91 Å) was usually contained in the reaction products. Single phase of  $\beta$ -LiAlO<sub>2</sub> was obtained by heating Al(OH)<sub>3</sub> (or Al<sub>2</sub>O<sub>3</sub>) with excess LiOH at 500°C for 4 h in air, washing its reaction product with distilled water, and then heating it at 400°C in air. At temperatures above  $850^{\circ}$ C both  $\alpha$ -LiAlO<sub>2</sub> and  $\beta$ -LiAlO<sub>2</sub> were converted into  $\gamma$ -LiAlO<sub>2</sub> (P4<sub>1</sub>2<sub>1</sub>2; a = 5.18 Å, c = 6.28 Å). Since the reaction conditions to prepare  $\alpha$ -LiAlO<sub>2</sub> were almost the same as those to prepare  $LiNiO_{2}^{2}$ ,<sup>2</sup> we intensively examined the conditions to prepare  $LiAl_y Ni_{1-y}O_2$  using a reaction mixture of  $LiNO_3$ ,  $Al(OH)_3$ , and NiCO<sub>3</sub>. Figure 1 shows the x-ray diffraction patterns of  $LiAl_yNi_{1-y}O_2$ . Miller indexes are given assuming a hexagonal lattice. All samples in Fig. 1 were prepared by heating a reaction mixture of  $LiNO_3$ ,  $Al(OH)_3$ , and  $NiCO_3$  at 750°C for 20 h under an oxygen stream. As can be seen in Fig. 1, a single phase of  $LiAl_yNi_{1-y}O_2$  can be prepared by this method. By increasing the aluminum content, the (0,0,6)line shifts toward the lower diffraction angles and conversely the (1,1,0) line shifts toward the higher diffraction angles, which result in a clear split of (0,0,6)(1,0,2) and (1,0,8)(1,1,0) lines for LiNiO<sub>2</sub>. Selective line broadening is observed especially for the (1,1,0) and (1,1,3) lines as the



Fig. 1. X-ray diffraction patterns of LiAl<sub>2</sub>Ni<sub>1-y</sub>O<sub>2</sub>; (a) y = 0, (b) y = 0.1, (c) y = 0.2, (d) y = 0.3, (e) y = 0.4, and (f) y = 0.5. LiAl<sub>2</sub>Ni<sub>1-y</sub>O<sub>2</sub> was prepared by heating a reaction mixture of LiNiO<sub>3</sub>, NiCO<sub>3</sub>, and Al(OH)<sub>3</sub> at 750°C for 20 h under an oxygen stream. Miller indexes were given by assuming a hexagonal lattice.



Fig. 2. Hexagonal unit cell parameters,  $a_h$  and  $c_h$ , as a function of y in LiAl<sub>y</sub>Ni<sub>1-y</sub>O<sub>2</sub>. The parameters were determined by a least squares method using 13-15 diffraction lines depending on the number of well-defined diffraction lines.

aluminum content increases, suggesting a microscopic stress in the basal plane. For  $LiAl_{1/2}Ni_{1/2}O_2$  well-defined diffraction lines are hardly obtained as seen in Fig. 1 (f).

Figure 2 shows the lattice parameters,  $a_h$  and  $c_h$ , as a function of y in LiAl<sub>y</sub>Ni<sub>1-y</sub>O<sub>2</sub>. These parameters were obtained by a least squares method using 10 to 15 diffraction lines depending on the number of well-defined diffraction lines for the samples. Substitution of nickel ions in LiNiO<sub>2</sub> for aluminum ions results in the *a*-axis shortening and *c*-axis enlarging as *y* increases until y = 1/4, after which the parameters level off. Consequently, the unit cell volume



Fig. 3. Hexagonal unit cell volume as a function of y in LiAl, Ni1-, O2.



