



Electrochemical and Structural Properties of a 4.7 V-Class $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Positive Electrode Material Prepared with a Self-Reaction Method

Koh Takahashi,^a Motoharu Saitoh,^a Mitsuru Sano,^{a,z} Miho Fujita,^b and Koichi Kifune^c

^aGraduate School of Environmental Studies, Nagoya University, Nagoya 464-8601, Japan

^bGraduate School of Natural Sciences, Nagoya City University, Nagoya 467-8501, Japan

^cFaculty of Science, Osaka Women's University, Sakai 590-0035, Japan

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as 4.7 V-class cathode materials were prepared with our self-reaction method at 650, 700, and 750°C calcination temperatures respectively, and their electrochemical properties and crystal structures were studied. The sample at 700°C was assigned to the space group $P4_332$ in the X-ray diffraction analysis. On the contrary, the space group of the sample calcined at 650 or 750°C fell into $Fd3m$ because diffraction peaks from $P4_332$ were missing. The sample at 700°C showed a one-step profile in the charge/discharge curve and this contrasted with the other samples showing two-step ones. In spite of their different structures, these three samples had the same initial capacities of about 123 mAh/g. They gave similarly good cycle performance as well, but the sample at 650 or 750°C maintained a little higher capacity after 50 cycles of charge/discharge than the sample at 700°C. From the analysis of transformation of the crystal structure of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ during charging, it was found that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ underwent the electrochemical reactions at three stages unlike LiMn_2O_4 with two stages.

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Lithium secondary batteries show great promise as power sources for portable electronic devices because of their high output voltages, high specific energy densities, and excellent cycle performances. However, there is a further demand for even higher specific energy density for use in large power devices such as electric vehicles etc. One plausible solution to such a higher specific energy density is to prepare cathode materials with higher working voltages.

Dahn and his group first prepared the 5 V class cathode of LiNiVO_4 with an inverse spinel structure.¹ Spinel type of lithium manganese oxides substituted with other transition metals for Mn, $\text{Li}[\text{M}_x\text{Mn}_{2-x}]\text{O}_4$ (M = Ni, Cr, Co, and Fe), also showed reversible lithium extraction-insertion at near 5 V vs. metal Li.²⁻⁹ $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ has a voltage plateau around 4.7 V vs. lithium metal whose voltage is about 0.3 V lower than those for 5 V-cathode materials of other spinels. In spite of this disadvantage, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has been one of the most interesting materials because of its phase stability and low electrolyte decomposition at the voltage, and in addition because of the high theoretical capacity at 4.7 V region.¹⁰⁻¹¹

Papers related to $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ have been published by Terada *et al.*,¹² Ooms *et al.*,¹³ and Myung *et al.*¹⁴ (After the submission and during processing of this paper, Yoshio *et al.*¹⁵ also published a report about the cycle performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$). However, their electrochemical and structural behavior have been examined well.

In the present study, we characterize electrochemically and structural properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared our own self-reaction method.¹⁶ The self-reaction method is one of the suitable preparative methods for complex metal oxide powders and we already applied this method for the preparations of a 4 V class cathode material, LiMn_2O_4 and Al-substituted LiMn_2O_4 , with good cycle performances, and a 3 V class cathode material, $\text{Li}_4\text{Mn}_5\text{O}_{12}$, with an initial capacity of 160 mAh/g, which was difficult to prepare with conventional methods.

Experimental

Materials.— $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was prepared using the self-reaction method.¹⁶ First, 0.1 mol of LiNO_3 (99%, Wako Pure Chemical In-

dustries, Ltd.), 0.05 mol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Wako Pure Chemical Industries, Ltd), and 0.15 mol of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, Wako Pure Chemical Industries, Ltd.) were dissolved together in 20 mL distilled water to form a mixed aqueous solution. Into the mixture was added 16, 24, 32, and 40 g of 20% poly-vinyl alcohol (PVA), Wako Pure Chemical Industries, Ltd.) aqueous solution. Then each solution was heated to 150°C to cause a reaction among them. The black powders obtained were ground and then calcined in an alumina crucible at 650, 700, and 750°C for 5 h in a conventional electric furnace. For comparison, $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$ was also prepared at 700°C.

