Hydrothermal Intercalation Reaction of Nickel Hydroxide into Layered Manganese Oxides

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A series of $Ni(OH)_2$−manganese oxide (NMO) compounds with a mixed layered structure were synthesized by inserting nickel hydroxide into layered manganese oxides, Na−birnessite (NaBir) and Ni−birnessite (NiBir), under hydrothermal conditions. The hydrothermal intercalation reaction and the NMO compounds were investigated by pH titration, XRD, IR, SEM, TG-DTA, and chemical composition analysis. $Ni(OH)_2$ is preferentially formed in the interlayer space of the birnessites. The mixed layered NMO with $Ni(OH)_2$ content up to Ni/Mn = 1/2 can be obtained by using the hydrothermal intercalation method. $Ni(OH)_2$ was more easily inserted into NiBir than into NaBir under the hydrothermal conditions. A mechanism of topotactic insertion reaction was proposed for the formation of the mixed layered compounds. The mixed layered NMO can be also prepared by hydrothermal treatment of NaBir in $Ni(Ac)_2$ solution below 250 °C. The NMO compounds were stable up to 300 °C in air, and transformed to other phases over this temperature.

Introduction

Layered metal oxides show interesting chemical properties, such as ion-exchange, intercalation, catalysis, and adsorption, as well as physical properties such as conductivity and magnetism. These compounds can be used as adsorbents, cathodic materials for batteries and precursors for syntheses of organic/inorganic composites and new compounds.[1−10] The development of a new technique for synthesis of mixed layered compounds is interesting in the preparation of new materials with special physicochemical properties.[11−15] Since the mixed layered compounds are made up by alternately stacking two or more kinds of structural unit layers, their properties can be predicted from the stacking structures as well as the properties of the structural unit layers, which means the design of the properties is possible.[16]

Since in most cases the mixed layered compounds are metastable phases, they are not easy to be synthesized by using a normal method. Soft chemical method is a powerful method for the synthesis of such metastable phases. Some mixed layered compounds have been synthesized by insertion of metal hydroxides into clay compounds with cation-exchange and pH titration methods, and it has been also found that these mixed layered compounds exhibit characteristics differing from the metal hydroxides and the clay precursors.[15,17,18] However, only a few studies have been reported on the synthesis of mixed layered metal oxides. Recently, Feng et al. synthesized a mixed layered manganese oxide from a birnessite-type manganese oxide with a layered structure by using a hydrothermal soft chemical process.[13] In the preparation of the mixed layered manganese oxide, $Li_xAl_n(OH)_m{}^{z+}$ complex ions are first inserted in the interlayer space of the birnessite by an ion-exchange reaction, and then the ion-exchanged birnessite is hydrothermally treated to polymerize the complex ions in the interlayer space. The resulted compound has a mixed layered structure of alternately stacking MnO_2 and $LiAl_2(OH)_6$ layers.

Asbolanes are naturally occurring manganese oxide minerals with uncontinuous metal hydroxide layers, such as $Ni(OH)_2$, CoOOH or $Co(OH)_3$, $Mn(OH)_2$, and $Cu(OH)_2$ in the interlayer spaces of layered manganese oxide.[19−23] Very recently we have successfully synthesized a mixed

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layered nickel hydroxide−manganese oxide (NMO) from a Ni−birnessite by using a hydrothermal intercalation method,[24] and found that the mixed layered compound can be used as a precursor for the synthesis of a $LiNi_xMn_{1-x}O_2$ layered compound which is an attractive material as an alternative of $LiCoO_2$ cathodic material in lithium rechargeable batteries. In this paper, we present the intercalation reactions of $Ni(OH)_2$ into Ni−birnessite and Na−birnessite in various solutions under hydrothermal and room-temperature conditions, and propose a formation mechanism of the mixed 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 0.3M $Mn(NO_3)_2$ (500 mL) under strong stirring conditions as described in the literature.[6] This suspension was aged in the mother solution at room temperature for 2 days. Then the product was filtered and washed with distilled water till pH = 8, and dried at room temperature. A Ni^{2+}-form of birnessite-type manganese oxide (NiBir) was prepared from NaBir (10 g) by ion-exchanging in 1 M $Ni(NO_3)_2$ solution (1 L) with stirring for 2 days.