Fig. 4. X-ray diffraction patterns of LiNiO<sub>2</sub> ( $a_h = 2.88$  Å,  $c_h = 14.19$  Å in hexagonal setting), LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> ( $a_h = 2.86$  Å,  $c_h = 14.24$  Å), and  $\alpha$ -LiAlO<sub>2</sub> ( $a_h = 2.80$  Å,  $c_h = 14.23$  Å).

decreases from 102 Å <sup>3</sup> to 100.5 Å <sup>3</sup> in  $0 \le y \le 1/4$  as shown in Fig. 3. The lattice parameters for the end members of LiAl<sub>y</sub>Ni<sub>1-y</sub>O<sub>2</sub> are a = 2.88 Å and c = 14.19 Å (102 Å <sup>3</sup> of unit cell volume) for LiNiO<sub>2</sub> *vs.* a = 2.80 Å and c = 14.23 Å (97 Å <sup>3</sup>) for  $\alpha$ -LiAlO<sub>2</sub>. The *c*-axis dimension of LiAl<sub>y</sub>Ni<sub>1-y</sub>O<sub>2</sub> in Fig. 2 quickly approaches 14.23 Å, or more than that value as *y* increases from 0 to 1/4, while the *a*-axis dimension follows a straight line from 2.88 Å for LiNiO<sub>2</sub> to 2.80 Å for  $\alpha$ -LiAlO<sub>2</sub> in the range  $0 \le y \le 1/4$ . Such an anisotropic



Fig. 5. First charge and subsequent discharge curves for LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> at a rate of 0.17 mA  $\cdot$  cm<sup>-2</sup> at 30°C. The cell was charged at a constant capacity of (a) 25, (b) 50, (c) 100, (d) 125, (e) 150, or (f) 200, or (g) 230 mAh  $\cdot$  g<sup>-1</sup> based on LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> sample weight and then discharged to 2.5 V. The electrolyte used was 1 M LiClO<sub>4</sub> dissolved in propylene carbonate.

change in lattice dimensions is characteristics of a layered structure.

As described above, a single phase of  $\text{LiAl}_{y}\text{Ni}_{1-y}\text{O}_{2}$  ( $0 \leq y \leq 1/4$ ) can be prepared by heating a reaction mixture of  $\text{LiNO}_{3}$ , Al(OH)<sub>3</sub>, and NiCO<sub>3</sub> at 750°C for 20 h under an oxygen stream.

Structural characterization of  $\text{LiAl}_{1/4}\text{Ni}_{3/4}\text{O}_2$ .—Our target material is  $\text{LiAl}_{1/4}\text{Ni}_{3/4}\text{O}_2$ , so we characterize it in more detail. The x-ray diffraction pattern of  $\text{LiAl}_{1/4}\text{Ni}_{3/4}\text{O}_2$ is shown in Fig. 4, comparing it with those of  $\text{LiNiO}_2$  and  $\alpha$ -LiAlO<sub>2</sub>. The *a*-axis dimension of  $\text{LiAl}_{1/4}\text{Ni}_{3/4}\text{O}_2$  is 2.86 Å, which is a quarter point between 2.88 Å for  $\text{LiNiO}_2$ and 2.80 Å for  $\alpha$ -LiAlO<sub>2</sub>. This suggests a homogeneous distribution of aluminum ions at nickel sites in  $\text{LiNiO}_2$ . We expected the appearance of superlattice lines from a [2 × 2] sublattice in a triangular lattice of sites, but could not detect such lines in spite of an extensive search (*a* = 2.86 × 2 Å for a hypothetical [2 × 2] sublattice).

The c-axis dimension of LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> is almost the same as that of  $\alpha$ -LiAlO<sub>2</sub> due to the change in force acting through plane by the substitution (van der Waals force). The unit cell parameters for LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> were determined to be a = 2.859 Å and c = 14.241 Å in a hexagonal setting by a least squares method using 15 diffraction lines. Batch-tobatch data were almost invariant in the *a*-axis dimension, but for some reason there was slight variability in the *c*axis dimension in the range 14.23 to 14.24 Å. In analyzing the structure, we assumed a space group R3m in which trivalent aluminum and trivalent nickel ions were randomly distributed at the octahedral 3(a) sites with an occupancy of 0.25 for aluminum and 0.75 for nickel. The lithium ions are located at the octahedral 3(b) sites, and oxygen ions at the 6(c) sites and we obtained an oxygen positional parameter of 0.26<u>2</u>. These results indicate that  $LiAl_{1/4}Ni_{3/4}O_2$  is a solid solution of  $\alpha$ -LiAlO<sub>2</sub> (R3m) and  $LiNiO_2$  (R3m) by the ratio 1:3.