The 1:2 solvent mixture of ethylenecarbonate (EC) to dimethylcarbonate (DMC) with 1 M LiPF_6 dissolved was donated by the Mitsui Chemical Company (Tokyo, Japan) and contained less than 10 ppm of H_2O . The 2:1 mixture (CB-2) of acetylene black binder to poly(tetrafluoroethylene) (PTFE) was made available from Soei Tsusho Company (Osaka, Japan).

Measurements.—Elemental analyses of the samples were done with an inductively coupled plasma (ICP) spectrophotometric technique (Seiko Instruments Industry, Ltd. SPS-4000). Cyclic voltammograms (CVs) were measured with a BTS100B electrochemical analyzer at a scan rate of 0.1 mV/s. The working electrode was lithium manganese oxide and both the counter and reference electrodes were lithium foil.

Identification and analysis of the crystal structure of the obtained powders were performed by a powder X-ray diffraction (XRD) using a diffractometer (Rigaku Electric Industry, Ltd. Rint-2001) or by use of the SPring8 (the synchrotron radiation source in Harima, Hyogo, Japan) for a further analysis.

Electrochemical cells and cycle performance tests.—The mixture of 2/3 lithium nickel-manganese oxide powder and 1/3 conductor, CB-2, was pressed carefully at 200 kg/cm² to make it into a disc for a positive electrode of a cell and the disc was then dried at 150°C for 6 h. Cycle performance tests in charge/discharge were done on a coin-type cell (CR-2032) assembled with Li metal/the electrolyte (EC/DMC = 1/2 with 1 M LiPF_6)/the positive electrode. Charge/discharge curves were recorded galvanostatically with a Nagano BTS-2004. The current rate was 0.5 mA/cm² with cutoff voltages of 3.5 and 4.3 to 4.9 V (vs. Li/Li^+). A cyclic voltammogram was measured at a sweep rate of 100 $\mu\text{V}/\text{min}$ between 3.5 and 5.1 V of the

^z E-mail: sano@info.human.nagoya-u.ac.jp

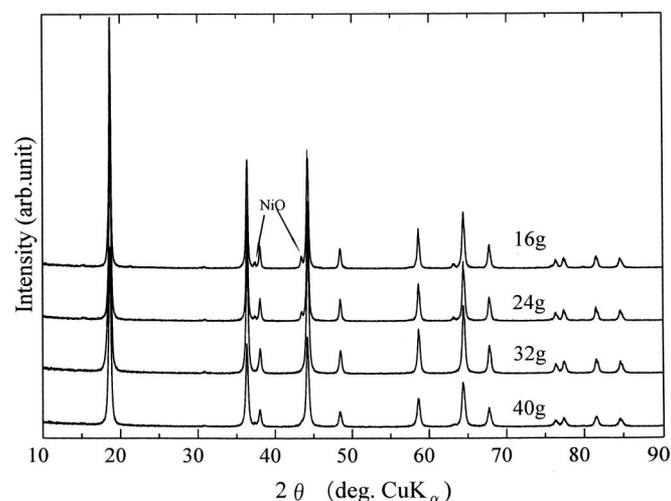


Figure 1. XRD profiles of the products reacted using each amount of PVA solution and calcined at 650°C for 5 h in air.

potential limits. All the processes of assembling and dismantling the cells were carried out in argon atmosphere in a glove box (Vacuum Atmosphere Co., California).

