Hydrothermal Syntheses of Layered Lithium Nickel Manganese Oxides from Mixed Layered $Ni(OH)_2$−Manganese Oxides

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A series of mixed layered $Ni(OH)_2$−manganese oxides with Ni/Mn molar ratios up to near 1 were prepared by using a novel exfoliation−restacking hydrothermal method and a hydrothermal intercalation method. A series of lithium nickel manganese oxides with hexagonal layered structure (space group $R\bar{3}m$) can be obtained by hydrothermal treatment of the mixed layered $Ni(OH)_2$−manganese oxides in a concentrated LiOH solution at 200 °C. Another type of lithium nickel manganese oxide with an α-$LiFeO_2$-like cubic structure can be obtained by using $NiMnO_3$ as precursor under similar hydrothermal conditions. The synthesis reactions and the products were investigated by XRD, TEM, TG−DTA, and XPS studies. The mixed layered structure of $Ni(OH)_2$−manganese oxides can be described by two sublattices having different hexagonal unit-cell parameters in the *ab* plane but a common periodicity perpendicular to them along *c*. The layered lithium nickel manganese oxides can be expressed by a general formula of $\{Li_x\}[Li_yNi_nMn_m]O_2$ ($x \le 1$, $y \le 1/3$, $(y + n + m) \le 1$). The cubic phase of lithium nickel manganese oxide is metastable, which transforms to the hexagonal layered phase after heating at 500 °C in air.

Introduction

It is well-known that lithium ion secondary batteries are very important energy carriers used in movable telephone and other electronic devices. $LiCoO_2$ is the most extensively used cathodic material for this kind of batteries.[1] However, cobalt is expensive and toxic. To search for ideal alternatives for this cathodic material, many attempts have been made.[2] Among so many examined compounds, lithium manganese oxides are attractive candidates due to the low cost, nontoxic nature, and high average potential of manganese. $LiMn_2O_4$ spinel with a three-dimensional tunnel structure has been studied extensively as the cathodic material for the lithium ion batteries.[3−6] However, the spinel phase shows two voltage plateaus between 4 and 3 V vs Li electrode in the Li^+ insertion−deinsertion processes, and the capacity is severely faded upon cycling over the two plateaus. To improve the electrochemical performance of $LiMn_2O_4$ spinel, many attempts including adding excess lithium and changing the preparation conditions as well as partly substituting Mn with other elements have been made.[7,8]

Two-dimensional layered lithium manganese oxides ($LiMnO_2$) are interesting due to their high theoretic capacities (Li/Mn = 1). A orthorhombic layered $LiMnO_2$ phase with a space group *Pmnm* shows a high initial capacity, but the capacity decreases rapidly due to the irreversible transformation to spinel phase during the charge−discharge cycling.[9] Armstrong and Bruce have reported a monoclinic layered $LiMnO_2$ phase prepared from a layered α-$NaMnO_2$ phase by ion-exchange of Li^+/Na^+. The monoclinic layered phase shows good stability over repeated charge−discharge cycling.[10] The discharge capacity of monoclinic $LiMnO_2$ is nearly 270 mA h/g, which is well compared with that of $LiCoO_2$. The monoclinic $LiMnO_2$ can be also prepared by hydrothermal reaction in LiOH−KOH mixed-alkaline solution.[11]

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The monoclinic phase has a similar structure to $LiCoO_2$ with an oxygen array of O3 type (O, alkali ion in octahedral site; 3, number of MO_2 layers within the unit cell) in the layered structure, in which the oxygen lattice is (to a very good approximation) cubic close packed, and both the lithium and manganese cations are located in octahedral sites yielding sandwiches of MnO_2 in the cubic [111] direction, separated by lithium ion layers.[12] The crystal structure is a monoclinic distortion (space group $C2/m$) of the "ideal" O3 phase which would be rhombohedral-hexagonal (space group $R\bar{3}m$). It was also found that the layered structure can be stabilized by Al-doping.[13] However, in both doped and undoped monoclinic $LiMnO_2$, there is still a partly irreversible transformation to spinel phase during cycling, which in some way damages the electrochemical performance in further applications.

Recently, Dahn et al. reported a new layered lithium transition metal oxide T2-$Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ (T: Li^+ in tetrahedral site) prepared from P2-$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ (P: Na^+ in prismatic site) by ion exchange Na^+ with Li^+.[14−16] It was found that T2-$Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ phase transforms to a layered O2−$Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ (O: Li^+ in octahedral site) phase during the first charge or discharge, and then the O2 phase remains stable during cycling. This material exhibits a large reversible capacity of 180 mA h/g with good capacity retention vs cycle number at both 30 and 50 °C, due to the fact that it does not transform to the spinel phase during cycling.

Recently, we have synthesized a mixed layered Ni-$(OH)_2$−manganese oxide (NMO) by hydrothermal intercalation of $Ni(OH)_2$ into a birnessite-type manganese oxide with a layered structure.[17,18] In this layered compound, $Ni(OH)_2$ layers and MnO_2 layers of the birnessite structure alternately pack together to form a sandwichlike structure. Our preliminary study[17] has indicated also that this kind of mixed layered $Ni(OH)_2$−manganese oxide can be used as precursor for the preparation of a layered lithium nickel manganese oxide. However, the content of nickel in the mixed layered compound synthesized by the hydrothermal intercalation method is limited to a molar ratio of Ni/Mn less than $^1/_2$.

In this paper, we present a novel exfoliation−restacking hydrothermal method for the synthesis of the mixed layered $Ni(OH)_2$−manganese oxide with a high Ni content, the synthesis of the layered lithium nickel manganese oxides from the mixed layered precursors, and characterization of the layered compounds.