Electrochemical charge and discharge.—Figure 5 shows the first charge and discharge curves for a Li /  $LiAl_{1/4}Ni_{3/4}O_2$ cell operated between 2.5 and 4.8 V. The open-circuit voltage of a freshly prepared cell was 3.13 to 3.20 V. During charge at  $0.17 \text{ mA} \cdot \text{cm}^{-2}$  the voltage rapidly increased to about 3.75 V, and then followed an ascending curve. A plateau was observed at 4.50 V, after which the voltage rose from 4.50 to 4.80 V. The charge capacity at 4.8 V of cutoff voltage was ca. 230 mAh  $\cdot$  g<sup>-1</sup> based on LiAl<sub>1/4</sub> Ni<sub>3/4</sub>O<sub>2</sub> sample weight. However, the first discharge capacity was observed to be  $ca. 170 \text{ mAh} \cdot \text{g}^{-1}$ . About 60 mAh  $\cdot \text{g}^{-1}$ of charge capacity is lost during the first charge and discharge. To examine how the charge capacity is lost during the first cycle, the cell was charged at constant capacity increments of 25, 50, 100, 125, 150, or 200 mAh  $\cdot$   $g^{-1}$  based on  $\rm LiAl_{1/4}Ni_{3/4}O_2$  sample weight and then discharged to 2.5 V. The results are shown in Fig. 5. Thirty to forty mAh .  $g^{-1}$  of charge capacity is lost when the charge capacities are 100-200 mAh  $\cdot$  g<sup>-1</sup>. Another 20-30 mAh  $\cdot$  g<sup>-1</sup> is lost when the cell is charged to 4.8 V (*ca*. 230 mAh  $\cdot$  g<sup>-1</sup> of charge capacity). These results indicate that the loss of charge capacity occurs in the initial and final part of the charging process. The loss of charge capacity is only observed in the first charge and discharge, after which the cell cycles with more than 99% of charge-discharge coulombic efficiency as shown in Fig. 6. In examining the rechargeability of  $LiAl_{1/}$  $4Ni_{3/4}O_2$ , the cells were cycled by charging at a constant capacity of 100 mAh  $\cdot$  g<sup>-1</sup> or 150 mAh  $\cdot$  g<sup>-1</sup> followed by discharging to 2.5 V at  $0.17 \text{ mA} \cdot \text{cm}^{-2}$ . As can be seen in Fig. 6, LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> is rechargeable in almost the same way as LiNiO<sub>2</sub> in nonaqueous lithium cells.

Detailed x-ray diffraction measurements of  $Li_{1-x}Al_{1/4}$  $Ni_{3/4}O_2$ .—In order to follow a change in the crystal stucture of LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> during charge and discharge, XRD examinations were carried out at the locations shown in the barcodelike indications in Fig. 7. The results are shown in Fig. 8 and 9. No new diffraction lines were observed; all diffrac-

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Fig. 6. Charge and discharge curves of LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> for a constant capacity charge of (a) 100 mAh  $\cdot$  g<sup>-1</sup> or (b) 150 mAh  $\cdot$  g<sup>-1</sup> based on LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> sample weight at a rate of 0.17 mA  $\cdot$  cm<sup>-2</sup>, followed by a constant-current discharge to 2.5 V. In drawing figures the 2nd to 11th charge and discharge curves were shown.

tion lines could be indexed assuming a hexagonal lattice. The XRD patterns in Fig. 8 were obtained for a charging process and their charge curves were shown in Fig. 7(a). The (1,1,0) line which is originally broader than the (1,0,8)line is getting sharper, shifting toward higher diffraction angles as the oxidation proceeds. This suggests a release of microscopic in-plane stress due to the accumulation of formal tetravalent nickel ions. Conversely, the (1,0,4), (1,0,5), (1,0,7), and (1,0,8) lines are getting broader than those for  $LiAl_{1/4}Ni_{3/4}O_2$ . The (0,0,3) line slightly shifts toward lower diffraction angles while retaining almost the same halfwidth as LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> until the charge capacity exceeds 200 mAh  $\cdot$  g<sup>-1</sup>, after which it slightly shifts back to higher diffraction angles while broadening the profile as shown in Fig. 8. The XRD patterns in Fig. 9 were obtained for a discharging process after charging to 4.8 V (about 230 mAh  $\cdot$  g<sup>-1</sup> of charge capacity). The charge and discharge curves for the cells used to prepare the XRD samples are shown in Fig. 7(b). As can be seen in Fig. 9, XRD observations for a discharging process are the same as those for the charging process in Fig. 8 in a reverse order. The XRD pattern in Fig. 9(e) is identical with that for  $LiAl_{1/4}Ni_{3/4}O_2$  in Fig. 8(a), indicating that  $LiAl_{1/4}Ni_{3/4}O_2$  is recovered after a charge-discharge cycle.