The positive electrode compounds at charged states were prepared for the measurement of XRD as follows; the mixture of 2/3 lithium nickel-manganese oxide powder and 1/3 conductor, CB-2, was pressed carefully at 300 kg/cm² to Al mesh (200 mesh) and the positive electrode was charged at each charged state at 0.5 C in a three-electrode cell. After being charged, the cathode was kept at each constant potential for 1 h and was taken out in the cell in the glove box. Then it was set in polyethylene tube and after about 1 day, its XRD was measured.

Results and Discussion

The preparation of LiNi_{0.5}Mn_{1.5}O₄ by the self-reaction.—Figure 1 shows the diffraction profiles of the samples which correspond, respectively, to 16, 24, 32, or 40 g of 20 wt % PVA solution as a starting material and calcined at 650°C for 5 h in the air. In the case of 32 g of PVA solution, only the spinel phase is observed with rather sharp diffractions, and for 16 and 24 g, the new diffractions corresponding to NiO also appear in addition to diffractions from a spinel phase. The NiO impurity has been identified as Li_xNi_{1-x}O with 0 < x < 0.33. For the product of the 40 g PVA solution, no diffractions from impurities are observed and the diffractions from the spinel phase are a little broader than those of other samples. These results suggest that 32 g of 20 wt % PVA solution would be best to synthesize 0.1 mol LiNi_{0.5}Mn_{1.5}O₄ successfully.

Table I summarizes the result of the elemental analyses of the reaction products. As seen from the Table, the Li/Ni/Mn ratios of all the samples were almost the same as the theoretical ratios. The carbon and nitrogen contents detected are impurities in the reaction product, which originate from the PVA and nitrate ions used.

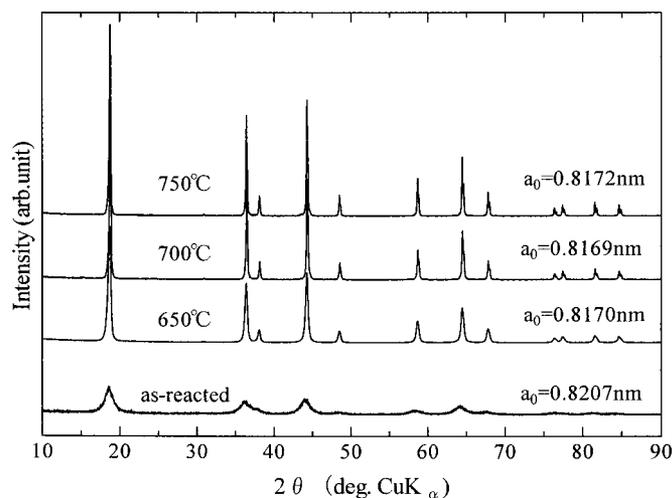


Figure 2. XRD profiles of the products reacted using 32 g of PVA solution and calcined at 650, 700, or 750°C for 5 h in air.

Crystal structures of the calcined samples.—Figure 2 shows the diffraction profiles of the products starting from 32 g of PVA solution used as the optimum amounts and calcined at 650, 700, or 750, for 5 h in the air. Every product looks to have more or less a single-phase spinel structure. Diffractions in each profile of all the products after the calcination shift slightly to higher angles than those before the calcination. In addition, as calcination temperatures are raised, diffraction intensities apparently increase. This implies that a calcination process at a higher temperature achieves a product of a higher crystalline state.

Lattice parameters were refined with a least square method and the resulting lattice parameters are also shown in Fig. 2. They have almost the same lattice constants; 0.817 Å. However, additional tiny diffractions are found in the sample calcined at 700°C. For further confirmation of the differences, we took finer profiles of powder XRD patterns using the synchrotron radiation source from Spring8. They are shown in Fig. 3. On the profile of the sample calcined at 700°C, diffractions denoted by asterisks (*) are additional ones to the diffractions expected in the crystal structure with the *Fd3m* space group, which is an ordinary one for a spinel structure. These diffractions cannot be refined to the *Fd3m* space group, but to the *P4₃32*. If a quarter of 16d sites in Mn are substituted with such an element as Ni in LiNi_{0.5}Mn_{1.5}O₄ and these elements dispose in order, it could happen that the space group falls into *P4₃32*.¹⁷ Therefore the product at 700°C could belong to the *P4₃32* space group due to the ordering of the substituted nickel ions.

