Peculiar Cycle Behavior of $LiAl_{0.1}Mn_{1.9}O_4$ Material in the 3 V Region

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$LiAl_{0.1}Mn_{1.9}O_4$ was synthesized using LiOH, $Al(NO_3)_3$, and two different Mn_3O_4 sources (Tosoh and Chuodenki, Japan). Two $LiAl_{0.1}Mn_{1.9}O_4$ showed similar physicochemical properties, but these presented very different cycle performance in the 3 V region. The ex-situ XRD measurements also revealed that the two materials showed different X-ray patterns after discharge to 2.2 V after 50 cycles. We found new phenomenon that the $LiAl_{0.1}Mn_{1.9}O_4$ materials might show an entirely different cycle behaviors in the 3 V region even if they were synthesized using Mn source of the same crystal structure.

Spinel $LiMn_2O_4$ and its derivatives are considered a promising cathode material for lithium secondary batteries with high energy density due to their low cost and nontoxicity.[1,2] However, a significant capacity loss of the spinel $LiMn_2O_4$ at high temperature during cycling prevents its wider use as cathode material for lithium secondary batteries.[3–5]

In Li / $Li_xMn_2O_4$ cell, when $0 \leqq x \leqq 1$, the cubic structure of $Li_xMn_2O_4$ spinel is maintained in the 4V region, while the crystal symmetry from the cubic into tetragonal due to a large anisotropic (Jahn–Teller) distortion occurred in the 3 V region during Li^+ intercalation and deintercalation process. The large Jahn–Teller distortion is believed to be mainly responsible for poor cycling performance of the $Li_xMn_2O_4$ electrode in the 3 V region. Therefore, it well explains why the cubic spinel $LiMn_2O_4$ is better cycleability in the 4 V region than in the 3 V region. We reported recently the cycle characterization of $LiAl_{0.1}Mn_{1.9}O_4$ spinel using two different Mn sources (Mn_3O_4 and γ-MnOOH) in the 3 V and 4 V regions. Although the two $LiAl_{0.1}Mn_{1.9}O_4$ materials showed excellent cycleability in the 4 V region, they showed entirely different electrochemical properties and a unique structural change in the low voltage region (~2.2 V).[6]

In this paper, we report new results that some $LiAl_{0.1}Mn_{1.9}O_4$ materials can show an excellent cycleability in the 3 V region as well as in the 4 V region. Furthermore, they might exhibit different cycle characterization and structural change in the 3 V region even if they were synthesized using the same manganese source by the same synthetic process.

The Mn_3O_4 used in this experiment was synthesized by different method. One is a hydrothermal method (Tosoh, Japan), the other is a conventional solid-state method (Chuodenki, Japan). The mixture of LiOH, $Al(NO_3)_3$ and Mn_3O_4 was precalcined at 470 and 530 °C for 5 h in O_2, respectively, and then post-calcined at 800 °C for 24 h in air. The powder X-ray diffraction (XRD) using Cu Kα radiation was employed to identify the crystalline phase of the synthesized material and the *ex-situ* electrode cell. The particle morphologies of the Mn_3O_4 and $LiAl_{0.1}Mn_{1.9}O_4$ material were observed using a scanning electron microscope (SEM). The specific surface area was measured in a Gemini 2375 instrument by the Brunauer, Emmett, and Teller (BET) method. The electrochemical characterizations were performed using a screw cell to investigate the structural change in the two different electrodes 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 graphite). The test cell was made of a cathode and a lithium metal anode separated by a porous polypropylene film. The electrolyte used was a mixture of 1 M $LiPF_6$–ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:2 by volume). The charge and discharge current density was 0.4 mA/cm^2 with the cut-off voltage of 3.0–4.3 V and 2.2–3.6 V for in the 4 V and 3 V region, respectively.

The lattice constants of the two Mn_3O_4 sources with a tetragonal unit cell calculated by Rietveld refinement using the X-ray data were the same (a, b = 5.76 Å, c = 9.46 Å). The average particle sizes are 20–30 μm for Tosoh Mn_3O_4 (herein referred to as T-Mn_3O_4) and 1–2 μm for Chuodenki Mn_3O_4 (herein referred to as C-Mn_3O_4). Meanwhile, T-$LiAl_{0.1}Mn_{1.9}O_4$ powder which was synthesized using T-Mn_3O_4 was about 0.2–0.5 μm and C-$LiAl_{0.1}Mn_{1.9}O_4$ using C-Mn_3O_4 was about 1–2 μm. The specific surface areas of the two resulting compounds were 2.27 m^2/g and 1.26 m^2/g and for T-$LiAl_{0.1}Mn_{1.9}O_4$ and C-$LiAl_{0.1}Mn_{1.9}O_4$, respectively.