As described above, the electrochemical reaction of  $\text{Li}_{1-x}\text{Al}_{1/4}\text{Ni}_{3/4}\text{O}_2$  proceeds topotactically in a rhombohedral phase, although the change in profile for each diffraction line during charge and discharge is quite complicated probably due to the existence of electrochemically inactive  $\text{Al}^{3*}$  species at the Ni<sup>3+</sup> sites in LiNiO<sub>2</sub> (R3m).

DSC measurements for fully charged LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub>.--Figure 10 shows the results on the DSC measurements for the fully charged  $LiAl_{1/4}Ni_{3/4}O_2$  and  $LiNiO_2$ . In preparing the samples for DSC measurements,  $LiAl_{1/4}Ni_{3/4}O_2$  or LiNiO<sub>2</sub> powder was pressed into a pellet and used as a cathode in a nonaqueous lithium cell. After constant-current charge at  $0.1\overline{7}$  mA  $\cdot$  cm<sup>-2</sup> up to 4.8 V the pellet was taken out of the cell, and the electrolyte (1 M LiClO<sub>4</sub> PC) was wiped off with a filter paper. A piece of the crushed pellet was mechanically sealed in an aluminum cell. The weight of the sample loaded in the aluminum cell, including the electrolyte, was estimated by weighing the aluminum cells with and without the sample. DSC signals (a heat flow in mW as a function of temperature) were measured at a heating and cooling rate of 5°C · min.<sup>-1</sup> The degree of oxidation was calculated from the charge capacity and a theoretical capacity based on one-electron transfer per a formula unit of  $\mathrm{LiAl}_{1/4}\mathrm{Ni}_{3/4}\mathrm{O}_2$  or  $\mathrm{LiNiO}_2.$ 

For LiNiO<sub>2</sub> containing the electrolyte, nothing happened except for endothermic signals at temperatures between 100 and 175°C. These were probably due to the thermal decomposition of propylene carbonate on LiNiO<sub>2</sub>. For a fully charged LiNiO<sub>2</sub>, specifically Li<sub>0 15</sub>NiO<sub>2</sub> which is close to nickel dioxide ( $\Box$ NiO<sub>2</sub>), two exothermic peaks at 155 and 210°C were observed in addition to an exothermic spike at 184°C. The onset temperature of an exothermic reaction is accelerated as temperature rises. To draw such a sharp spike an endothermic reaction whose onset temperature is 184°C would be necessary. A possible reaction is the bulk decomposition of nickel dioxide which releases oxygen. If such an endothermic reaction is involved, an endothermic



Fig. 7. Continuous charge (and discharge) curves at a rate of 0.17 mA  $\cdot$  cm<sup>-2</sup> for Li/LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> cells to prepare XRD samples of Li<sub>1-x</sub>Al<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> for (a) a charging process and (b) discharging process. Barcode-type indications in figures show the locations at which the XRD examinations were undertaken.



Fig. 8. X-ray diffraction patterns of Li<sub>1-x</sub>Al<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> after (a) 0, (b) 75, (c) 150, and (d) 230 mAh  $\cdot$  g<sup>-1</sup> of charge capacity. Charge curves for the cells were shown in Fig. 7(a).

peak is estimated to occur at about 190°C which is in good agreement with the results on the thermal gravimetric study on the decomposition reaction of  $\text{Li}_{0.3}\text{NiO}_2$ .<sup>14</sup> Although it is difficult to specify each endothermic or exothermic reaction by DSC data alone, it is clear that the thermal behavior of  $\text{Li}_{0.15}\text{NiO}_2$  containing the electrolyte is a haystack-type reaction associated with thermal runaway.<sup>15</sup> The thermal behavior of the fully charged LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub>, specifically Li<sub>0.28</sub>Al<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub>, is quite different from that for Li<sub>0.15</sub>NiO<sub>2</sub>. Although some exothermic and endothermic reactions are involved, these reactions are mild, resulting in rounded exothermic and endothermic signals.