Ooms *et al.*¹³ have reported X-ray and neutron diffraction studies about LiNi_{0.5}Mn_{1.5}O₄ prepared from a combination of a sol-gel synthesis and solid-state processing. Although they have not observed any XRDs refined with the *P4₃32* space group, they concluded that the neutron diffraction data could be fitted with this space group.

For the present study, because the sample calcined at 700°C showed XRDs refined with the *P4₃32* space group, the sample is

Table I. Elemental analyses of the reaction products.

Sample	Li (mass %)	Ni (mass %)	Mn (mass %)	Li:Ni:Mn	C (mass %)	N (mass %)
As-reacted	3.34	13.71	39.52	1.00:0.49:1.49	1.34	0.82
Calcined at 650°C	3.81	15.69	45.12	1.00:0.49:1.50	<0.1	<0.1
Calcined at 700°C	3.84	15.81	45.40	1.00:0.49:1.50	<0.1	<0.1
Calcined at 750°C	3.84	15.80	45.35	1.00:0.49:1.49	<0.1	<0.1
Theoretical	3.80	16.07	45.11	1.00:0.50:1.50	—	—

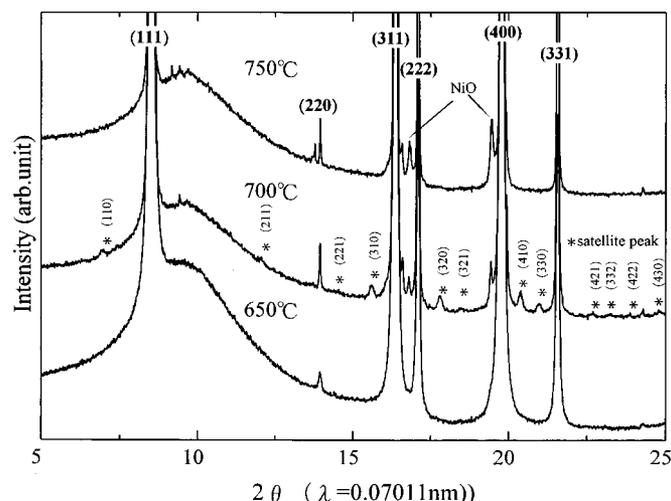


Figure 3. XRD patterns for the samples of Fig. 3 using a diffractometer in the synchrotron radiation source from SPring8.

considered to have a highly Ni-ordering structure. On the contrary, the Ni-ordering in the samples at 650 and 700°C is not thought completed well, presumably from the fact that they gave no XRDs due to the $P4_332$ space group.

Electrochemical properties of the calcined samples.—Figure 4 shows the charge/discharge curves at the second cycle and the corresponding cyclic voltammograms of the samples prepared at each calcination temperature. The result of $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$ prepared simi-