Mixed layered $Ni(OH)_2$−manganese oxides (NMO) were prepared by two methods. In the first method, NiBir or NaBir was dispersed into a certain $Ni(NO_3)_2$ solution, and added 0.5M NaOH solution until pH = 11−12, then the mixture was filtered and washed with distilled water for 10 times, and was autoclaved in distilled water at 150−200 °C for 1−3 days. In the second method, NaBir was directly hydrothermally treated in $Ni(Ac)_2$ solution at 150 and 200 °C for 1 day.

pH Titration. A pH titration of the suspension solutions of NaBir or NiBir in $Ni(NO_3)_2$ solution was carried out similarly as that for preparation of $Ni(OH)_2$−montmorillonite mixed layered compound described by Yamanaka et al.[15] Separate 1.0 g samples of NaBir and NiBir (dried at 80 °C) were dispersed in 25 mL of $Ni(NO_3)_2$ solution (0.1M), and agitated by ultrasonic vibration for 30 min. Then these suspensions were potentionmetrically titrated with a 0.1139M NaOH solution. The pH value at each stage of the titration was measured by a HORIBA F-22 pH meter. The titrated suspension was stirring for 10 min before the pH measurement at each stage of the titration before pH = 8, 5 min before pH = 10, and 2 min to the end. A pure water and one with dispersed NiBir as well as a pure $Ni(NO_3)_2$ solution (0.1M, 25 mL) were also similarly titrated for comparison.

Chemical Analysis. The contents of sodium, nickel, and manganese in the samples were determined by Seiko Instruments SPS7000A induced couple plasma (ICP) spectrometer after dissolved 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 K ($\lambda = 0.15418$ nm) radiation. Infrared spectra (IR) were recorded by the KBr method on a Perkin-Elmer 1600 Series FTIR infrared spectrometer. Thermogravimetric (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 10 °C/min in air on a Seiko SSC5200 thermal analyzer. Scanning electron microscopy (SEM) was performed on a Hitachi S-530 scanning electron microscope.

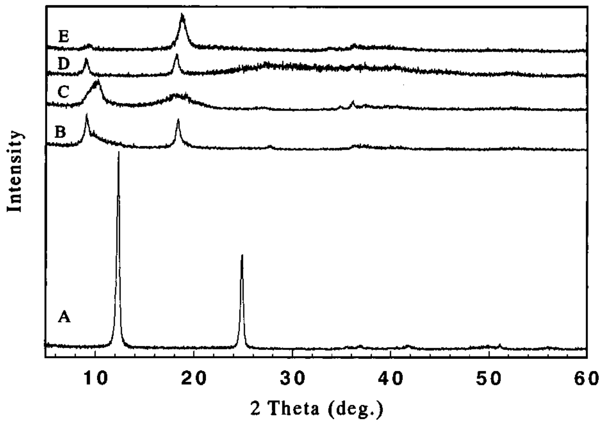

Figure 1. The XRD patterns of (A) NaBir, (B) NiBir, (C) sample obtained by pH titration of NaBir in $Ni(NO_3)_2$ with NaOH at room temperature, (D) $Ni(OH)_2$−NiBir mixture with Ni/Mn = 1/2, and (E) hydrothermally treated sample (D) at 200 °C for 2 days.

Table 1. The Chemical Compositions of the Samples

no.	samples	Mn (mmol/g)	Ni (mmol/g)	Na (mmol/g)	Ni/Mn (mol)	Na/Mn (mol)
1	NaBir	9.01	0	2.84	0	0.315
2	NiBir	8.45	1.21	0	0.14	0
		$Ni(OH)_2$−NiBir Reaction System				
3	NMO-1/7	9.36	1.84	0	0.197	0
4	NMO-2/7	7.43	2.50	0.087	0.337	0.012
5	NMO-3/8	8.10	2.78	0	0.343	0
6	NMO-1/2	6.68	3.44	0.030	0.515	0.0045
		$Ni(OH)_2$−NaBir Reaction System				
7	(Ni/Mn = 3/8)	8.26	2.78	0.48	0.335	0.057
8	(Ni/Mn = 1/2)	7.39	3.19	0.35	0.431	0.047
		$Ni(Ac)_2$−NaBir Reaction System				
9	Ac-A	7.92	3.71	0	0.469	0
10	Ac-B	7.34	4.05	0	0.552	0

Results and Discussion

Preparation of NaBir and NiBir. The XRD pattern of NaBir prepared as the precursor is shown in Figure 1A. The XRD pattern and chemical composition (Table 1) of NaBir are in agreement with those in the literature,[13,25] which indicates that a pure birnessite phase with a basal spacing of 0.72 nm was obtained. After two ion-exchange treatments of NaBir with a $Ni(NO_3)_2$ solution, Na^+ ions were completely exchanged with Ni^{2+} ions (Table 1). The XRD pattern of NiBir (Figure 1B) shows two main diffraction peaks at 0.97 and 0.49 nm, which is very similar to that of buserite.[26,27] This fact suggests that the layered structure of the birnessite retains after the ion-exchange reaction, while the basal spacing increases from 0.72 to 0.97 nm. However, there is a hump at the right side of the first diffraction peak at 0.97 nm and the intensity of peak at 0.49 nm is as strong as that at 0.97 nm. This is perhaps due to the formation of distorted layered structure in the product.

