



## Effect of Mn Source and Peculiar Cycle Characterization for $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ Material in the 3 V Region

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$\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  was synthesized using  $\text{LiOH}$ ,  $\text{Al}(\text{NO}_3)_3$ , and two different  $\text{Mn}_3\text{O}_4$  sources (Tosoh and Chuodenki, Japan). Rietveld analysis revealed that the two  $\text{Mn}_3\text{O}_4$  and  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  compounds exhibited the same structures, respectively.  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  materials showed similar physicochemical properties, but they presented very different cycle retention rates in the 3 V region after 50 cycles (Tosoh, 36.2%; Chuodenki, 98.6%). The *ex situ* X-ray powder diffraction measurements also revealed that the two  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  materials showed different X-ray patterns after discharge to 2.2 V after 50 cycles. It was seen that  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  synthesized using Tosoh  $\text{Mn}_3\text{O}_4$  showed a mixture of distinct cubic and many tetragonal phases, but the other one using Chuodenki  $\text{Mn}_3\text{O}_4$  maintained an almost perfect cubic phase after cycling. We found that the  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  material might show an entirely different cycle characterization in the 3 V region although it was synthesized using the Mn source of the same crystal structure. © 2001 The Electrochemical Society. [DOI: 10.1149/1.1397935] All rights reserved.

Manuscript submitted April 2, 2001; revised manuscript received June 4, 2001. Available electronically August 14, 2001.

Spinel  $\text{LiMn}_2\text{O}_4$  and its derivatives are considered promising cathode materials for lithium secondary batteries with high energy density, due to their low cost and nontoxicity.<sup>1,2</sup> However, a significant capacity loss of the spinel  $\text{LiMn}_2\text{O}_4$  at high temperature during cycling prevents its wider use as cathode material for lithium secondary batteries.<sup>3-8</sup>

Many research groups have reported some reasons for the capacity loss of the  $\text{LiMn}_2\text{O}_4$  electrode in the 4 V region, such as (i) manganese dissolution, (ii) an unstable two-phase structure in the high voltage region, (iii) the surface area of the spinel in contact with the electrolyte, and (iv) Jahn-Teller distortion in the deeply discharged state.<sup>3-6</sup> On the other hand, when lithium is inserted into an octahedral vacancy (16c site) of the spinel ( $\text{Li}_x\text{Mn}_2\text{O}_4$ ) structures ( $1 < x \leq 2$ ) in the 3 V region, this process brings about a Jahn-Teller distortion, which induces an increase in the *c/a* ratio of the spinel unit cell of about 16%. The distorted spinel structure results in abrupt capacity fading in this voltage range.<sup>7,8</sup> Therefore, it has been reported that most of  $\text{LiMn}_2\text{O}_4$ -based materials showed poor cyclability in the 3 V region and were limited to use only in the 4 V region.<sup>7,8</sup>

Recently, we have synthesized Al-doped spinel ( $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ ) and reported the cycle characterizations of  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  using two different kinds of Mn sources ( $\text{Mn}_3\text{O}_4$  and  $\gamma\text{-MnOOH}$ ) in the 3 and 4 V regions.<sup>9,10</sup> Although the two  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  materials exhibited excellent cyclability in the 4 V region, they showed entirely different electrochemical properties and a unique structural change in the low voltage region ( $\sim 2.2$  V).<sup>10</sup> Based on these results, we had presented the opinions that the cycle performance in the 3 V region is influenced by the Mn starting material and that there may be many possibilities which induce different electrochemical characterizations in the 3 V region.

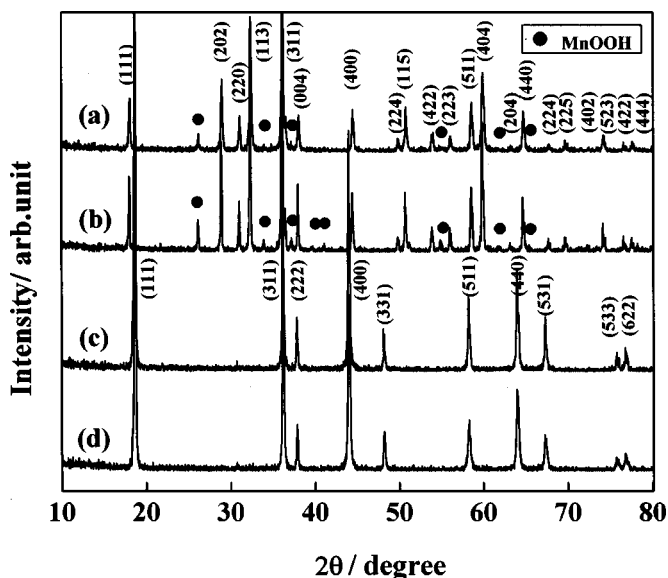
In this paper, we report new interesting observations in which some  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  materials can show very stable cycle performance in the 3 V region as well as in the 4 V region at the same time. Furthermore, they show different cycle characterization and structural change in the 3 V region even if they were synthesized using the same Mn source ( $\text{Mn}_3\text{O}_4$ ) by the same synthetic route.