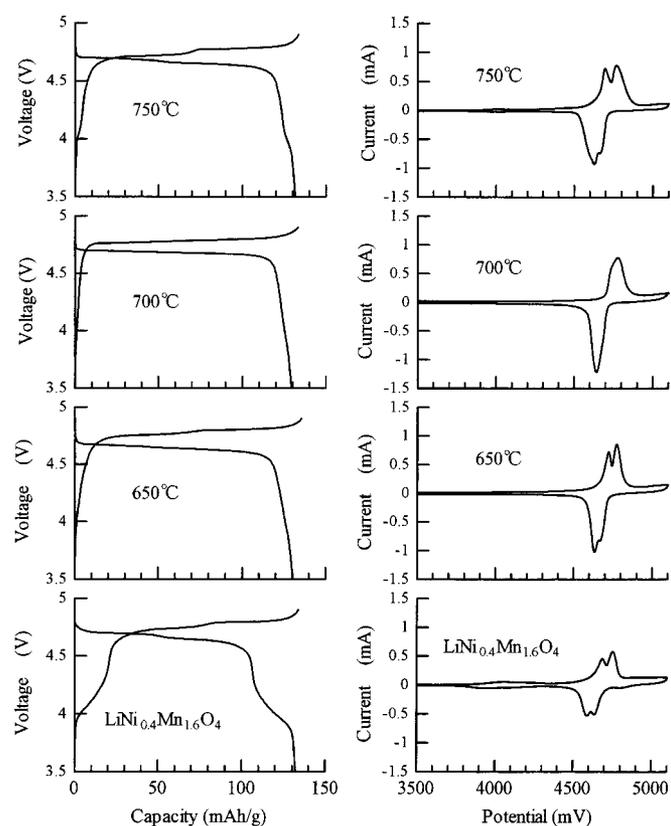
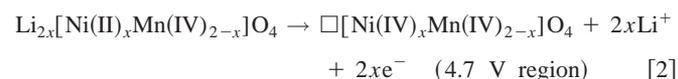
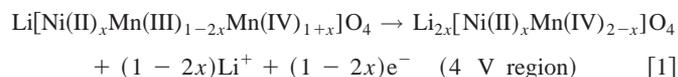


Figure 4. Charge/discharge curves at the second cycle and the cyclic voltammograms of the samples prepared at 650, 700, or 750°C calcination temperature.

larly to the above $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is also shown for comparison. The sample prepared at 650 or 700°C had only one plateau around 4.7 V on the charge-discharge curve, while the sample at 750°C showed a faint 4 V region plateau in addition to a 4.7 V region plateau. The 4.7 V plateau of the sample at 650 or 750°C has a two-step profile. On the other hand, the sample at 700°C shows a one-step profile. The discharge capacities of all the samples are almost the same values of about 130 mAh/g when the cutoff voltages are fixed between 3.5 and 4.9 V.

Electrochemical reactions of $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ are expressed as follows:^{3,10}



Then, the theoretical capacity of $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ can be calculated from the following equations

$$\begin{aligned} \text{total capacity} &= 96500 \times \{2x + (2-x) \\ &\quad \times [4 - (7-2x)/(2-x)]\} / (3600 \times M) \\ &= 26.8/M \quad (\text{Ah/g}) \quad [3] \end{aligned}$$

$$4 \text{ V region capacity} = 26.8 \times (1-2x)/M \quad (\text{Ah/g}) \quad [4]$$

$$4.7 \text{ V region capacity} = 26.8 \times 2x/M \quad (\text{Ah/g}) \quad [5]$$

where M denotes the molecular weight of $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$. Thus, the theoretical capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is estimated to be 146.6 mAh/g. Therefore, the observed charge capacities in the present study are 92% of the theoretical capacity.

In the CVs of the samples at 650 and at 750°C, two peaks were observed as expected from two-step plateaus in their charge/discharge curves. On the contrary, only one broad band was observed for the sample at 700°C. For this sample, the potential gap between peaks would be narrower than those of the other samples and as a result two peaks look like one broad peak. These differences correspond to those of XRD results; in the sample at 700°C, the diffractions from $P4_332$ were observed, and on the other hand the samples at 650 and 750°C did not show such diffractions. It suggests that the narrower potential gap has something to do with the ordering of the Ni ions in the structure.

The $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$ sample shown for comparison has two ordinary plateaus both in the 4.7 and in 4 V regions. The capacities of each voltage are 118 and 29 mAh/g, and their ratio corresponds to that calculated theoretically from the equation.

