

Anomalous step at $x=0.7$ in potential–composition profiles of $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_4$ spinels at low temperature

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Abstract

In order to investigate the relation between spinel type structure and anomaly in potential–composition profile of stoichiometric LiMn_2O_4 spinel at low temperature ($T \leq 278$ K), several $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ type spinels ($y = 0.01–0.25$) have been synthesized by conventional solid-state reaction and their potential–composition (ϕ – x ; $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_4$) profiles at 273 K have been recorded. The ϕ – x profiles of the specimens ($y = 0.01–0.03$) show an anomalous stepwise feature as one that stoichiometric LiMn_2O_4 shows at low temperature. However, the step at $x=0.7$ becomes weak with increase of the value y , and finally disappears. In the specimens, Mn and Cr are considered to occupy only 16d sites of spinel type structure. As compared with the ϕ – x profiles of lithium-excess type spinels $\text{Li}_{1+\delta}\text{Mn}_{2-\delta}\text{O}_4$ and lithium-deficient type spinels $\text{Li}_{1-\delta}\text{Mn}_2\text{O}_4$, the gradual result suggests that state of Mn lattice strongly affects the appearance of anomalous step at $x=0.7$.

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1. Introduction

In recent years, lithium manganese oxides have attracted as a cathode material for lithium ion battery in the viewpoint of cost, consideration to environment and so on. Especially, spinel type oxide LiMn_2O_4 has received much attention, and its electrochemical and structural feature have been studied so far [1–7].

Stoichiometric LiMn_2O_4 shows a characteristic potential–composition (ϕ – x ; $\text{Li}_x\text{Mn}_2\text{O}_4$) profile having a step voltage change at $x = 1/2$. Furthermore, the anomaly has been found in the ϕ – x curves at low temperature ($T \leq 278$ K) as previous report [8]. That is, the slope at $x = 1/2$ becomes far steeper. Moreover, a new voltage step (or kink) appears at $x=0.7$ in the profile.

In the anomaly, the slope at $x = 1/2$ is assumed ordering of Li ions, because the host diamond-type lattice has a commensurate ZnS arrangement at $x = 1/2$. On the other hand, the origin of the new step at $x=0.7$ is still unknown. Stoichiometric LiMn_2O_4 undergoes a reversible phase transition from cubic ($Fd3m$) to orthorhombic ($Fddd$) symmetry

close to room temperature [9,10], and relation between the phase transition and the anomalous step was a matter of concern. However, it was proved that the anomalous behavior of the compounds at low temperature is not directly related to the structural transition associated with Jahn–Teller effect [11]. The distortion is canceled when only a very small amount of Li ions are extracted by charging. Investigation concerning the anomaly was continued further, then it was clarified that composition of the specimen at the stage of synthesis is very sensitive whether the anomaly in the potential profile at low temperature undergoes or not.

We paid attention to lithium chromium manganese oxides $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$, because Mn and Cr are considered to occupy only 16d sites in the spinel type compounds, and lithium ions (8a) are slightly affected by substitution of Mn with Cr.

Guohua et al. have reported synthesis and cycle performance of spinel oxides $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ ($y = 1/9, 1/6$ and $1/3$) [12]. They asserted that improvement in cycle performance of $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ is attributed to stabilization of structure by substitution of Mn. Further, they also predicted that interaction between Li ions and M–O structure becomes weak with increasing of the amount of substitution [13], on the basis of measurements of chemical diffusion coefficient of $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$.

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In this research, several $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ type specimens ($y = 0.01\text{--}0.25$) were synthesized, and their potential–composition curves were recorded at low temperature ($T = 273\text{ K}$). Assuming that the anomalous step at $x=0.7$ appears regardless of the value y , the step originates from distribution of Li ions. On the other hand, a kind of ordering in Mn lattice has some influence on forming the anomalous step, if some dependence on y in the profile is found. The result is reported in this paper.

2. Experimental

Powder specimens of $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ type spinels ($y = 0.01\text{--}0.25$) were prepared from Li_2CO_3 , MnCO_3 (both of the products of Soekawa Chemical Co.) and Cr_2O_3 (Wako Pure Chemical Industries Ltd.) by conventional solid-state reaction. The mixture at an atomic ratio $\text{Li}:\text{Cr}:\text{Mn} = 1:y:(2-y)$ was sintered at $750\text{ }^\circ\text{C}$ in air for 72 h, after pre-sintering for 48 h at $550\text{ }^\circ\text{C}$. The mixture was finally quenched with liquid nitrogen. The final quench treatment was done for preventing decomposition of specimens in the process of cooling in air [14].