Experimental Section

Preparation of Materials. A Na^+-form of birnessite-type manganese oxide (NaBir), which was used as a precursor, was prepared by pouring a mixed solution of 3% H_2O_2 and 0.6 M NaOH (1000 mL) into a solution of 0.3 M $Mn(NO_3)_2$ (500 mL) under strong stirring as described in the literature.[19] The product was aged in the reaction solution at room temperature for 2 days. Then the product was filtered and washed with distilled water until pH = 8−8.5, and dried at room temperature. A Ni^{2+}-form of birnessite-type manganese oxide (NiBir) was prepared from NaBir by ion-exchange treatment in 1 M $Ni(NO_3)_2$ solution for 2 days.[18] A H^+-form of birnessite-type manganese oxide (HBir) was prepared from NaBir by ion-exchange of H^+/Na^+ in 0.1 M HNO_3 solution as reported in the literature.[20,21]

The mixed layered $Ni(OH)_2$−manganese oxides (NMO) were prepared by two methods. The NMO samples with molar ratios of Ni/Mn less than $^1/_2$ were prepared by hydrothermal intercalation method.[17,18] In this method, NiBir was dispersed into a solution with stoichiometric amount of $Ni(NO_3)_2$, then a 0.5 M NaOH solution was added until pH = 11−12 to prepare a $Ni(OH)_2$−NiBir mixture. The mixture was filtered, washed with distilled water, and autoclaved in distilled water at 200 °C for 2 days. The NMO samples with molar ratio of Ni/Mn larger than $^1/_2$ were prepared by an exfoliation−restacking hydrothermal method. HBir was dispersed in 0.05 M tetramethylammonium hydroxide (TMAOH) solution with molar ratio of TMA/Mn = $^5/_2$ under stirring to exfoliate the layered manganese oxide into a nanosheet colloidal suspension solution.[21] A solution (0.03 M) with stoichiometric amount of $Ni(NO_3)_2$ was dropwise added into the exfoliated suspension solution under vigorous stirring. A black-brown precipitate was obtained with a final pH value between 11 and 14. After 4 h of stirring, the precipitate was filtered and washed with distilled water until the pH was between 7 and 8. Then this precipitate was autoclaved in water at 150 to 200 °C for 1 to 3 days. The final product was filtered, washed, and dried at room temperature in air.

Lithium nickel manganese oxides (LNMO) were prepared by using mixed layered NMO as precursors. The mixture with weight ratio of NMO:$LiOH\cdot H_2O$:H_2O = 1:10:20 was autoclaved at 200 °C for 1−3 days. Then the product was filtered, washed with distilled water, and dried at room temperature.

Chemical Analysis. The metal element contents in the samples were determined by Seiko Instruments SPS7000A induced couple plasma (ICP) spectrometer after dissolving the samples in a mixed solution of HCl and H_2O_2.

Physical Analysis. Powder X-ray diffraction (XRD) patterns of the samples were carried out on a Rigaku RTP300−RC X-ray diffractometer with Cu Kα (λ = 0.15418 nm) radiation. The lattice constants were refined against an internal KBr standard. Infrared spectra (IR) were performed by the KBr method on a Perkin-Elmer 1600 Series FTIR infrared spectrometer. Thermogravimetric (TG) data and differential thermal analysis (DTA) curves were obtained at a heating rate of 10 °C/min in air on a Seiko SSC5200 thermal analyzer. X-ray photoelectron spectroscopy (XPS) was performed on a Shimadzu ESCA K1 using an Mg Kα 1253.6 eV X-ray source. Transmission electron microscope (TEM) observation and selected-area electron diffraction (SAED) studies were performed on a JEOL JEM3010 at 300 kV. The powdered sample was dispersed and supported on a microgrid, and a gold element was evaporated in a vacuum on half the area of the microgrid to exactly measure lattice distances of the sample.

Results and Discussion

Synthesis of the Mixed Layered $Ni(OH)_2$—Manganese Oxide (NMO). A series of NMO samples with

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Table 1. Composition, Synthesis Method, and Structure of NMO Samples

sample[a]	synthesis method	Ni/Mn	Na/Mn	structure
NMO-1	intercalation	0.20	0.000	layered
NMO-2	intercalation	0.34	0.012	layered
NMO-3	intercalation	0.36	0.000	layered
NMO-3#	intercalation	0.36	0.015	layered
NMO-5	intercalation	0.52	0.004	layered
NMO-5#	intercalation	0.56	0.129	layered
NMO-6	exfoliation−restacking	0.83		layered
NMO-7	exfoliation−restacking	0.98		$NiMnO_3$

[a] NMO-3# and NMO-5# were obtained by oxidation of NMO-3 and NMO-5 in NaClO solution, respectively.