Intercalation of $Ni(OH)_2$ into Birnessites by pH Titration. The intercalation reaction of $Ni(OH)_2$ into NiBir and NaBir at room temperature was investigated by pH titration method. When NaOH solution was

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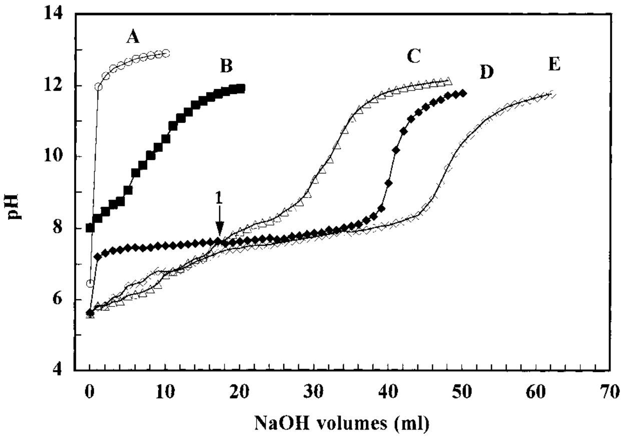

Figure 2. The pH titration curves of (A) blank, (B) distilled water with NiBir, (C) 0.1M $Ni(NO_3)_2$ solution with NaBir, (D) 0.1M $Ni(NO_3)_2$ solution, and (E) 0.1M $Ni(NO_3)_2$ solution with NiBir.

added into $Ni(NO_3)_2$ solution without the presence of the birnessites, the pH of the solution increased from pH 5.6 to 7.2, immediately, and then increased very slowly (Figure 2D). This was accompanied the formation of $Ni(OH)_2$ precipitate at the same time. The $Ni(NO_3)_2$ solution showed the end-point of the titration at pH = 9.5, around which the pH increased rapidly.

The titration curve of NaBir−$Ni(NO_3)_2$ system showed dibase behavior (Figure 2C), which was different from that of $Ni(NO_3)_2$ solution. The titration curve C can be separated into two stages, before the point (1) crossing with curve D and after that. Before the point (1), the pH values are lower than that of curve D, which corresponds to the formation of $Ni(OH)_2$ precipitate in the interlayer space of NaBir by a reaction as follows:

$$Na_{0.32}MnO_2 + yNi(NO_3)_2 + (x + 2y - 0.32)NaOH \rightarrow Na_xNi_y(OH)_{x+2y-0.32}MnO_2 + 2yNaNO_3 \quad (1)$$

After the point (1), the pH values are higher than those of curve D, which corresponds to the formation of free $Ni(OH)_2$ precipitate. The amount of $Ni(OH)_2$ inserted into NaBir by the titration estimated from the amount of NaOH at the point (1) is 2.03 mequiv/g of NaBir (Ni/Mn = 0.12 in mol). The added amount of NaOH at the end-point (pH = 9.5) of the titration curve C is less than that of the curve D. The difference of the added NaOH amounts between the end points of curves C and D is 1.53 meq/g of NaBir, which is attributed to the amount of nickel ion that is inserted into NaBir by Ni^{2+}/Na^+ exchange reaction during the titration.[15] Since the Na^+ content in NaBir is 2.84 mequiv/g (Table 1), so only 54% of Na^+ was exchanged by Ni^{2+} ion after the titration, and 46% of Na^+ (Na/Mn = 0.15) was still in the sample to balance the charge. The XRD study on the $Ni(OH)_2$−NaBir sample obtained by the titration indicated that the basal spacing of the layered structure increased from 0.72 nm of NaBir to 0.87 nm after the titration, revealing that $Ni(OH)_2$ was inserted into the interlayer space of NaBir, and NMO was formed (Figure 1C). The small peak at 0.46 nm is attributed to the free $Ni(OH)_2$. The titration result suggests that $Ni(OH)_2$ is precipitated preferentially in the interlayer space of NaBir rather than as free $Ni(OH)_2$, and partial Na^+ in NaBir was exchanged by Ni^{2+} during the titration.

The titration curve of NiBir−$Ni(NO_3)_2$ system also shows a dibase behavior similar to that of NaBir−$Ni(NO_3)_2$ system (Figure 2E). In the first stage, the pH value increases with the increasing of the amount of NaOH with almost the same manner as that of curve C until it approaches the point (1), which can be attributed to the formation of $Ni(OH)_2$ in the interlayer space of NiBir. The amount of $Ni(OH)_2$ inserted into NiBir is 2.33 mequiv/g of NiBir (Ni/Mn = 0.14). In the second stage (after the point (1)), the curve E shows a similar behavior to the curve D, which can be ascribed to the formation of free $Ni(OH)_2$. It is interesting that the amount of NaOH required to complete the titration is more than that of $Ni(NO_3)_2$ solution (curve D). To clear this phenomenon, a titration of distilled water containing NiBir and a blank titration were performed. The pH value increases rapidly with the addition of NaOH in a blank titration (Figure 2A), but with the presence of NiBir, the titration curve shows a different behavior (Figure 2B), implying that Ni^{2+} ions in NiBir transformed to $Ni(OH)_2$, and some Na^+ ions were inserted into NiBir to balance the charge during the titration. The reaction can be written as follows:

$$Ni_{0.14}MnO_2 + xNaOH \rightarrow Na_xNi_{0.14}(OH)_xMnO_2 \quad (2)$$

The amount of inserted Na^+ is 0.77 mequiv/g of NiBir (Na/Mn = 0.093) based on the difference of the added NaOH amounts between the end points of curves B and A.