#### Discussion

Reaction mechanism of  $Li_{1-x}Al_{1/4}Ni_{3/4}O_2$ .—As seen in Fig. 7-9, there is no doubt about a single-phase reaction over the entire range. This is better illustrated in Fig. 11. In calculating x in of  $Li_{1-x}Al_{1/4}Ni_{3/4}O_2$ , we assume one electron transfer per a formula unit of  $LiAl_{1/4}Ni_{3/4}O_2$  (298 mAh  $\cdot g^{-1}$  of capacity for an assumed reaction). To represent a series of  $\alpha$ -NaFeO<sub>2</sub>-structural types having a rhombohedral lattice, we usually use a hexagonal setting.<sup>2,16-18</sup> The relation-ship between rhombohedral ( $a_R$  and  $\alpha$ ) and hexagonal lattice constants ( $a_h$  and  $c_h$ ) is as follows

$$a_{\rm R} = \frac{1}{3} \sqrt{3a_{\rm h}^2 + c_{\rm h}^2}$$
,  $\alpha = 2 \sin^{-1} \left[ \frac{3}{2\sqrt{3 + (c_{\rm h}/a_{\rm h})^2}} \right]$ 

so we can convert one lattice constant to another. In Fig. 11 the hexagonal lattice constants,  $a_h$  and  $c_h$ , as a function of x in  $\text{Li}_{1-x}\text{Al}_{1/4}\text{Ni}_{3/4}\text{O}_2$  are shown. In calculating x-values from the charge and discharge capacity, we assumed 100% coulombic efficiency. Open-circles in Fig. 11 are the lattice parameters,  $a_h$  and  $c_h$ , calculated from XRD data in Fig. 8 obtained for a charging process (shown in Fig. 7(a)). The triangles in Fig. 11 are the lattice parameters similarly calculated from the XRD data in Fig. 9 for a discharging process (shown in Fig. 7(b)). If the coulombic efficiency is

100% to oxidize LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub>, the two curves of open circles and triangles must merge into a single curve. However, about 0.1 shift in x-value (corresponding to 30 mAh  $\cdot$  g<sup>-1</sup> of capacity) is observed in Fig. 11, indicating the loss of charge capacity in the high voltage region mainly above 4.50 V, which is consistent with the observations in Fig. 5. Another loss of charge capacity is observed in charge capacifies below 100 mAh  $\cdot g^{-1}$  for which operating voltage is below 4.0 V as seen in Fig. 5. In this region the lattice parameters in Fig. 11 are not affected by the charge capacity. If we assume the change in lattice parameters is directly proportional to the amount of charge accumulated in the solid matrix, the charge capacity below  $100 \text{ mAh} \cdot \text{g}^{-1}$  is not effectively consumed to oxidize LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> as seen in Fig. 5 and 11. Since the loss of charge capacity in this region is only observed in the first charge and discharge as seen in Fig. 5 and 6, the oxidation of impurity such as combined water probably participated in this loss although we cannot specify a reaction.

As can be seen in Fig. 8 and 9, the rapid increase in charging voltage at about 230 mAh  $\cdot$  g^{-1} of charge capacity strongly suggests the formation of an electronically insulating material  $\Box_{3/4} Li_{1/4} Al_{1/4} Ni_{3/4} O_2$  in which the electronic structures of Al<sup>3+</sup> and Ni<sup>4+</sup> are 3s<sup>0</sup> and presumably  $t_{5g}^6 \cdot e_g^o$  (3d<sup>6</sup>) in  $O_h$  symmetry,<sup>2</sup> respectively. It should be noted that in the fully charged state for LiAl\_{1/4} Ni\_{3/4} O\_2 ( $\Box_{3/4} Li_{1/4} Ni_{3/4} O_2$  in this case) lithium ions are available, but no electrons can be removed in an appropriate voltage range, called electrons-source (or sink) limiting capacity.<sup>5</sup> This is the reverse of the situation for Li[Li\_{1/3}Ti\_{5/3}]O\_4 for which lithium-ion site limiting capacity was observed.<sup>19</sup>