### Experimental

$\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  material was synthesized using  $\text{LiOH}$ ,  $\text{Al}(\text{NO}_3)_3$ , and  $\text{Mn}_3\text{O}_4$  by the melt impregnation method. The two  $\text{Mn}_3\text{O}_4$  starting materials used in this research were synthesized by different synthetic processes. One is a hydrothermal method (Tosoh, Japan),

the other is a conventional solid-state method (Chuodenki, Japan). The mixture of  $\text{LiOH}$ ,  $\text{Al}(\text{NO}_3)_3$ , and  $\text{Mn}_3\text{O}_4$  was precalcined at 470 and 530°C for 5 h in  $\text{O}_2$  and then postcalcined at 800°C for 24 h in air. The two mixtures were calcined in the same box furnace at the same time. The powder X-ray diffraction (XRD) (Rint 1000, Rigaku, Japan) using  $\text{Cu K}\alpha$  radiation was employed to identify the crystalline phase of the synthesized material and the *ex situ* electrode cell. Rietveld refinement analysis was performed on the Mn starting materials using XRD data to distinguish its original structure. The Li, Al, and Mn contents in the resulting materials were determined using inductively coupled plasma-atomic emission spectrometry (Seiko Instruments Inc., SPS 7800, Japan). The particle morphologies of the  $\text{Mn}_3\text{O}_4$  and  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  materials were observed using a scanning electron microscope (SEM) (JSM-5300E, Japan Electron, Ltd., Japan). The specific surface area was measured in a Gemini 2375 instrument by the Brunauer, Emmett, and Teller method.

In order to calculate the average oxidation state of Mn, titration with excess  $\text{FeSO}_4$  solution with standard  $\text{KMnO}_4$  solution was carried out. The total Mn ion was determined by a complexometric titration method, in which excess ethylenediaminetetraacetic acid



**Figure 1.** XRD patterns for (a) Tosoh- $\text{Mn}_3\text{O}_4$ , (b) Chuodenki- $\text{Mn}_3\text{O}_4$ , (c) Tosoh- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ , and (d) Chuodenki- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ .

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**Table I. Properties and chemical analysis data of  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ .**

$\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ (LiOH + $\text{AlNO}_3$ + Mn)	Li (wt %)	Al (wt %)	Mn (wt %)	Average Mn valence	Lattice parameter (Å)	Surface area ( $\text{m}^2/\text{g}$ )
T- $\text{Mn}_3\text{O}_4$	3.91	1.32	58.79	3.52	8.2273	2.57
C- $\text{Mn}_3\text{O}_4$	3.91	1.32	58.77	3.53	8.2253	1.26

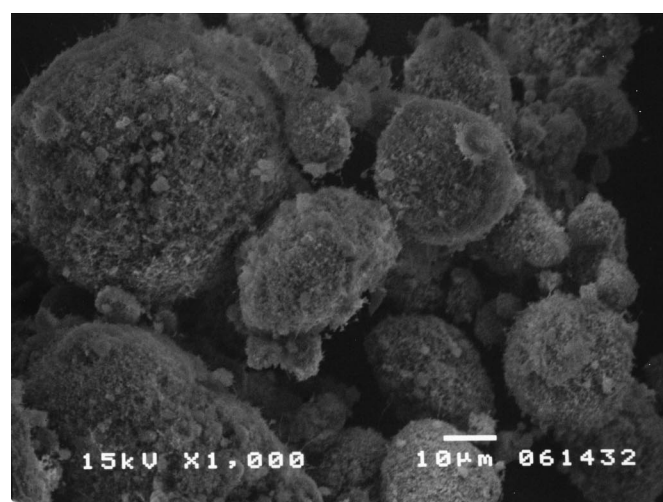
(EDTA) was analyzed by back titration using a standard zinc solution. The sample was first dissolved in hydroxylammonium chloride solution containing EDTA in advance.