On the basis of the reaction 2, the reaction in curve E for NiBir-$Ni(NO_3)_2$ system before the point (1) can be written as follows:

$$Ni_{0.14}MnO_2 + (y - 0.14)Ni(NO_3)_2 + (x + 2y - 0.28)NaOH \rightarrow Na_xNi_y(OH)_{x+2y-0.28}MnO_2 + 2(y - 0.14)NaNO_3 \quad (3)$$

Since more amount of $Ni(OH)_2$ was formed in NiBir−$Ni(NO_3)_2$ system than that in $Ni(NO_3)_2$ solution only, more amount of NaOH was required to complete the titration in NiBir−$Ni(NO_3)_2$ system than that in Ni($NO_3)_2$ solution.

Hydrothermal Intercalation of $Ni(OH)_2$ into NiBir. Although $Ni(OH)_2$ can be inserted into the birnessites by the pH titration at room temperature, the titration needs a relatively long time to reach the reaction equilibrium, and the amount of inserted $Ni(OH)_2$ is very little. A hydrothermal method was used in the preparation of NMO. In the hydrothermal intercalation, NiBir (or NaBir) was first dispersed in a $Ni(NO_3)_2$ solution, and a NaOH solution was then added in the NiBir−$Ni(NO_3)_2$ system to prepare a $Ni(OH)_2$−NiBir mixture. The mixture was hydrothermally treated in distilled water to intercalate $Ni(OH)_2$ into the NiBir.

Figure 1D shows the XRD pattern of the $Ni(OH)_2$−NiBir mixture with a molar ratio of Ni/Mn = 1/2. The broad peak between 20 and 40° is attributed to amorphous phase of the free $Ni(OH)_2$. After hydrothermal treatment in distilled water at 200 °C for 2 days, the intensity of peak at 0.46 nm increased while that at 0.92 nm decreased (Figure 1E), and the broad peak of the free $Ni(OH)_2$ disappeared. This suggests that the free $Ni(OH)_2$ is inserted into NiBir under the hydrothermal conditions. The XRD profile of the hydrothermally

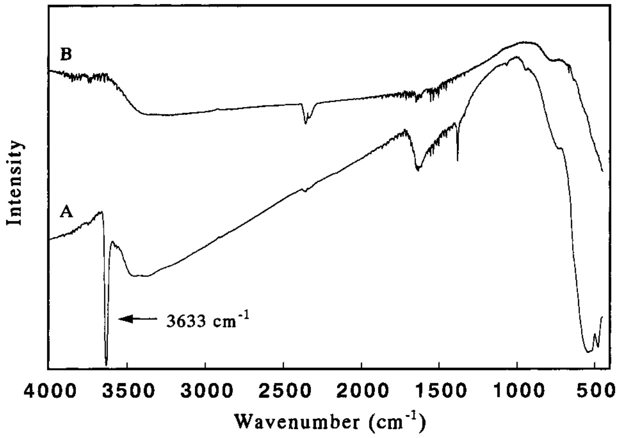

Figure 3. IR spectra of (A) $Ni(OH)_2$−NiBir mixture and (B) hydrothermally treated sample (A) at 200 °C for 2 days.

treated sample is similar to that of natural asbolane with the mixed layered structure.[21,23] Since the hydrothermally treated sample has low crystallinity, it is difficult to confirm the mixed layered structure only from the XRD profile, because the XRD profile is also similar to that of todorokite with a (3 × 3) tunnel structure.[28−30] A IR study was carried out on the $Ni(OH)_2$ insertion reaction and the NMO sample (Figure 3). A strong vibration band at 3633 cm^{-1}, which is attributed to the free $Ni(OH)_2$, was observed in the $Ni(OH)_2$−NiBir mixture before the hydrothermal reaction (Figure 3A). The vibration band disappeared after the hydrothermal reaction (Figure 3B), implying that $Ni(OH)_2$ was completely inserted into the layered compound. The IR spectrum (Figure 3B) of the hydrothermally treated sample corresponds to that of natural asbolane.[21] This suggests that the hydrothermally treated sample has the mixed layered structure.