General observations, such as the shrinkage in the *a*-axis dimension down to *ca*.2.80 Å and the dilution in the *c*-axis dimension up to 14.5 Å as *x* increases, are the same as those for LiCoO<sub>2</sub>,<sup>18</sup> LiNiO<sub>2</sub>,<sup>2</sup> or LiNi<sub>1/2</sub>Co<sub>1/2</sub>O<sub>2</sub>.<sup>17</sup> A dramatic change in the *c*-axis dimension to below 14.0 Å is observed



Fig. 9. X-ray diffraction patterns of  $Li_{1-x}AI_{1/4}Ni_{3/4}O_2$  after (a) 0, (b) 50, (c) 100, (d) 122, and (e) 170 mAh  $\cdot g^{-1}$  of discharge capacity, which followed 230 mAh  $\cdot g^{-1}$  of charge. Charge and discharge curves for the cells were shown in Fig. 7(b).



Fig. 10. DSC curves for (a)  $Li_{0.15}NiO_2$  (23.2 mg), (b)  $Li_{0.28}Al_{1/4} Ni_{3/4}O_2$  (17.0 mg), and (c)  $LiNiO_2$  (24.1 mg) containing electrolyte (1 *M* LiClO<sub>4</sub>PC).  $Li_{0.15}NiO_2$  and  $Li_{0.28}Al_{1/4}Ni_{3/4}O_2$  were prepared by charging  $LiNiO_2$  or  $LiAl_{1/4}Ni_{3/4}O_2$  without the addition of acetylene black and Teflon to 4.8 V at a rate of 0.17 mA  $\cdot$  cm<sup>-2</sup>. Heating and cooling rates were  $5^{\circ}C \cdot min^{-1}$ .

in the range 0.75 < x < 1 for  $\text{Li}_{1-x}\text{CoO}_2$ ,<sup>18</sup>  $\text{Li}_{1-x}\text{NiO}_2$ ,<sup>2</sup> or  $\text{Li}_{1-x}\text{Ni}_{1/2}\text{Co}_{1/2}\text{O}_2$ .<sup>17</sup> This gives a limitation in applying these materials to lithium-ion batteries, such that we need to set proper cutoff voltages for charging in order to safely cycle



Fig. 11. Unit cell parameters,  $a_h$  and  $c_h$ , as a function of x in  $Li_{1-x}Al_{1/4}Ni_{3/4}O_2$ . In calculating x-values 100% coulombic efficiency was assumed. Open circles were obtained for a charging process shown in Fig. 7(a) and triangles for a discharging process shown in Fig. 7(b).



Fig. 12. Unit cell volumes as a function of x in  $\text{Li}_{1-x}\text{Al}_{1/4}\text{Ni}_{3/4}\text{O}_2$ .

for thousands of cycles to prevent overcharging. As seen in Fig. 11, such as dramatic change in the *c*-axis dimension (below 14.0 Å) during charging is not observed for  $\text{Li}_{1-x}\text{Al}_{1/4}\text{Ni}_{3/4}\text{O}_2$ . The *c*-axis dimension remains above 14.3 Å even for a fully charged state (we are expecting 14.5 Å of the *c*-axis dimension by optimizing the composition and structure of the material). Figure 12 shows the change in unit cell volume for a hexagonal lattice as a function of *x* in  $\text{Li}_{1-x}\text{Al}_{1/4}\text{Ni}_{3/4}\text{O}_2$ . The unit cell volume changes monotonically from 100.5 Å <sup>3</sup> to 98 Å <sup>3</sup> (about 2.5% change in volume) during the reaction.



Fig. 13. Comparison between (a) LiNiO<sub>2</sub> and (b) LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> in terms of the change in voltage and interlayer distance on charge.

Although some ambiguities exist about the relationship between the structural parameters and x in  $\mathrm{Li}_{1-x}\mathrm{Al}_{1/4}\mathrm{Ni}_{3/4}\mathrm{O}_2$ , we formulate the topotactic reaction as

[Li] [Al<sub>1/4</sub>Ni<sub>3/4</sub>]O<sub>2</sub> 
$$\rightleftarrows$$
 [Li<sub>1-x</sub>□<sub>x</sub>] [Al<sub>1/4</sub>Ni<sub>3/4</sub>]O<sub>2</sub> + xLi<sup>+</sup> + xe<sup>-</sup>  
3(b) 3(a) 6(c) 3(b) 3(a) 6(c)  
(0 ≤ x < 0.75)

in which 3(a), 3(b), and 6(c) is the number of equivalent positions combined with Wyckoff letter in a space group R3m to represent the sites for each species. From this formulation the theoretical capacity is calculated to be 224 mAh  $\cdot$  g<sup>-1</sup> based on LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> weight (1.0 Ah  $\cdot$  g<sup>-3</sup> in volumetric capacity).