The electrochemical characterizations were performed using a screw cell for the structural change in the two  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  materials after 50 cycles. The cathode was fabricated with 25 mg of accurately weighed active material and 18 mg of conductive binder (12 mg of Teflonized acetylene black (TAB) and 6 mg of graphite). It was pressed on a 250  $\text{mm}^2$  stainless steel mesh used as the current collector under a pressure of 300  $\text{kg}/\text{cm}^2$  and dried at 200°C for 5 h in an oven. The test cell was made of a cathode and a lithium metal anode (Cyprus Foote Mineral Co.) separated by a porous polypropylene film (Celgard 3401). The electrolyte used was a mixture of 1 M  $\text{LiPF}_6$ -ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:2

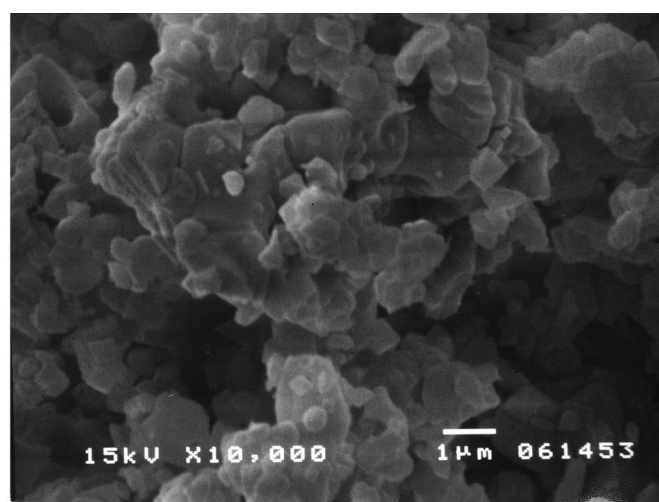
by volume). The charge or discharge current density was 0.4  $\text{mA}/\text{cm}^2$  (C/3) with a voltage of 3.0 to 4.3 V for the 4 V test (or 2.2 to 3.6 V for the 3 V test).

### Results and Discussion

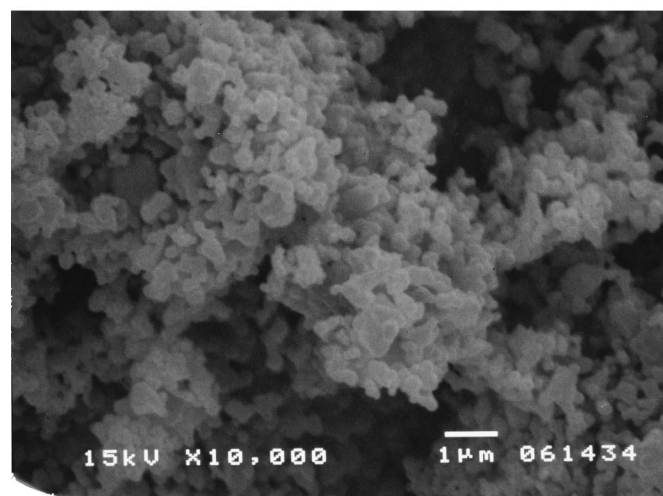
Figure 1 shows the XRD patterns of the  $\text{Mn}_3\text{O}_4$  sources and the resulting  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  materials. The two  $\text{Mn}_3\text{O}_4$  sources had almost the same XRD pattern without the stronger impurity peak of  $\text{MnOOH}$  in the Chuodenki  $\text{Mn}_3\text{O}_4$  (Fig. 1a, b). The lattice constants of the two  $\text{Mn}_3\text{O}_4$  sources with a tetragonal unit cell calculated by Rietveld refinement using the XRD data were  $a$ ,  $b$  = 5.76 Å,  $c$  = 9.46 Å. All the peaks appearing on the XRD patterns were identified with the characteristic peaks of  $\text{Mn}_3\text{O}_4$  reported in the