Golden et al. have studied the synthesis of todorokite by hydrothermal treatment of divalent metal ion exchanged birnessites and the structures of the products.[30] A single phase of todorokite was obtained from Mg−birnessite, but a mixture of todorokite and asbolane phases was obtained from Ni−birnessite. Our synthesis experimental results indicate that under our synthesis condition the hydrothermal product is a mixed layered compound rather than a tunnel compound.[24] We think it is due to that our sample has high Ni content in the precursor, and the $Ni(OH)_2$ in the interlayer space acts as pillar to hinder the structural transformation from the layered structure to the tunnel structure. The natural asbolanes usually contain Ni, Co, Fe, or Cu, due to their hydroxides are easily form in the interlayer space of the layered manganese oxide. The above titration study indicates that formation of the hydroxides in the interlayer space correspond to the increase of the metal contents in the compounds.

A series of NMO with different molar ratio of Ni/Mn were prepared (labeled as sample no.'s 3−6 in Table 1) by this hydrothermal reaction. These samples show similar XRD patterns (Figure 4), indicating that these compounds have similar layered structure. The composition analysis (Table 1) shows that the molar ratio of Ni/Mn is closed to the designed one in the starting mixture. It is expected that the interlayer space of the birnessite could accommodate $Ni(OH)_2$ up to a maximum molar ratio of about Ni/Mn = 1. However, under our experimental conditions, the $Ni(OH)_2$ content was limited to below Ni/Mn = 1/2. If the molar ratio of Ni/Mn in the starting $Ni(OH)_2$−NiBir mixture was larger than 1/2, the hydrothermal product was a mixture of NMO and $Ni(OH)_2$. This may be ascribed to the difficulty of diffusion of $Ni(OH)_2$ in the interlayer space. It is considered that there are some spaces surrounded by $Ni(OH)_2$ species between the MnO_2 layers.

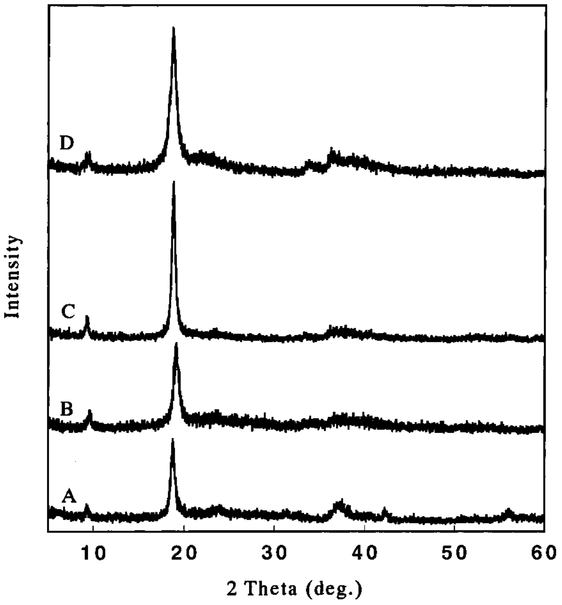

Figure 4. XRD patterns of (A) NMO-1/7, (B) NMO-2/7, (C) NMO-3/8, and (D) NMO-1/2 obtained by hydrothermal treatment of $Ni(OH)_2$−NiBir mixtures at 200 °C for 2 days.

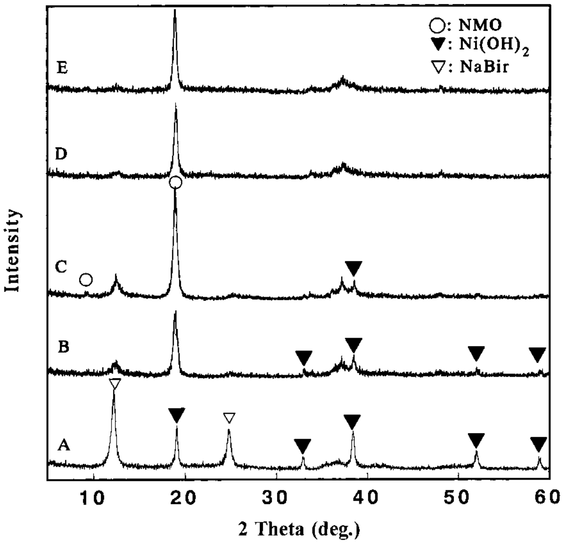

Figure 5. XRD patterns of (A) $Ni(OH)_2$−NaBir mixture with Ni/Mn=3/8, and the samples obtained by (B) one, (C) two, (D) four, and (E) six hydrothermal treatments of sample (A) at 200 °C for 3 days, respectively.