Significance of LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> for lithium-ion batteries.— One of the objectives in this research is to design a resistive characteristic against overcharging by replacing Ni<sup>3+</sup> ions with  $Al^{3+}$  ions in  $LiNiO_2$  while retaining the high voltage characteristic of LiNiO<sub>2</sub>. To discuss whether or not such a beneficial effect is expected from a fundamental point of view, we compare electrochemical and structural results for  $Li_{1-x}Al_{1/4}Ni_{3/4}O_2$  with those for  $Li_{1-x}NiO_2$ . Figure 13 shows the comparison of the charge curves and structural data between  $Li_{1-x}NiO_2$  and  $Li_{1-x}Al_{1/4}Ni_{3/4}O_2$ . To make a comparison in the same measure, we calculated the interlayer distances between  $NiO_2$  or  $Al_{1/4}Ni_{3/4}O_2$  sheets from the structural data obtained during charging processes. As seen in Fig. 13,the general features of charge curves for  $LiNiO_2$  and  $LiAl_{1/4}Ni_{3/4}O_2$ , such as voltage level, a plateau voltage at *ca*.4.50 V, and rapid increase in voltage from 4.5 to 4.8 V, are the same. This strongly suggests that both reactions consist of solid-state redox reactions between a lowspin  $\rm Ni^{3_{+}}$  ( $t^6_{2g} \cdot e^1_g$  in Oh symmetry) and low-spin  $\rm Ni^{4_{+}}$  ion  $(t_{2g}^6 \cdot e_g^0)$ . For Li<sub>1-x</sub>NiO<sub>2</sub> we observed a monoclinic phase in the range  $0.25 \leq x \leq 0.55$  (shown in triangles in Fig. 13(a)) and two rhombohedral phases in 0.75 < x < 1. A monoclinic phase which results from a cooperative Jahn-Teller effect of low-spin Ni<sup>3+ 2</sup> is not observed over the entire range for  $Li_{1-x}Al_{1/4}Ni_{3/4}O_2$  probably due to a microscopic stress induced by the substitution of nickel ions for aluminum ions as was previously described regarding the diffraction profile for the (1,1,0) line in Fig. 1 and 8. A two-phase reaction in the region 0.75 < x < 1 for  $\text{Li}_{1-x}\text{NiO}_2$ , which is associated with *ca*. 0.3 Å of dimensional change in the interlayer distance, is also eliminated for Li<sub>1-x</sub>Al<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> because Al<sup>3+</sup> ions together with lithium ions keep the interlayer distance to be about 4.8 Å. For LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub>,  $\Box_{3/4} Li_{1/4} Al_{1/4} Ni_{3/4} O_2$  is the fully charged state and an electronic insulator. The formation of an insulating material may give a beneficial effect upon overcharging because the insulating material behaves like an ideally polarizable electrode. Consequently, nothing will happen even when high voltages are imposed. This also prevents a haystacktype reaction associated with thermal runaway as seen in Fig. 10. LiNiO<sub>2</sub> shows 200 mAh  $\cdot$  g<sup>-1</sup> of rechargeable capacity with a changing interlayer distance between 4.72 and 4.80 Å. Therefore, we can expect 200 mAh  $\cdot$   $g^{-1}$  of rechargeable capacity out of 224 mAh  $\cdot$  g<sup>-1</sup> of the theoretical capacity for LiAl<sub>1/4</sub>Ni<sub>3/4</sub>O<sub>2</sub> and also resistivity against overcharging. The current results on the rechargeable capacity are about 150 mAh  $\cdot$  g<sup>-1</sup> as shown in Fig. 5, partly because the processing methods for preparing materials and electrodes including the selection of carbon and binder materials together with electrolyte composition have not been optimized. Such approaches are in progress in our laboratory. Although more thorough studies are necessary, we believe that the combination of  $\text{LiAl}_{1/4}\text{Ni}_{3/4}O_2$  (R3m) and (natural) graphite<sup>20</sup> is a most attractive system for lithium-ion batteries.

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