Figure 1 shows the discharge capacity as a function of cycle number for two $LiAl_{0.1}Mn_{1.9}O_4$ materials at different voltage regions. In the 4 V region, both compounds showed excellent cycle performance as well as high initial discharge capacity. The capacity retention rate of T-$LiAl_{0.1}Mn_{1.9}O_4$ is over 96% and C-$LiAl_{0.1}Mn_{1.9}O_4$ also presented a fairly good cycleability of over 91% after 50 cycles even though it showed a big capacity loss compared to that of T-$LiAl_{0.1}Mn_{1.9}O_4$. However, the cycle performance of two $LiAl_{0.1}Mn_{1.9}O_4$ materials in the 3 V

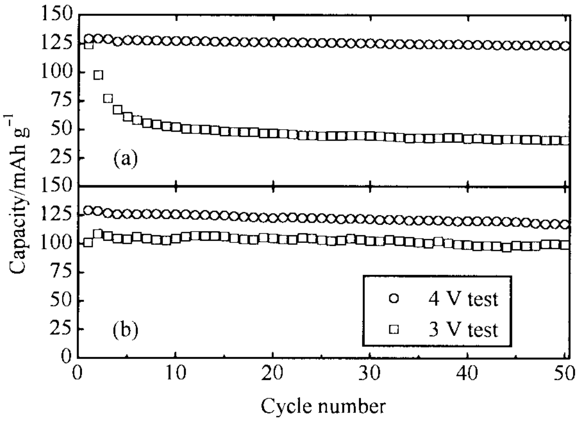

Figure 1. Cycle test of $LiAl_{0.1}Mn_{1.9}O_4$ (a) using Tosoh Mn_3O_4 (b) using Chuo Mn_3O_4.

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region was quite different even though they had the same composition and had similar physicochemical properties. T-$LiAl_{0.1}Mn_{1.9}O_4$ showed an abrupt capacity loss within the 5th cycle, which steadily decreased by 50th cycle in the 3 V region. We have already reported that this indication resulted from the co-effect of Jahn–Teller distortion and a unique aluminum effect (aluminum prevents a complete structural change from $LiMn_2O_4$ to $Li_2Mn_2O_4$ in the 3 V region).[7] On the other hand, the C-$LiAl_{0.1}Mn_{1.9}O_4$ material exhibited steady discharge capacity in the 3 V region. The cycle retention rate of C-$LiAl_{0.1}Mn_{1.9}O_4$ in this region was 98.6% after 50 cycles. This is a very interesting result in which the spinel based material commonly showed a poor cycleability in the 3 V region due to Jahn–Teller distortion when the lithium ion is inserted into the 16c site of $Li_xMn_2O_4$ ($1 < x \leqq 2$). In order to investigate this different cycling behavior observed with the $LiAl_{0.1}Mn_{1.9}O_4$ materials, ex-situ XRD measurements were taken of both $LiAl_{0.1}Mn_{1.9}O_4$ electrodes in the discharged state after 50 cycles as shown in Figure 2. Figure 2 (a) shows that the two $LiAl_{0.1}Mn_{1.9}O_4$ materials had the same crystalline structure. On the other hand, Figure 2 (b) and (c) show that the two electrodes had quite different XRD patterns in the discharged state after 50 cycles. The T-$LiAl_{0.1}Mn_{1.9}O_4$ electrode still keeps both distinct cubic and small tetragonal phases together, whereas C-$LiAl_{0.1}Mn_{1.9}O_4$ maintains an almost perfect cubic structure after 50 cycles. On the basis of these data, we concluded that some $LiAl_{0.1}Mn_{1.9}O_4$ materials could show a very stable cycleability in the 3 V region as well as in the 4 V region. Furthermore, the $LiAl_{0.1}Mn_{1.9}O_4$ materials can show conflicting cycle performance in the 3 V region even though these were synthesized using the same manganese sources, but which were made by a different synthetic process and/or from a different raw material. Actually, we found some other elements and higher amount of Ca in one starting material using ICP analysis. Further work is now in progress on the reaction mechanism and the main reason for inducing the different electrochemical performance of $LiAl_{0.1}Mn_{1.9}O_4$ in the 3 V region.

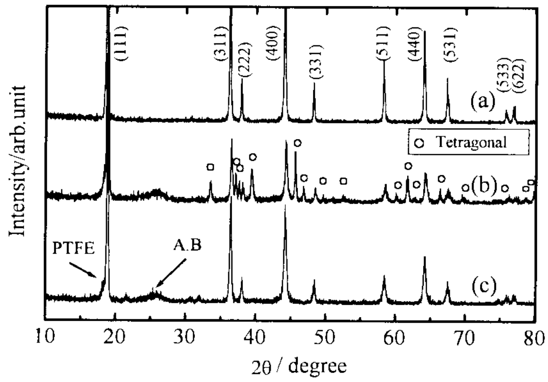

Figure 2. XRD patterns of (a) $LiAl_{0.1}Mn_{1.9}O_4$ (b)$LiAl_{0.1}Mn_{1.9}O_4$ using Tosoh Mn_3O_4 after 50 cycles (c) $LiAl_{0.1}Mn_{1.9}O_4$ using Chuo Mn_3O_4 after 50 cycles. Cut-off voltage : 3.6–2.2 V.

References and Notes

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