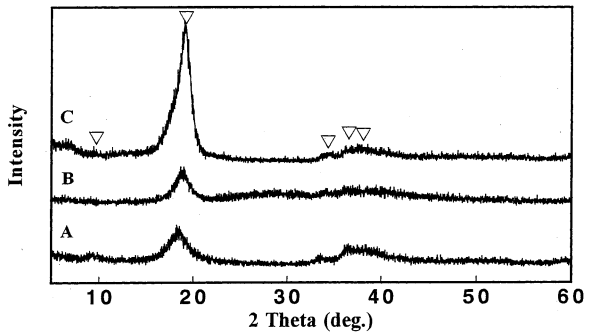

Figure 1. XRD patterns of (A) as-prepared $Ni(OH)_2$−manganese oxide precipitate and hydrothermally treated samples for (B) 7 h and (C) 4 days at 150 °C. Key: (▽) mixed layered $Ni(OH)_2$−manganese oxide phase.

different Ni contents, which were used as the precursor for the synthesis of the layered lithium nickel manganese oxides, were obtained by using the hydrothermal intercalation method and the exfoliation−restacking hydrothermal method. We have described the synthesis of the NMO by the hydrothermal intercalation method in the previously study.[17,18] It has found that NiBir and NaBir can be used as the precursors for the NMO by the hydrothermal intercalation method, and the molar ratio of Ni/Mn in the compound is limited to less than $^1/_2$. The samples of NMO-1, -2, -3, and -5 in Table 1 were prepared by hydrothermal treatment of the $Ni(OH)_2$−NiBir mixture at 200 °C for 2 days.

To synthesize NMO with high Ni content, we used the exfoliation−restacking hydrothermal method. In this method, the mixed layered NMO was stepwise synthesized from HBir. First, HBir was treated with TMAOH solution to exfoliate the layered manganese oxide into a manganese oxide nanosheet colloidal solution,[21] and then a $Ni(NO_3)_2$ solution was added into the colloidal solution. When the $Ni(NO_3)_2$ solution was added into the colloidal solution, a black-brown precipitate of $Ni(OH)_2$−manganese oxide was formed, immediately. Figure 1A shows the XRD patterns of the as-prepared $Ni(OH)_2$−manganese oxide precipitate. The precipitate shows a weak broad diffraction peak at 0.48 nm, suggesting that the manganese oxide nanosheets retain the sheet structure, but they are in low ordering arrangement in the precipitate. An IR study indicated that there is some free amorphous $Ni(OH)_2$ in the precipitate. The precipitate can be crystallized to the mixed layered NMO under hydrothermal conditions. Parts B and C of Figure 1 show the XRD patterns of the hydrothermally treated samples in distilled water at 150 °C. After the hydrothermal treatment, the diffraction peak at 0.48 nm shifted to 0.46 nm, and the intensity increased with increasing reaction time. The hydrothermally treated samples show the same XRD pattern as the NMO prepared by hydrothermal intercalation method,[18] but the diffraction peaks are broad. This fact revealed that the NMO can be prepared by the exfoliation−restacking hydrothermal method, and the layered structure is in low ordered arrangement. IR analysis shows that there is no free $Ni(OH)_2$ in the hydrothermally treated samples, meaning all $Ni(OH)_2$ is accommodated into the layered structure.

The formation of the NMO from the manganese oxide nanosheets solution is a restacking process of manganese oxide nanosheets, which accompanies accommodation of $Ni(OH)_2$ into the layered manganese oxide. This process can be described with a reaction model, as shown in Figure 2. When $Ni(NO_3)_2$ solution is added into the manganese oxide nanosheets colloidal solution, a strong basic solution, nickel hydroxide complex ions, $Ni_x(OH)_y^{z+}$ are formed immediately, and the complex cations attract negatively charged manganese oxide nanosheets together, resulting in the formation of a reassembled $Ni(OH)_2$−manganese oxide precipitate. The low crystallinity of the as-prepared precipitate suggests that a housing stacking occurs in the as-prepared precipitate. The housing stacking structure can be changed to an orderly stacking structure under the hydrothermal conditions, which corresponds to the crystallization into the mixed layered NMO.

The temperature effect on the formation of NMO under the hydrothermal conditions was also investigated. Figure 3 shows the XRD patterns of the samples obtained by hydrothermal treatment of the as-prepared precipitate in distilled water at 200 °C. After 8 h of hydrothermal reaction, the product is a mixed layered NMO (Figure 3A), but the crystallinity is still poor. A NMO with good crystallinity is obtained after 3 days of hydrothermal treatment, but the product contains a small amount of impurity from the $NiMnO_3$ phase (Figure 3B). After 9 days of hydrothermal treatment, the product is mainly $NiMnO_3$ (Figure 3C). The above results show that the as-prepared precipitate can be crystallized into the mixed layered NMO in the temperature range 150−200 °C. At a low reaction temperature (150 °C), a long hydrothermal reaction time is necessary to prepare NMO with good crystallinity. At high temperature (200 °C), a good crystallized NMO can be synthesized in a relatively short hydrothermal reaction time, but the metastable NMO phase transforms to the stable $NiMnO_3$ phase after a long time hydrothermal treatment. The compositions of the samples (NMO-6 and -7) prepared by the exfoliation−restacking hydrothermal method are given in Table 1. NMO-6 and NMO-7 have mixed layered and $NiMnO_3$ structures, respectively, which are prepared by hydrothermal treatment at 150 and 200 °C. These samples have higher nickel contents than the samples prepared by the hydrothermal intercalation method.