Figure 5 shows the change of discharge capacities with cycles for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$ when the cutoff voltages were between 4.3 and 4.9 V. The initial discharge capacities of all $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples were about 123 mAh/g, but that of $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$ was lowered to 108 mAh/g. After 50 cycles, capacities of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ calcined at 650, 700, and 750°C, respectively got to 118, 116, and 118 mAh/g. As seen from this, the capacity losses of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ sample at 650 and 750°C were only 4% after 50 cycles and they are better in the cycle performance than the sample at 700°C.

After the submission of the present paper, Yoshio *et al.*¹⁵ published the study of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized with a composite carbonate process. The cathode material showed good initial capacity and cycle performance, and its discharge curve had a very small 4.1 V plateau. However, they had not observed XRDs deriving from the $P4_332$ space group.

This seems to correspond to our result that our sample calcined at 650 or 750°C and refined to the $P4_332$ space group has better cycle performance than the sample at 700°C. Thus, it could be said

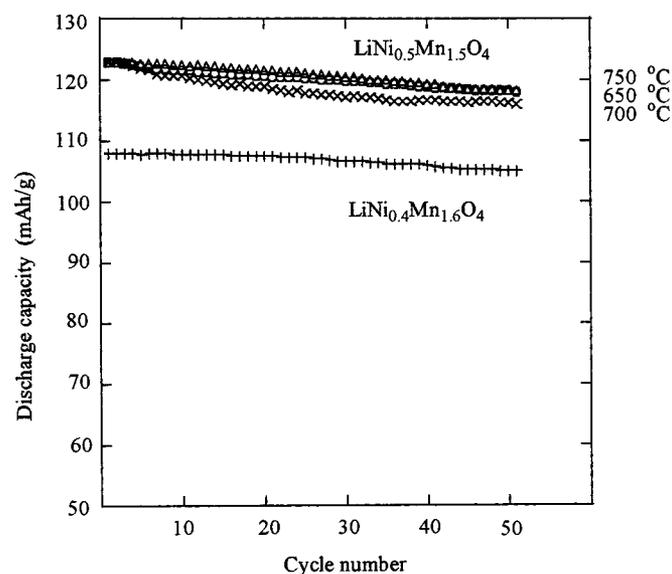


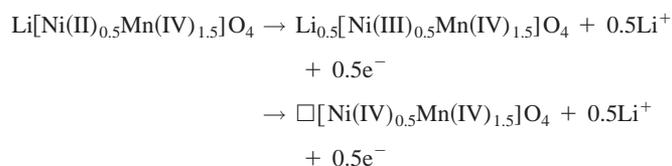
Figure 5. Cycle performances of the discharge capacities for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared at 650, 700, or 750°C calcination temperature and for $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$ when the range of cutoff voltages is between 4.3 and 4.9 V.

that cathode materials, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, with the highly Ni-ordering structure are worse in cycle performance than the other samples without the Ni-ordering structure.

Phase transitions of crystal structures during charging.—In order to study crystal structures at each charged state, XRDs were measured *ex situ* for $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($0 < x < 1$) at each calcination temperature. The results are shown in Fig. 6. At $x = 0$, the diffractions of the cubic spinel structures were observed with the lattice constant of 0.816 nm, though diffractions of Al mesh also appeared at the same time. The new and additional diffractions appeared at higher angle as charging proceeded. They were still indexed to their cubic spinel structures but their lattice parameters were reduced to 0.809 and 0.800 nm, respectively. Each parameter maintained a roughly constant value within the same stage.

However, we did not find the new diffractions with the lattice constant 0.809 nm at $x = 0.33$ in the sample at 650°C. This suggests that the sample may have self-discharged during the measurement of *ex situ* XRD. Although there are some uncertainties in the measurements in the charged state of the samples, note that three structures, as expected from the three stages of lattice constants, exist in charging, though this is different from the existence of double layers in LiMn_2O_4 in charging.