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT2100 using monochromatized $\text{Cu K}\alpha$ radiation. The measurements were carried out in the step-scan mode with a 2θ step width of 0.02° . The lattice constants were determined by calculation of least-square refinements.

Measurements of the ϕ - x profiles were performed using a gas-tight three electrode glass cells. Preparation of the cathode electrode and construction of the cells are according to the previous report [8]. The electrolyte was 1 M LiClO_4 /propylene carbonate (PC) solution (supplied by Kishida Chemical Co. or Mitsubishi Chemical Co.), and lithium foil (Soekawa Chemical Co.) pressed onto a nickel mesh (Nilaco Co.) was used as the anode and the reference electrodes.

The ϕ - x profiles were recorded using HJ-101SM6 system (Hokuto Denko Co.) under a constant current condition for the first charging (deintercalating process). To suppress polarization overpotential, a very small value of the current density, i.e. 0.428 mA per 1 g of each specimen was used. It was confirmed that ϕ - x curves obtained by this continuous method are almost near to OCV profiles by intermittent mode. The cut off voltage was 4.3 V in the recording. The cell temperature was controlled within $\pm 0.1\text{ }^\circ\text{C}$ using a Peltier thermostatic bath (DW621-A/DR62B, Komatsu Electronics Inc.).

3. Results and discussion

Fig. 1 shows XRD patterns for the specimens of $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ type spinels ($y = 0.02, 0.05, 0.1$ and 0.2). All of the specimens ($y = 0.01\text{--}0.25$) obtained in the research is in a single cubic phase ($Fd3m$) at room tem-

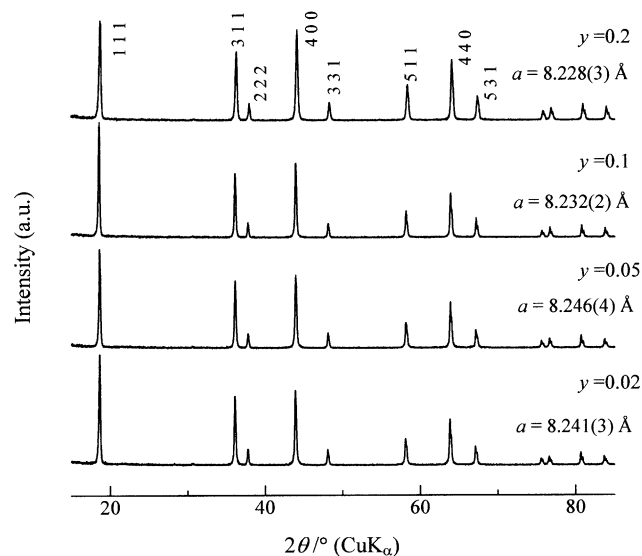


Fig. 1. XRD patterns for the $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ specimens ($y = 0.02, 0.05, 0.1$ and 0.2).

perature. The lattice parameters of $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ type spinels are described in Fig. 2. Baochen et al. [15] have reported that substitution of manganese (Mn^{3+}) in LiMn_2O_4 spinel by chromium (Cr^{3+}) caused monotonous decrease of the lattice constant. The result in this research agrees with the foregoing reports [12,15–17] in the region $0.05 < y$. However, the lattice parameter seems to increase with substitution by Cr^{3+} slightly in the region $0 < y \leq 0.05$. The driving force of the tendency is not clearly understood. Taking into account of error bars in the figure, lattice parameter is probably almost constant in the region.

Potential–composition curve of $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ ($y = 0.03$) at 298 K is described in Fig. 3. While the ϕ - x curves of $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ do not exhibit stepwise feature at 298 K , the potential profiles change into almost stepwise feature at low temperature, 273 K . Their shapes are shown in Fig. 4. That is, certainly the ϕ - x profiles of $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ have temperature dependence as one that ϕ - x profile of LiMn_2O_4 shows (Fig. 5).