We also tried to oxidize Ni^{2+} in the NMO to Ni^{3+} by treatment of the NMO in NaClO solution. This is useful to adjust the Ni valence in the NMO, which will be important when the NMO is used as precursor for the synthesis of lithium nickel manganese oxide. Figure 4 shows the XRD patterns of NMO-5 and oxidation-treated sample (NMO-5#) in NaClO solution at 50 °C

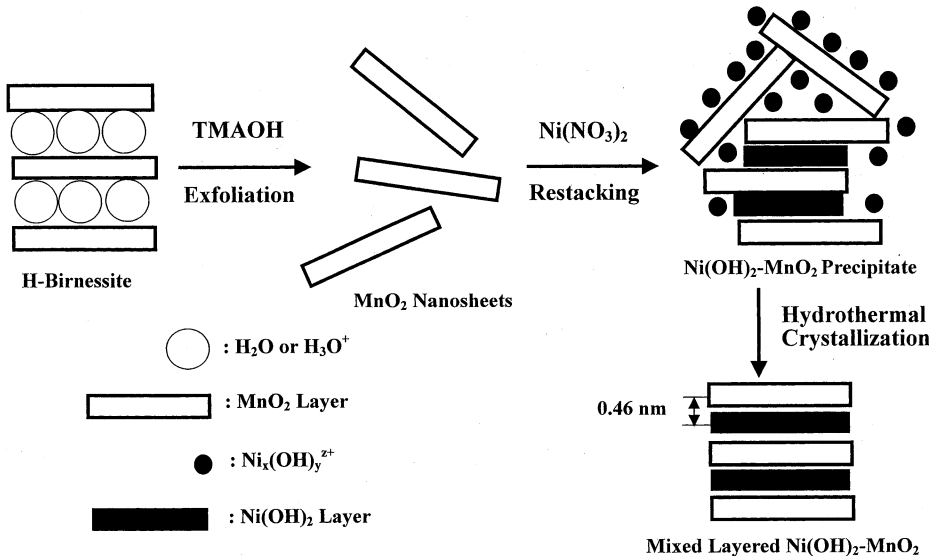

Figure 2. Model of formation mixed layered $Ni(OH)_2$−manganese oxide by exfoliation−restacking hydrothermal method.

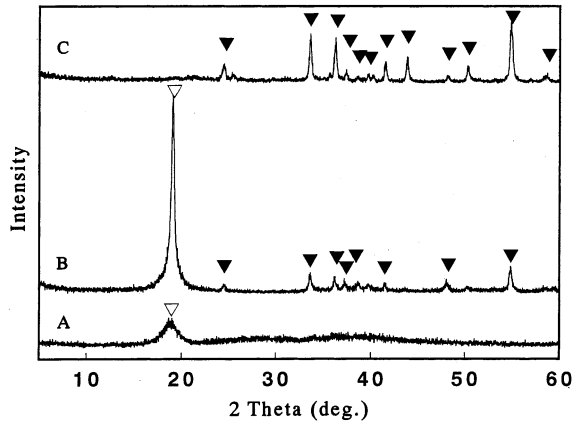

Figure 3. XRD patterns of samples obtained by hydrothermal treatment of as-prepared $Ni(OH)_2$−manganese oxide precipitate at 200 °C for (A) 8 h, (B) 3 days, and (C) 9 days. Key: (▽) mixed layered $Ni(OH)_2$−manganese oxide phase; (▼) $NiMnO_3$ phase.

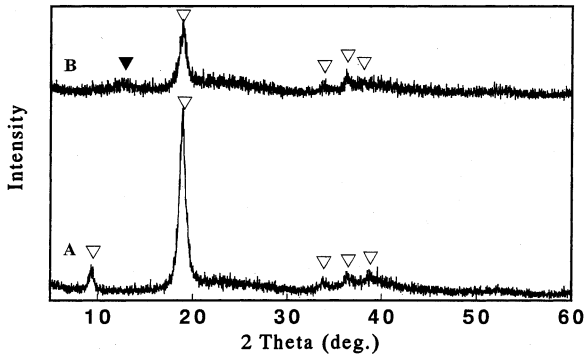

Figure 4. XRD patterns of (A) NMO-5 and (B) NMO-5# obtained by oxidation treatment of NMO-5 with NaClO solution. Key: (▽) mixed layered $Ni(OH)_2$−manganese oxide phase; (▼) NaBir phase.

for 6 h. After the oxidation treatment, this sample retains the layered structure, although the crystallinity decreased. Elemental analysis (Table 1) shows that the composition of the oxidized sample is a little different from that of its precursor. After oxidation treatment, the sodium contents in the sample increased. In fact, during the oxidation treatment, the solution became violet, suggesting the formation and dissolution of a small amount of MnO_4^- in the solution. A small amount of layered phase with a basal spacing of 0.72 nm, which corresponds to NaBir phase, is observed in the oxidized sample (Figure 4B). This suggests that a small amount of Na^+ was inserted into the layered structure during the oxidation treatment.

Electron Diffraction of NMO. To confirm the structure of NMO, TEM observation and selected-area electron diffraction (SAED) studies were carried out on NMO samples. NMO-6 has a platelike particle morphology (Figure 5A). When the electron beam is perpendicular to the basis plane, the SAED pattern contains two incommensurate hexagonal networks of (*hk*0) reflections (Figure 5B). The diffraction pattern is in agreement with that of asbolane, a nature mineral with mixed layered $Ni(OH)_2$−manganese oxide structure.[22−24] The mixed layered structure can be described by two sublattices (sublattices I and II) having different hexagonal unit-cell parameters in the *ab* plane but a common periodicity perpendicular to them along *c*. The lattice parameters for the sublattices are given in Table 2. The sublattice I with small *a* corresponds to the sublattice of MnO_6 octahedral layer, and sublattice II with large *a* to the sublattice of $Ni(OH)_6$ octahedral layer.[22] The SAED patterns for NMO-5 and NMO-3 are similar to that for NMO-6 (Figure 5), but with larger *a* than that for NMO-6 (Table 2). The relative intensity of sublattice II reflections decreases in an order of NMO-6 > NMO-5 > NMO-3, which is in agreement with the decreasing order of $Ni(OH)_2$ content in the samples, indicating that sublattice II corresponds to the sublattice of $Ni(OH)_2$ layer in the mixed layered structure.