Hydrothermal Intercalation of $Ni(OH)_2$ into NaBir. NaBir shows different behavior from NiBir in the hydrothermal insertion reaction. Figure 5 shows the XRD patterns of the samples obtained by hydrothermal

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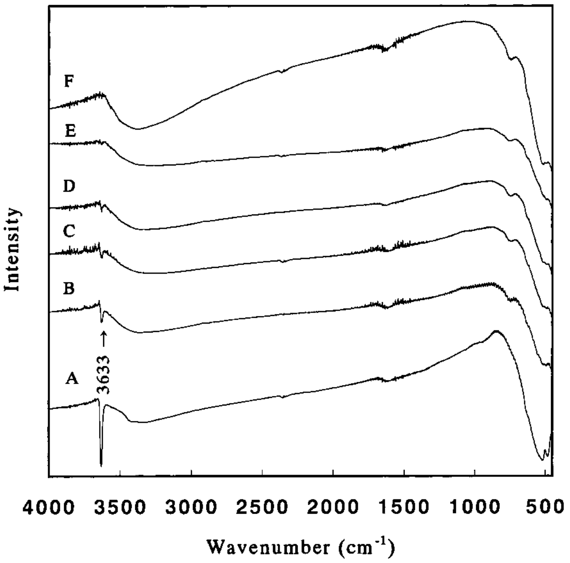

Figure 6. IR spectra of (A) Ni(OH)2−NaBir mixture with Ni/Mn =3 /8, and samples obtained by (B) one, (C) two, (D) three, (E) four, and (F) six times hydrothermal treatments of sample (A) at 200 °C for 3 days, respectively.

treatment of Ni(OH)$_2$−NaBir mixture with molar ratio of Ni/Mn = 3/8 at 200 °C. It is very easy to distinguish NaBir and Ni(OH)$_2$ before the hydrothermal reaction (Figure 5A). After the hydrothermal treatment in distilled water at 200 °C for 3 days, the intensities of diffraction peaks of Ni(OH)$_2$ and NaBir decreased, but product is a mixture of NaBir, Ni(OH)$_2$, and NMO. To prepare a pure NMO phase, the product was washed and hydrothermally treated in distilled water again. The hydrothermal treatment and washing of the product were repeated for several times to promote the Ni(OH)$_2$ insertion reaction. After four hydrothermal treatments, no more free Ni(OH)$_2$ can be detected by XRD analysis in the product (Figure 5D). However, a little amount of NaBir remained in the product, even after six hydrothermal treatments (Figure 5E).

The Ni(OH)$_2$ insertion reaction was also confirmed by IR study. The IR analysis is more sensible than XRD analysis in detection of the free Ni(OH)$_2$. The starting mixture shows the sharp vibration band of free Ni(OH)$_2$ at 3633 cm^{-1} (Figure 6A). The intensity of the vibration band decreases gradually with the increasing of the repeat times of the hydrothermal treatment, indicating that the amount of free Ni(OH)$_2$ decreases gradually (Figure 6). After six hydrothermal treatments, there was no free Ni(OH)$_2$ detectable by IR analysis, implying that Ni(OH)$_2$ was completely inserted into the layered compound.

It was also found that more times of repeating hydrothermal treatment were needed in order to insert more amount of Ni(OH)$_2$ into NaBir. When the molar ratio of Ni/Mn in the starting mixture increased to about 1/2, eleven repeated hydrothermal treatments were necessary to obtain the product without free Ni(OH)$_2$. The compositions of the two final products are listed in Table 1 (labeled as sample no.'s 7 and 8). The molar ratio of Na/Mn decreases with the increase of the molar ratio of Ni/Mn, indicating that the ion-exchange of Ni^{2+}/Na^{+} took place during the hydrothermal reaction.

Mechanism of Insertion of Ni(OH)$_2$ into the Birnessites. The dissolution−deposition reaction 4 of Ni(OH)$_2$ under hydrothermal conditions is important in the Ni(OH)$_2$ insertion reactions.

$$\mathrm{Ni(OH)_2} \rightarrow \mathrm{Ni^{2+}} + 2\mathrm{OH^-} \qquad (4)$$

The pH titration study suggests that the solubility of free Ni(OH)$_2$ is higher than that of Ni(OH)$_2$ in the interlayer space of the manganese oxide. This is the reason Ni(OH)$_2$ is preferentially formed in the interlayer space rather than as free Ni(OH)$_2$. The insertion reaction of Ni(OH)$_2$ into NiBir can be written as follows:

$$\mathrm{Ni_{0.14}MnO_2} + x\mathrm{Ni^{2+}} + 2x\mathrm{OH^-} \rightarrow \mathrm{Ni}_{x+0.14}(\mathrm{OH})_{2x}\mathrm{MnO_2} \qquad (5)$$

The reaction rate of reaction 4 and diffusion of Ni^{2+} and OH^{-} into the interlayer space of the birnessite in the reaction 5 are speeded up under the hydrothermal conditions, which promotes the formation reaction of NMO.