This figure also reveals that the potential profile changes with the value of y obviously. Here, it is remarkable that

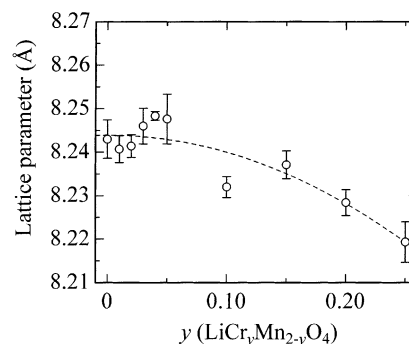


Fig. 2. Lattice parameters of the $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ specimens ($y = 0\text{--}0.25$).

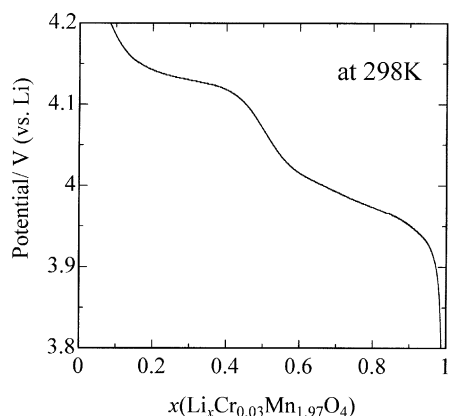
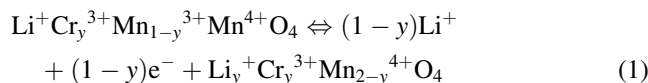


Fig. 3. The potential–composition (ϕ - x) profile of $\text{LiCr}_{0.03}\text{Mn}_{1.97}\text{O}_4$ at 298 K.

lithium composition (x) at 4.3 V increases with the amount of substitution of Mn with Cr.

The lithium deintercalation/intercalation reaction of 4 V range process in $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ spinel can be presented in



Theoretically, Li^+ deintercalation of 4 V range process finishes when Li ions are deintercalated to the point of lithium composition (y). Fig. 6 shows the relation between lithium composition (x) at 4.3 V and the value of y in the specimens. In the graph, the relation $x = y$ is almost achieved in all of the specimens. There is small difference, because 4 V range deintercalation process does not finish at 4.3 V completely. The result shows that each specimen synthesized in this research has almost objective composition.

In the ϕ - x profiles of $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ at 273 K, the steep slope at $x = 1/2$, which is assumed to be caused by ordering of Li ions, are little changed by the amount of substitution. Therefore, substitution of Mn with Cr has little influence on distribution of lithium ions ($8a$) in the specimens. On the

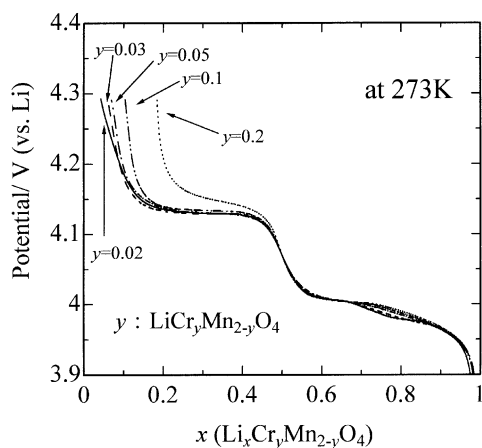


Fig. 4. Anomalous feature of the potential–composition (ϕ - x) profiles of the $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ specimens ($y = 0.02$ – 0.2) at 273 K.

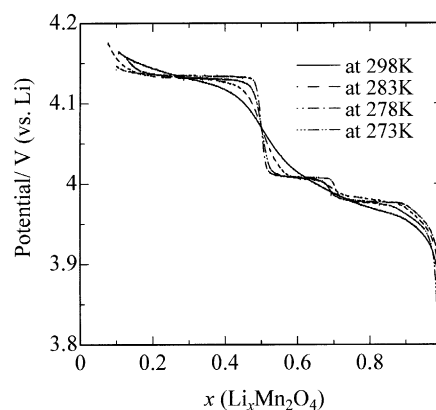


Fig. 5. Temperature dependence in potential–composition profile of stoichiometric LiMn_2O_4 .

contrary, the step at $x=0.7$ changes in accordance with the substitution (Fig. 7). The step becomes weak with increasing of the value y , and then finally disappears at $y = 0.2$. It is very attractive that the profiles show gradual change with y .