Synthesis of Lithium Nickel Manganese Oxides (LNMO). Lithium nickel manganese oxides (LNMO) with layered structures can be synthesized by hydrothermal treatment of the mixed layered NMO in a concentrated LiOH solution at 200 °C. The crystallinity of the LNMO samples increased with increasing reac-

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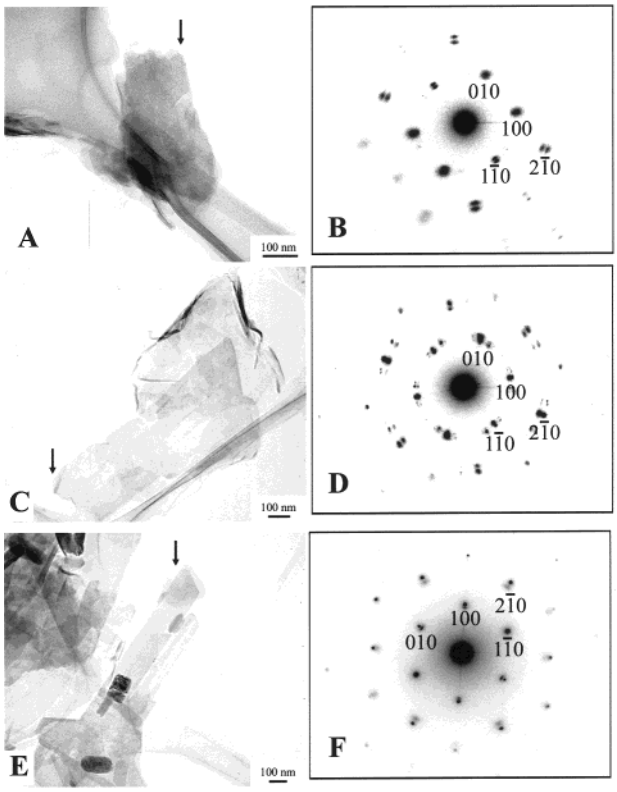

Figure 5. TEM images and selected-area electron diffraction (SAED) patterns from the *c* axis direction (perpendicular to the basis plane of the platelike crystal particle) for NMO-6 (A, B), NMO-5 (C, D), and NMO-3 (E, F), respectively.

Table 2. Crystal Data for Mixed Layered Ni(OH)$_2$−Manganese Oxides

		a (nm)[a]		
sample	Ni/Mn	sublattice I	sublattice II	*c* (nm)[b]
NMO-6	0.83	0.276	0.296	0.92
NMO-5	0.52	0.284	0.302	0.92
NMO-3	0.36	0.282	0.304	0.92

[a] Data from electron diffractions. [b] Data from X-ray diffractions.

tion time. Figure 6 shows the XRD patterns of LNMO prepared from the NMO with different Ni contents by hydrothermal treatment under the conditions of NMO: LiOH·H_2O:H_2O = 1:10:20 at 200 °C for 2 days. All these LNMO samples show the XRD pattern of the O3 type layered structure, which can be indexed in the layered hexagonal system (space group $R\bar{3}m$). When the nickel content was low, such as Ni/Mn = 0.20 (Figure 6A), small peaks around 22° were observed, and the peaks of (006) and (102), and peaks of (108) and (110) were observed separately, respectively. However, when the nickel content was high, such as in Figure 6F, the small peaks disappeared, and the peaks of (006) and (102), and peaks of (108) and (110) overlapped together, respectively. This XRD pattern corresponds to that of $LiNi_{1/2}Mn_{1/2}O_2$ prepared by a coprecipitation-calcination method, which has the layered hexagonal structure (space group $R\bar{3}m$).[16,25] Figure 6D shows the XRD pattern of LNMO-3# prepared from NMO-3# which is oxidation-treated with NaClO solution. This sample has the same XRD pattern as that of the other layered

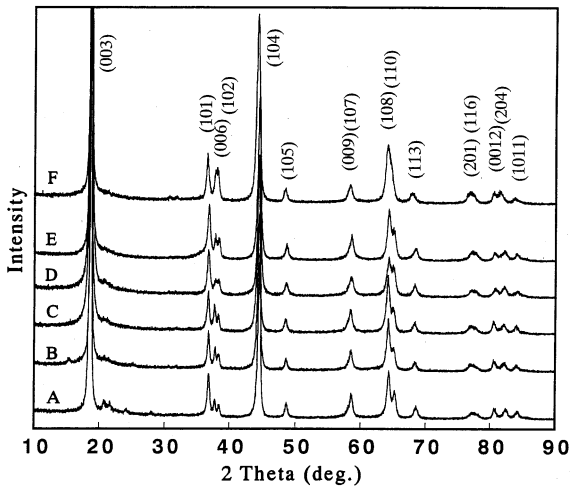

Figure 6. XRD patterns of (A) LNMO-1, (B) LNMO-2, (C) LNMO-3, (D) LNMO-3#, (E) LNMO-4, and (F) LNMO-6 obtained by hydrothermal treatment of NMO samples with different Ni contents at 200 °C for 2 days in LiOH solution with mass ratio of NMO:LiOH·H_2O:H_2O = 1:10:20.