In the Ni(OH)$_2$−NaBir reaction system, the insertion reaction is more complex than that in the Ni(OH)$_2$−NiBir system. To understand the reaction, the pH values of the reaction solutions in the Ni(OH)$_2$−NaBir system were measured before and after each hydrothermal treatment. Before the first hydrothermal reaction, the pH value of the solution was about 9.5, while after the hydrothermal reaction, the pH value of the solution increased to about 11. In the following repeating process, the pH values of the solutions were within 8−9 before hydrothermal treatment and within 9−10 after hydrothermal treatment. The pH value of the hydrothermal reaction solution shows two main characteristics. One is that the pH value of the solution increases after hydrothermal reaction, and another is that the pH value of the solution after hydrothermal reaction decreases with the increase of the hydrothermal treatment times. These results can be explained by formation of OH^{-} and ion-exchange reaction of Ni^{2+}/Na^{+} during the hydrothermal treatment, and the hydrothermal reaction can be summarized as follows:

$$\begin{aligned}&\mathrm{Na_{0.32}MnO_2} + x\mathrm{Ni(OH)_2} \rightarrow\\ &\qquad \mathrm{Na}_y\mathrm{Ni}_x(\mathrm{OH})_{2x+y-0.32}\mathrm{MnO_2} + (0.32 - y)\mathrm{NaOH} \qquad (6)\end{aligned}$$

This formula includes both Ni(OH)$_2$ insertion reaction and Ni^{2+}/Na^{+} ion-exchange reaction. In fact, NMO was transformed to a mixture of NaBir and free Ni(OH)$_2$ when it was hydrothermally treated in 2M NaOH solution at 200 °C. This indicates that the reaction 6 is reversible, and the removal of formed NaOH from the reaction system will promote the Ni(OH)$_2$ insertion reaction 6. This fact indicates also that NMO has the mixed layered structure, but not the (3 × 3) tunnel structure. If the tunnel structure was formed, the reaction would not be a reversible.

Direct Synthesis of NMO in Ni(Ac)$_2$ Solution. It has been reported that Ni(OH)$_2$ can be formed by hydrothermal treatment of nickel acetate solution.[31] This suggests that NMO can be prepared by hydrothermal treatment of the birnessite in Ni(Ac)$_2$ solution. The

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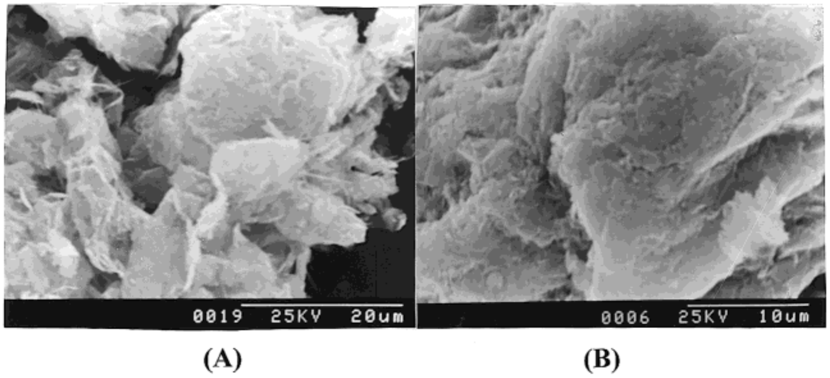
[31] Nishizawa, H.; Kishikawa, T.; Minami, H. In *Proceedings of the Joint Sixth International Symposium on Hydrothermal Reactions & Fourth International Conference on Solvent-Thermal Reactions*; 2000; p 92.



(A) (B)

Figure 7. SEM micrographs of microstructures of (A) NMO-2/7 and (B) NMO-1/2.

Table 2. The Reaction Conditions and Products in $Ni(Ac)_2$−NaBir Reaction System[a]

starting materials Mn:Ni (mol)	concentration of $Ni(Ac)_2$ (mol/L)	reaction temp (°C)	products
1:1	0.05	150	NMO
1:2	0.10	150	NMO
1:3	0.15	150	NMO
1:5	0.25	150	NMO + $Ni(OH)_2$
2:1	0.15	150	NMO
1:1	0.15	150	NMO$^{(1)}$
1:2	0.30	150	NMO + $Ni(OH)_2$$^{(2)}$
1:3	0.45	150	NMO + $Ni(OH)_2$
1:1	0.15	200	NMO + $Ni(OH)_2$
2:1	0.15	250	NMO + NiO

[a] Reaction time is 1 day. NMO = nickel hydroxide manganese oxide. (1) is sample Ac-A, and (2) is sample Ac-B in Table 1.

conditions of the hydrothermal reactions and products are listed in Table 2. The final products were dependent on the molar ratio of Ni/Mn in the reaction system, the concentration of $Ni(Ac)_2$, and reaction temperature. The high $Ni(Ac)_2$ concentration leads to the formation of free $Ni(OH)_2$. The formation of $Ni(OH)_2$ was also promoted by increasing the hydrothermal reaction temperature. Since $Ni(Ac)_2$ can be transformed to NiO over 250 °C, the temperature for the preparation of NMO should be controlled below 250 °C. The compositions of the two samples (no.'s 9 and 10) prepared by this method are listed in Table 1. Sample Ac-A (no. 9) with a molar ratio of Ni/Mn = 0.469 is a pure NMO phase, and sample Ac-B (no. 10) with a molar ratio of Ni/Mn = 0.552 contains a little free $Ni(OH)_2$. Similar to the $Ni(OH)_2$−NiBir system, the Ni content in NMO was also limited to the molar ratio of Ni/Mn = 1/2 for the $Ni(Ac)_2$−NaBir system.