From the X-ray absorption study Terada *et al.*¹² proposed that Ni^{2+} is first oxidized to the low-spin Ni^{3+} and then Ni^{3+} is oxidized to Ni^{4+} in electrochemical reaction of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, as expressed below.



Thus, according to these reactions, the three structures are considered to correspond to $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with Ni^{2+} , $\text{Li}_{0.5}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with Ni^{3+} , and $\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with Ni^{4+} , respectively, and during charging, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ would undergo a different electrochemical reaction from LiMn_2O_4 .

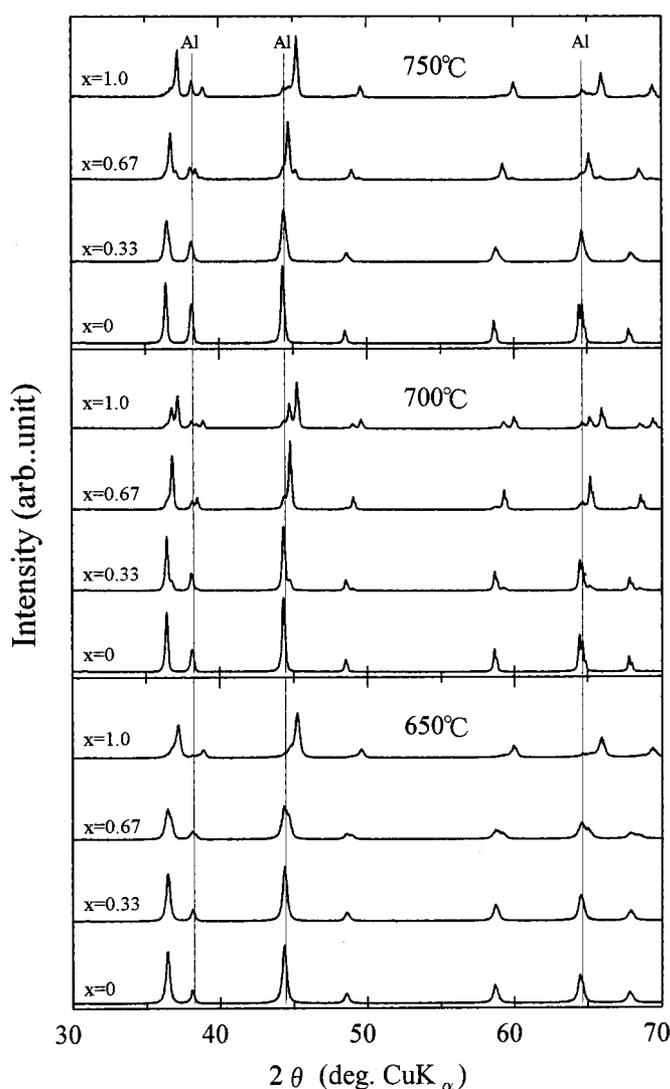


Figure 6. *Ex situ* XRD profile at each charged state in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared at 650, 700, or 750°C calcination temperature.

Conclusions

A 4.7 V class cathode material, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, was prepared with the self-reaction method and by successive calcination. The optimum amount of 20 wt% PVA solution used was found to be 32 g for the preparation of 0.1 mol $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

The resulting sample at the calcinations temperature of 700°C showed XRD peaks assigned to the space group $P4_332$. On the contrary, the space group of the sample calcined at 650 or 750°C fell into $Fd3m$ in the XRD analysis because diffraction peaks from $P4_332$ were missing.

The above sample at 700°C showed a one-step profile in the charge/discharge curve and this was contrasted with the other samples showing a two-step one. In spite of their different structures, these samples had the same initial capacities of about 123 mAh/g. Both of the samples gave similarly good cycle performance, but the sample at 650 or 750°C maintained a little higher capacity after 50 cycles of charge/discharge than the sample at 700°C.

The XRD pattern in each charged state suggests the existence of three structures with different lattice parameters; 0.816, 0.809, and 0.800 nm.

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