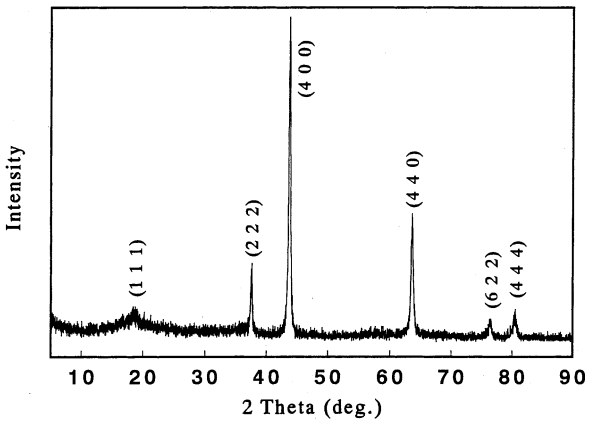

Figure 7. XRD pattern of C-LNMO obtained by hydrothermal treatment of NMO-7 at 200 °C for 2 days in LiOH solution with mass ratio of NMO:LiOH·H_2O:H_2O = 1:10:20.

Table 3. Crystal Data for Layered Lithium Nickel Manganese Oxides

sample	*a* (nm)	*c* (nm)	*V* (nm^3)
LNMO-1	0.2856	1.426	0.1007
LNMO-2	0.2867	1.428	0.1017
LNMO-3	0.2868	1.428	0.1017
LNMO-3#	0.2869	1.426	0.1016
LNMO-4	0.2866	1.427	0.1015
LNMO-6	0.2886	1.428	0.1030

LNMO samples. The lattice parameters of the layered LNMO samples are given in Table 3, in which the *a* axis trends to increase with increasing the Ni content.

When $NiMnO_3$ (NMO-7), which was prepared by hydrothermal treatment of as-prepared Ni(OH)$_2$−manganese precipitate at 250 °C was hydrothermally treated in a concentrated LiOH solution at 200 °C, a lithium nickel manganese oxide (C-LNMO) with an α-$LiFeO_2$-like structure was obtained (Figure 7). The sample shows an XRD pattern similar to that of α-$LiFeO_2$ except for a small peak at d = 0.4767 nm. Usually α-$LiFeO_2$ has a cubic disordered NaCl-type structure.[26] However, it has been reported also that

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Table 4. Composition and Structure of Lithium Nickel Manganese Oxides Prepared from NMO Samples in Table 1 and Electron Binding Energies of Ni $2P_{3/2}$ from XPS Investigation for LNMO and NMO Samples

sample	Ni/Mn	Li/(Mn + Ni)	structure	binding energy (eV)
LNMO-1	0.19	1.4	layered	859.2
LNMO-2	0.34	1.2	layered	857.3
LNMO-3	0.36	1.2	layered	856.7
LNMO-3#	0.36	1.2	layered	858.7
LNMO-4	0.45	0.98	layered	854.6
LNMO-5#	0.56	0.96	layered	
LNMO-6	0.88	0.88	layered	
C-LNMO	0.99	0.82	cubic(α-$LiFeO_2$)	
NMO-3	0.36			854.7
NiO (ref 32)				853.8/854.4
Ni_2O_3 (ref 32)				855.8/857.3

α-$LiFeO_2$ with a short-range cation ordering is possible, which shows a diffraction peak around $d = 0.4767$ nm.[27,28] We found that C-LNMO can be indexed in the cubic system with a superlattice structure with cation ordering. The observed diffraction data are in very good agreement with the calculated ones by indexing them as the cation-ordered system with a lattice constant a (=0.8270 nm) that is twice that of the disordered structure.

On the basis of the fact that the mixed layered NMO is suitable as a precursor for the synthesis of layered LNMO under the hydrothermal conditions, we propose an in situ topotactic structural transformation mechanism for the formation of the layered LNMO from the mixed layered NMO. In this reaction, Li^+ can diffuse into the mixed layered structure through the interlayer space, and react with the MnO_2 and $Ni(OH)_2$ layers in the crystal bulk to transform the mixed layered structure to the layered structure of LNMO in situ. This reaction accompanies a dehydration of $Ni(OH)_2$ or an ion-exchange of Li^+/H^+ and a rearrangement of Ni and Mn positions in subnanometer order distances. This is different from the normal hydrothermal synthesis, where usually a dissolution−deposition reaction occurs.

Chemical Composition and Cation Distribution of the Layered LNMO. The compositions of LNMO prepared by using NMO samples of Table 1 as precursors are listed in Table 4. It is interesting that the molar ratio of Li/(Ni + Mn) decreases with increasing the Ni content of the layered LNMO. This result can be explained from the characteristic of LNMO structure. On the basis of an assumption that Ni occupies the same site as Mn,[16,29] the layered LNMO can be expressed by a general formula as follows

$$\{Li_x\}[Li_yNi_nMn_m]O_2 \quad (1)$$

where { } and [ ] are octahedral sites in the layer of Li atom and octahedral sites in the layer of Mn atom, respectively, with $x \le 1$, $y \le 1/3$, $(y + n + m) \le 1$. Ni and a part of the Li atoms can be located in the Mn site.[12]

When $n = 0$, $x = 1$, $y = 1/3$, and $m = 2/3$, without Ni in the layered structure, the formula corresponds to

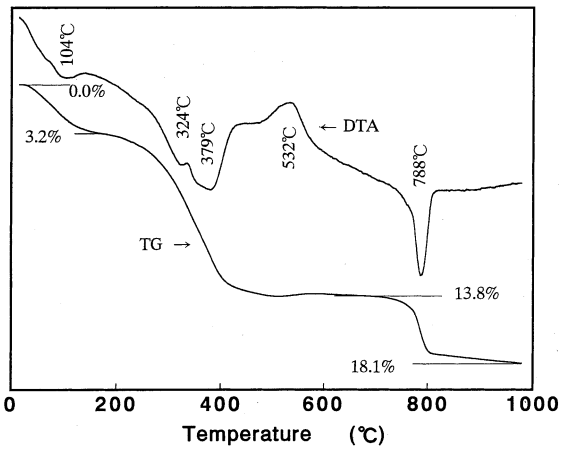

Figure 8. TG−DTA curves for NMO-6.