In the previous report, lithium-excess type $\text{Li}_{1+\delta}\text{Mn}_{2-\delta}\text{O}_4$ ($[\text{Li}]_{8a}[\text{Li}_\delta\text{Mn}_{2-\delta}]_{16d}[\text{O}_4]_{32e}$, $\delta = 0.01$ – 0.05) compounds and lithium-deficient type specimens $\text{Li}_{1-\delta}\text{Mn}_2\text{O}_4$ ($[\text{Li}_{1-\delta}]_{8a}[\text{Mn}_2]_{16d}[\text{O}_4]_{32e}$, $\delta = 0.02$ – 0.05) were synthesized, and their ϕ - x curves at 273 and 298 K were recorded [11]. As a result, lithium-excess type compounds do not show the anomalous step at $x=0.7$ except for only one sample ($\delta = 0.01$), which has the least extent of excess lithium in the specimens. On the contrary, lithium-deficient type specimens $\text{Li}_{1-\delta}\text{Mn}_2\text{O}_4$ ($\delta = 0.02$ – 0.05) show the anomalous curve regardless of composition (Fig. 8). In the $\text{Li}_{1-\delta}\text{Mn}_2\text{O}_4$ type compounds, there is only lack of Li ion in $8a$ sites, and Mn occupies all of $16d$ sites in spinel type structure [14].

From the above results, it is clear that state of the manganese lattice (for example, charge ordering of Mn^{3+} and Mn^{4+}) is strongly related to anomaly at $x=0.7$. Recently,

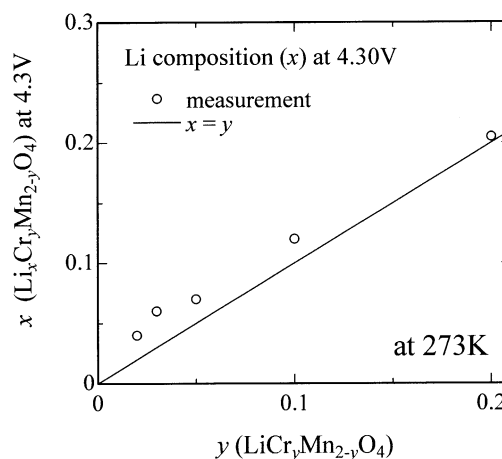


Fig. 6. The relation between the amount of substitution (y) in $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ and lithium composition (x) at 4.30 V in the ϕ - x profiles at 273 K.

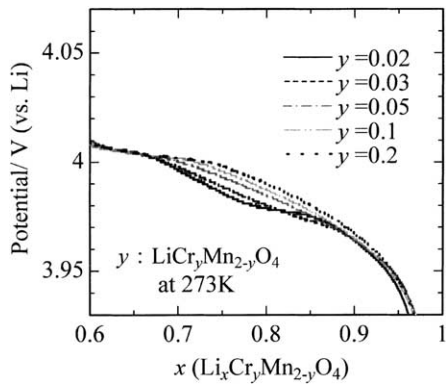


Fig. 7. Gradual change of the step at $x=0.7$ with the value of y at 273 K.

it is revealed that structural phase transition (cubic \leftrightarrow orthorhombic) in stoichiometric LiMn_2O_4 ($\text{Mn}^{3+}/\text{Mn}^{4+} = 1$) close to room temperature is accompanied with charge ordering on Mn sites. Rodríguez-Carvajal and coworkers have reported about a partial charge ordered state at $T = 230$ K using neutron scattering and electron diffraction experiments [18,19]. Further, Paolone et al. have observed