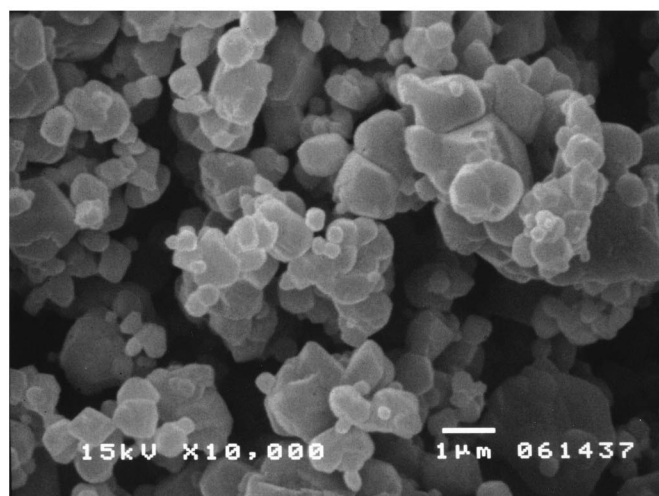
(a)



(b)

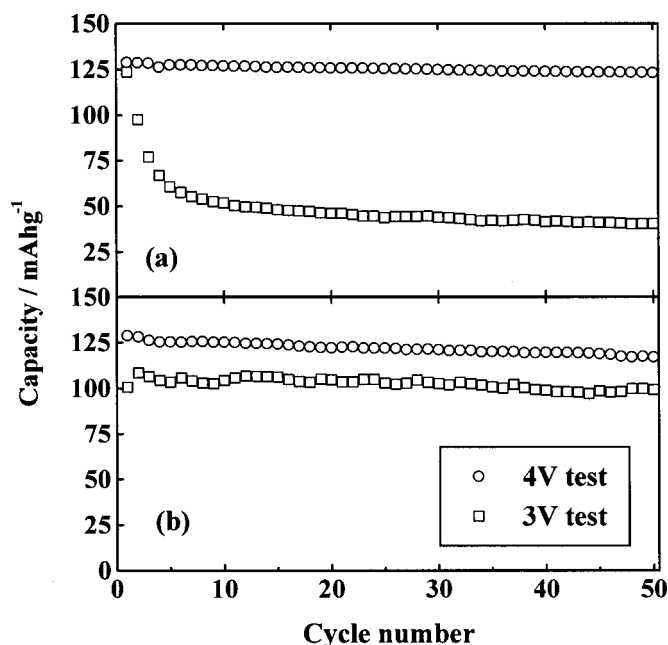


(c)



(d)

**Figure 2.** SEM images of (a, top left) Tosoh- $\text{Mn}_3\text{O}_4$ , (b, top right) Chuodenki- $\text{Mn}_3\text{O}_4$ , (c, bottom left) Tosoh- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ , and (d, bottom right) Chuodenki- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ .



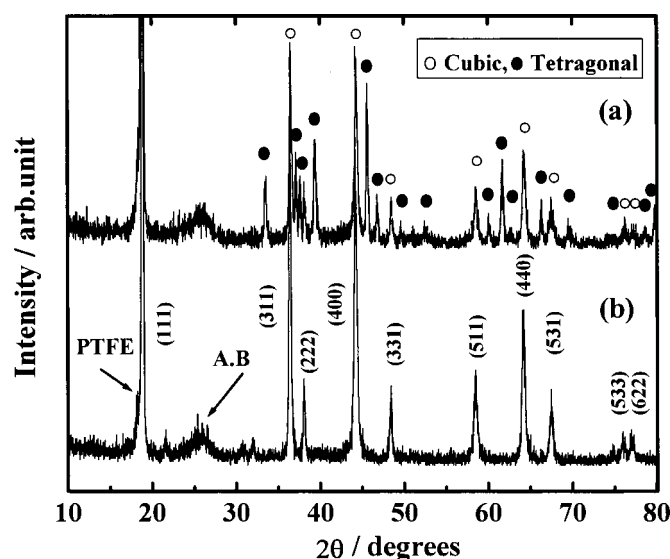
**Figure 3.** Charge/discharge curves of (a) Tosoh- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  and (b) Chuodenki- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  at different voltage regions. Cycling was carried out at a constant charge/discharge current density of  $0.4 \text{ mA/cm}^2$  between 4.3 and 3.0 V for the 4 V test (3.6-2.2 for the 3 V test).

X-ray powder data file of JCPDS. Figures 1c and d show that the two  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  materials were of the same crystalline structure and that all peaks were an indexed single cubic phase with the space group ( $Fd\bar{3}m$ ). Table I also shows that the two compounds are the same material and have the typical physicochemical properties of  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ .

The morphology of the powders was observed with a scanning electron micrograph (SEM). Figures 2a and b show SEM photographs of the  $\text{Mn}_3\text{O}_4$  starting materials. The average particle sizes are 20-40  $\mu\text{m}$  for Tosoh  $\text{Mn}_3\text{O}_4$  (herein referred to as T- $\text{Mn}_3\text{O}_4$ ) and 1-2  $\mu\text{m}$  for Chuodenki  $\text{Mn}_3\text{O}_4$  (herein referred to as C- $\text{Mn}_3\text{O}_4$ ). The colors of the powders were dark brown for T- $\text{Mn}_3\text{O}_4$  and dark orange for C- $\text{Mn}_3\text{O}_4$ , respectively. Meanwhile, the T- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  powder which was synthesized using T- $\text{Mn}_3\text{O}_4$  was about 0.2-0.5  $\mu\text{m}$  and C- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  using C- $\text{Mn}_3\text{O}_4$  was about 1-2  $\mu\text{m}$ , but its average particle size is slightly decreased compared to that of the original C- $\text{Mn}_3\text{O}_4$ . A great volume change was observed from T- $\text{Mn}_3\text{O}_4$  to T- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  in the synthetic process. The surface areas of the two resulting compounds were  $2.57 \text{ m}^2/\text{g}$  (for T- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ ) and  $1.26 \text{ m}^2/\text{g}$  (for C- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ ), as shown in Table I.

Figure 3 shows the discharge capacity as a function of cycle number for two  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  materials in the different voltage regions. In the 4 V region, the two compounds showed excellent cycle performance as well as a high initial discharge capacity. The capacity retention rate of T- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  was over 96% after 50 cycles (from 129 to 123  $\text{mAh/g}$ ). C- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  also presented a fairly good cyclability of over 91% after 50 cycles (from 129 to 117  $\text{mAh/g}$ ), even though it showed a big capacity loss compared to that of T- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ .

However, the cycle performance of two  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  materials in the 3 V region was quite different even if these had the same composition and showed similar physicochemical properties. T- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  showed an abrupt capacity loss within the 5th cycle from 124 to 61  $\text{mAh/g}$ , which steadily decreased to about 45  $\text{mAh/g}$  by the 50th cycle. We already reported that this indication



**Figure 4.** *Ex situ* XRD patterns of (a) Tosoh- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  and (b) Chuodenki- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  after 50 cycles.

resulted from the co-effect of Jahn-Teller distortion and a unique aluminum effect in which aluminum prevents a complete structural change from  $\text{LiMn}_2\text{O}_4$  (cubic) to  $\text{Li}_2\text{Mn}_2\text{O}_4$  (tetragonal) in the 3 V region.<sup>11</sup> On the other hand, the C- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  material exhibited a steady discharge capacity in the 3 V region. The cycle retention rate of C- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  in this region was 98.6% after 50 cycles (from 100.6 to 99.2  $\text{mAh/g}$ ). Furthermore, it also did not show an abrupt capacity loss in the early stage which was a unique cycle characterization in the 3 V region. This is a very interesting result in which the Mn-based spinel material (specially,  $\text{LiMn}_2\text{O}_4$ ) commonly showed poor cyclability in the 3 V region as a result of Jahn-Teller distortion when the lithium ion is inserted into the 16c site of  $\text{Li}_x\text{Mn}_2\text{O}_4$  ( $1 < x \leq 2$ ).

In order to investigate this different cycling behavior observed with the  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  materials, *ex situ* XRD measurements were taken of both  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  electrodes in the discharged state after 50 cycles as shown in Fig. 4. Each cell was left in a dry room for 2 days to reach equilibrium after being tested from 2.2 to 3.6 V, and the electrode was washed with DMC solution to remove the  $\text{LiPF}_6$  salt. Figure 4 shows that the two electrodes had quite different XRD patterns in the discharged state after 50 cycles. The T- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  electrode showed a distinct cubic and many tetragonal phases together, whereas C- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  maintained an almost perfect cubic ( $\text{LiMn}_2\text{O}_4$ ) structure after 50 cycles. The same result, which sustained the cubic structure of the  $\text{LiMn}_2\text{O}_4$ -based material helps to maintain good cycle retention in the 3 V region, was already reported by other research groups.<sup>12,13</sup> However, it is worth noting that this is a new observation even if the same material could show different cycle characterization and structural changes in the 3 V region. On the basis of these data, we concluded that C- $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  material showed a very stable cyclability in the 3 V as well as in the 4 V region. Furthermore, the  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$  materials, which were synthesized using the same manganese source (but they were made by a different synthetic process or a different raw material), can show conflicting cycle performance in the 3 V region, although they showed a similar cycle performance in the 4 V region. Actually, we found some other elements and a higher amount of sulfur in C- $\text{Mn}_3\text{O}_4$  starting material using electron probe microanalysis (EPMA) as shown in Fig. 5. These images were taken at the cross section of the particles after grinding completely. The test conditions were 30 kV and 0.1  $\mu\text{A}$ . Although, we still cannot explain clearly the meaning of this observation, we assume that a small