(Li)$[Li_{1/3}Mn_{2/3}]O_2$ (Li_2MnO_3). A study on the Li_2MnO_3 structure has indicated that it has a rock-salt-type structure with a cubic-close-packed oxygen anion array in which layers of Li atoms alternate with layers containing Li and Mn atoms in a 1:2 ratio,[30] which is in agreement with formula 1. The structure of Li_2MnO_3 is a monoclinic distortion of the "ideal" O3 phase of the hexagonal system (space group $R\bar{3}m$). This suggests that when the Ni content is low, the monoclinic distortion of the hexagonal layered LNMO phase is possible. The monoclinic Li_2MnO_3 phase can be obtained also by hydrothermal treatment of Li−birnessite in a concentrated LiOH solution.[31] In the samples of LNMO-1, -2, and -3 which have low nickel contents, the Li/(Ni + Mn) molar ratios are larger than 1 (Table 4), suggesting that some lithium atoms occupy the octahedral sites in the manganese layer. These facts indicate that a series of layered LNMO with general formula 1 can be prepared by using the present method.

The layered LNMO with low Ni content show the small diffraction peaks around 22° (Figure 6), which is similar to Li_2MnO_3. The structural study on Li_2MnO_3 has shown that Li and Mn atoms are ordering arrangement in the Li−Mn mixed layers.[30] A similar Ni and Mn ordering arrangement has been also observed in Ni−Mn mixed layers of $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ layered structure.[15,16] In the later case, when the molar ratio of Ni/Mn increases to 1, there is no superlattice in the sodium nickel manganese oxide. A superlattice structure is also possible in the layered LNMO prepared here when Ni content is low. The present of small diffraction peaks around 22° for the layered LNMO with low Ni content may be due to the metal ordering in the transition metal layer and the monoclinic distortion of the hexagonal layered structure.

TG—DTA Analysis. Figure 8 shows the TG−DTA curves for NMO-6 sample. The weight loss of 3.2% below 200 °C is attributed to the loss of water absorbed on the surface. The endothermic peaks at 324 and 379 °C in the DTA curve with about 10.6% weight loss between 200 and 500 °C are ascribed to the loss of water by the dehydration of the interlayer $Ni(OH)_2$, accompanying the transformation of the mixed layered phase to an

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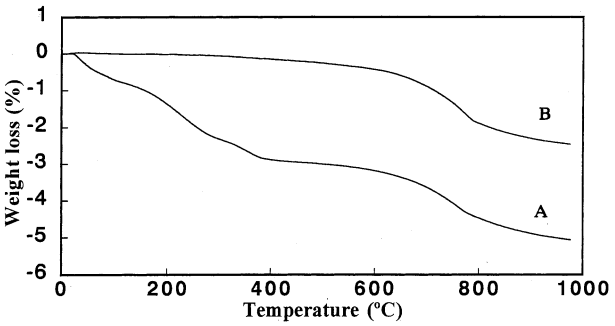

Figure 9. TG curves of (A) first heating and (B) second heating for LNMO-6.

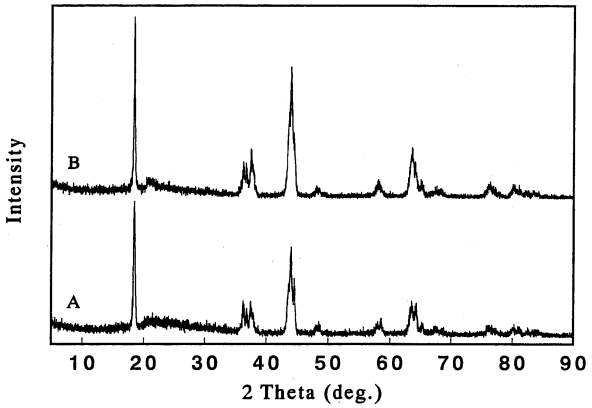

Figure 10. XRD patterns of samples obtained by heat-treatment of (A) LNMO-6 and (B) C-LNMO at 1000 °C in air.

amorphous phase. The exothermic peak at 532 °C in the DTA curve with no apparent weight loss is referred to the transformation of the amorphous phase to $NiMnO_3$. The endothermic peak at 788 °C in the DTA curve with about 4.4% weight loss between 600 and 950 °C in the TG curve is attributed to the transformation of $NiMnO_3$ to a spinel phase of $Ni_xMn_{3-x}O_4$ with O_2 evolution. These results indicate that the mixed layered $Ni(OH)_2$−manganese oxide can be stable up to 300 °C.

Figure 9 shows the TG curves of LNMO-6 that has the hexagonal layered structure with high nickel content. In the first heating TG curve (Figure 9A), the weight loss of 0.8% below 150 °C is attributed to the loss of water absorbed on the surface. The weight loss of 2.2% between 150 and 500 °C can be ascribed to the loss of water by dehydration of lattice −OH or crystal water in the structure. The weight loss of 2.1% between 500 and 950 °C is attributed to the release of O_2. Figure 9B shows the second heating TG curve for the sample. The weight loss behavior over 500 °C is similar to that of the first heating, suggesting that reversible release of O_2 and recombination of O_2 reactions occur during the heating and cooling in air, respectively. Since there is only very little weight loss below 500 °C in the second heating, the dehydration of the lattice −OH is an irreversible reaction. The presence of the lattice −OH in the LNMO sample suggests that some Li^+ ions are substituted by H^+ ions in the layered structure. This is the reason the molar ratio of Li/(Ni + Mn) is less than 1 in the sample (Table 4).