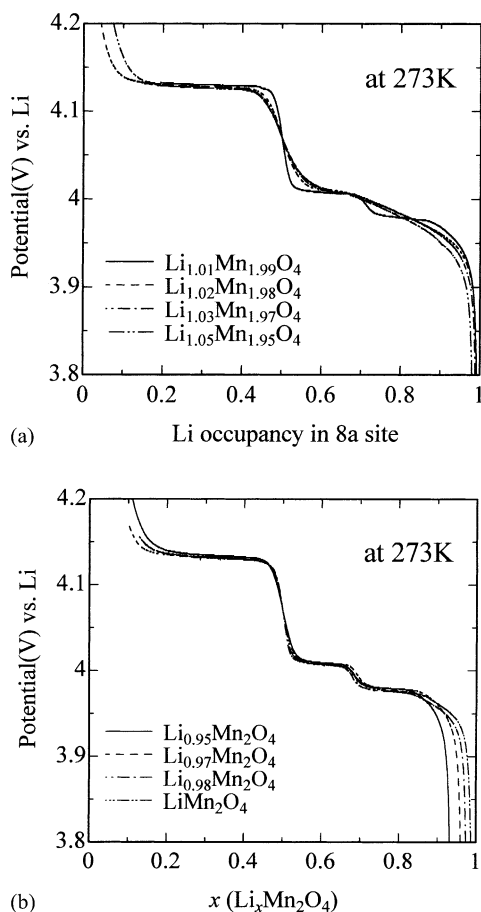


Fig. 8. Potential–composition curves of some non-stoichiometric LiMn_2O_4 spinels at 273 K. (a) Li-excess type samples $\text{Li}_{1+\delta}\text{Mn}_{2-\delta}\text{O}_4$ ($\delta = 0.01$ – 0.05). (b) Li-deficient type samples $\text{Li}_{1-\delta}\text{Mn}_2\text{O}_4$ ($\delta = 0.02$ – 0.05), as compared with stoichiometric LiMn_2O_4 .

appearance of the charge ordering around $T = 280$ K upon cooling with infrared spectroscopy [20,21].

In transition metal ($3d$, including Mn) oxides, interactions among electrons can not be negligible. There are many researches explored physical properties of the compounds from standpoints of charge, spin and orbital [22]. Especially in recent years, charge ordering on Mn sites in several manganese oxides has been studied eagerly. The appearance of ordering phase in perovskite type oxides $\text{Sm}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.5$, $\text{Mn}^{3+}:\text{Mn}^{4+} = 1$) [23] and $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.48 < x < 0.52$, $12:13 < \text{Mn}^{3+}:\text{Mn}^{4+} < 13:12$) [24,25] have been confirmed by magnetic field study. In addition, the compound $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ occurs the ordering phase in wide region of x ; $0.3 < x < 0.75$ ($7:3 > \text{Mn}^{3+}:\text{Mn}^{4+} > 1:3$) [25–28]. In this way, various compounds show the ordering in a different range of $\text{Mn}^{3+}:\text{Mn}^{4+}$.

It is reasonable to expect charge ordering phase in $\text{Li}_x\text{Mn}_2\text{O}_4$; $0.7 < x < 1$ ($7:13 < \text{Mn}^{3+}:\text{Mn}^{4+} < 1$) around $T = 280$ K from these results. However, extensive state on Mn sites in $\text{Li}_x\text{Mn}_2\text{O}_4$ remains still unsolved, particularly in Li deintercalation/intercalation process. It is important to know more detail of the state of Mn lattice in LiMn_2O_4 , which is a key factor of the anomaly in the ϕ – x profiles at low temperature.

4. Conclusions

Chromium-substituted spinel type lithium manganese oxides $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ ($[\text{Li}]_{8d}[\text{Cr}_y\text{Mn}_{2-y}]_{16d}[\text{O}_4]_{32e}$) show an anomaly identical with one of stoichiometric LiMn_2O_4 in potential–composition profiles at low temperature. Here, the anomalous step at $x=0.7$ in the profiles of $\text{Li}_x\text{Cr}_y\text{Mn}_{2-y}\text{O}_4$ becomes weak as the value of y increases, and finally disappears at $y = 0.2$. As compared with the potential curves and structures of several non-stoichiometric LiMn_2O_4 , the result indicates that state on Mn sites ($16d$) in spinel type structure is strongly related to the origin of the anomalous step at $x=0.7$ in the ϕ – x profiles of LiMn_2O_4 . Especially, charge ordering phase on Mn sites in $\text{Li}_x\text{Mn}_2\text{O}_4$; $0.7 < x < 1$ ($7:13 < \text{Mn}^{3+}:\text{Mn}^{4+} < 1$) is expected to be the origin of the anomaly. The effect of charge ordering state in LiMn_2O_4 upon potential–composition profile is also a matter of concern for practical use of Li ion battery under various operating conditions.

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