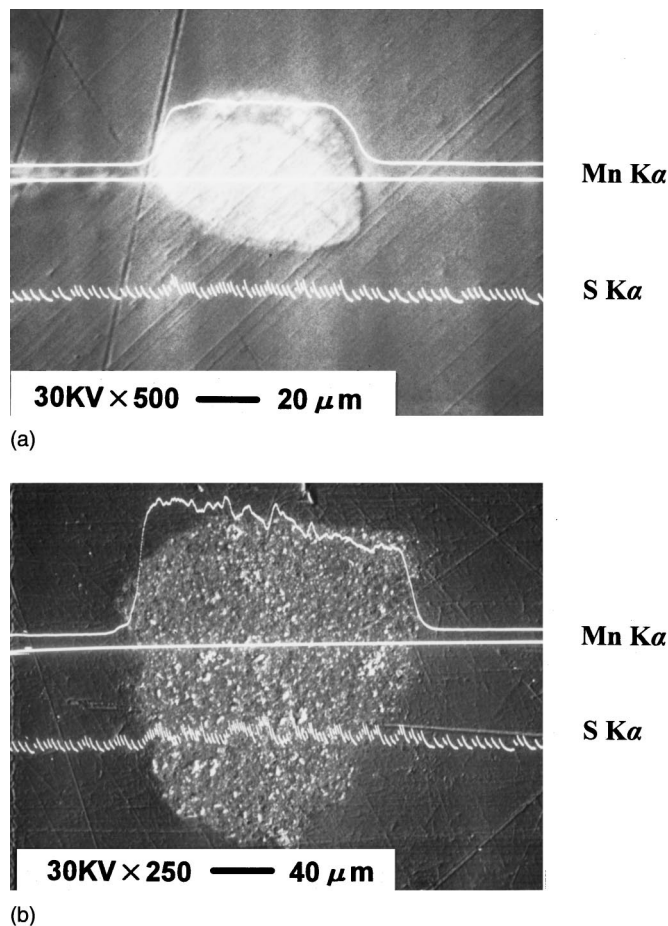


Figure 5. EPMA images (a) Tosoh-Mn<sub>3</sub>O<sub>4</sub> and (b) Chuodenki-Mn<sub>3</sub>O<sub>4</sub>.

amount of sulfur in the manganese source plays an important role in improving the cycle characterization of the Mn-based cathode materials in the 3 V region. Further work is now in progress on the reaction mechanism and the main reason for inducing the different

electrochemical performance of LiAl<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub> in the 3 V region. The results will be reported elsewhere.

### Conclusions

LiAl<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub> was synthesized using LiOH, Al(NO<sub>3</sub>)<sub>3</sub>, and two kinds of Mn<sub>3</sub>O<sub>4</sub> sources by the melt impregnation method. LiAl<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub> materials showed the same composition and similar physicochemical properties, but they presented very different cycle performances in the 3 V region. The *ex situ* XRD measurements also revealed that the two LiAl<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub> materials showed different XRD patterns after discharge to 2.2 V after 50 cycles. The T-LiAl<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub> showed as a mixture of a distinct cubic phase and many tetragonal phases, whereas C-LiAl<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub> maintained an almost perfect cubic phase after cycling. We found that the LiAl<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub> material might show entirely different cycle characterization in the 3 V region, although it was synthesized using the same manganese source.

### Acknowledgment

The author would like to thank Dr. Ikeda of the Instrumental Analysis Center in Saga University for EPMA work and technical discussions.

*Saga University assisted in meeting the publication costs of this article.*

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