Figure 10A shows the XRD pattern of LNMO-6 after heat treatment in air at 1000 °C. Some diffraction peaks, e.g., (101), (104), and (110), are split, indicating that LNMO-6 is transformed to a mixture of more than

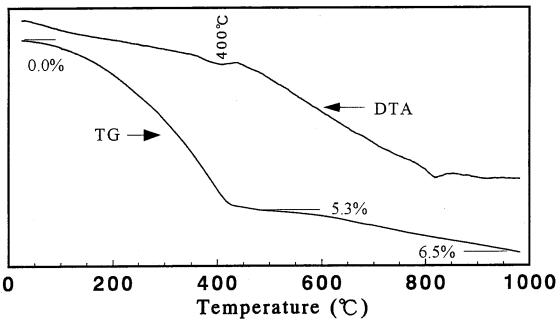

Figure 11. TG−DTA curves for C-LNMO.

two phases, such as hexagonal layered phase, spinel phase as well as Li_2MnO_3 phase. Since the diffraction peaks of these phases are close to each other, the distinction of these phases is difficult from the XRD pattern.

The C-LNMO sample shows a weight loss of 5.3% up to 500 °C with an endothermic peak at 400 °C (Figure 11), which can be attributed to a dehydration of lattice −OH. There is a weight loss of 1.2% between 500 and 950 °C, which can be ascribed to the evolution of O_2. The cubic C-LNMO is a metastable phase, which transforms to the hexagonal layered phase after heating at 500 °C in air. Both C-LNMO and LNMO-6 show almost same XRD pattern after heating at 1000 °C (Figure 10).

X-ray Photoelectron Spectroscopy (XPS). An XPS study was carried out on the NMO and LNMO samples to investigate the oxidation state of nickel in the samples. The values of binding energy of Ni $2P_{3/2}$ are summarized in Table 4. The values of binding energy of Ni $2P_{3/2}$ for NiO and Ni_2O_3 are also given in Table 4 as references.[32] NMO-3 has a Ni $2P_{3/2}$ binding energy of 854.7 eV, which is close to that of NiO. LNMO-3 has a higher binding energy (856.7 eV) than its precursor of NMO-3. This indicates that an oxidation reaction of Ni^{2+} to Ni^{3+} occurs during the hydrothermal treatment of NMO-3 in the LiOH solution. Since most manganese ions in the birnessite precursor are Mn^{4+},[33] it is expected that Mn^{4+} can act as an oxidant in the redox reaction. The binding energy for the LNMO samples is dependent on the nickel content of the samples; it decreases with increasing the nickel content, except for LNMO-3#. This fact suggests that the fraction of Ni^{2+} increases, while the fraction of Ni^{3+} decreases with increasing nickel content of the LNMO samples. LNMO-3# shows a higher Ni $2P_{3/2}$ binding energy (858.7 eV) than LNMO-3, due to that its precursor NMO-3# is obtained by oxidation treatment of NMO-3 in NaClO solution. Moriga et al.[29] have investigated the binding energies of Ni in $LiNi_{0.8}Mn_{0.2}O_2$ and $LiNiO_2$, and found that Ni^{2+} and Ni^{3+} in the compounds have binding energies of 853.7 and 855.3 eV, respectively, which are somewhat lower than that in our LNMO samples. This may be due to the low Ni content in our samples.

Electrochemical Properties of the Layered LNMO. A preliminary investigation on electrochemical properties of the layered LNMO samples as cathodic material

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for lithium rechargeable battery was carried out. LNMO-6 with high Ni content (Ni/Mn = 0.88) shows a higher initial discharge capacity (120 mA h/g), and better cyclability than LNMO-4 with lower Ni content (Ni/Mn = 0.45) in a charge−discharge voltage range of 2.0 to 4.2 V. LNMO-5#, which was prepared from the oxidation-treated NMO precursor, shows quite different charge−discharge behavior from the untreated samples. The results suggest that the electrochemical properties of the LNMO samples are dependent on the chemical composition and oxidation states of Ni and Mn. Detailed electrochemical results will be published elsewhere.

Conclusions

The mixed layered $Ni(OH)_2$−manganese oxide with a molar ratio of Ni/Mn up to 1 can be stepwise synthesized by the exfoliation−restacking hydrothermal method. This mixed layered compound is in the metastable phase. It transforms to the $NiMnO_3$ phase over 200 °C under hydrothermal conditions and over 530 °C in air. A series of the hexagonal layered lithium nickel manganese oxides with different Ni/Mn molar ratios can be hydrothermally synthesized in concentrated LiOH solutions by using the mixed layered compound as the precursor. The layered lithium nickel manganese oxides can expressed with the general formula of $\{Li_x\}[Li_yNi_nMn_m]O_2$ ($x \leq 1$, $y \leq {}^1/_3$, $(y + n + m) \leq 1$). The cubic lithium nickel manganese oxide with α-$LiFeO_2$-like structure can be obtained by using $NiMnO_3$ as the precursor. This cubic phase is metastable and transforms to the hexagonal layered phase after heating at 500 °C in air.

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