Morphology of NMO. The SEM photographs for NMO-2/7 and NMO-1/2 are shown in Figure 7. All these samples have similar sheety crystal morphology as that of NaBir precursor.[32] This result suggests that the hydrothermal insertion of $Ni(OH)_2$ is a topotactic reaction, in which almost no dissolution−deposition of NaBir or NiBir occurs. The sheety crystal morphology also suggests that the $Ni(OH)_2$ inserted samples have a layered structure, rather than a tunnel structure, such as (3 × 3) tunnel structure of todorokite. The crystal with the tunnel structure usually shows fibrous crystal morphology.[30]

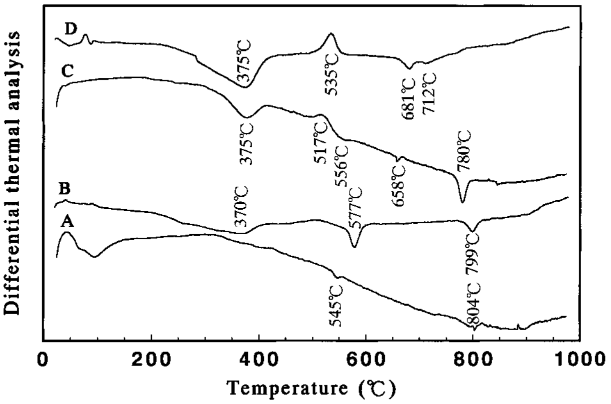


Figure 8. The DTA curves of (A) NiBir, (B) NMO-1/7, (C) NMO-3/8, and (D) NMO-1/2.

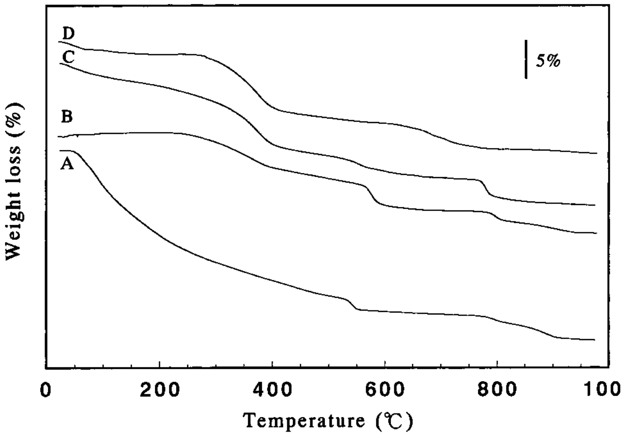


Figure 9. The TG curves of (A) NiBir, (B) NMO-1/7, (C) NMO-3/8, and (D) NMO-1/2.

Thermal Analysis. Thermal analyses (TG-DTA) were carried out on NiBir and NMO samples. The TG and DTA curves of NMO samples are different from those of NiBir (Figures 8 and 9). To well understand what happened at each temperature stage, the products of the samples heated at each temperature were investigated by XRD analysis, and the results are summarized in Table 3. On the basis of the XRD result, the weight loss of 19.7% between 50 and 500 °C in the TG curve of NiBir (Figure 9A) is attributed to the loss of surface adsorptive water and crystal water in the interlayer space. The weight loss of 2.9% between 500 and 700 °C with an endothermal peak at 546 °C in the DTA curve (Figure 8A) is ascribed to the formation of

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[32] Feng, Q.; Liu, L.; Yanagisawa, K. J. *Mater. Sci. Lett.* **2000**, *19*, 1567.

Table 3. The Products from the Samples Calcined at Various Temperatures

sample	250 °C	400 °C	540 °C	600 °C	680 °C	720 °C	800 °C	1000 °C
NiBir	NiBir	NiBir		γ-Mn_2O_3 $NiMnO_3$			γ-Mn_2O_3 $NiMn_2O_4$	$Ni_xMn_{2-x}O_4$
NMO-1/7	NMO	NMO	$NiMnO_3$		γ-Mn_2O_3 $NiMnO_3$ $NiMn_2O_4$	γ-Mn_2O_3 $NiMnO_3$ $NiMn_2O_4$		$Ni_xMn_{2-x}O_4$
NMO-3/8	NMO	NMO	$NiMnO_3$	γ-Mn_2O_3 $NiMnO_3$			γ-Mn_2O_3 $NiMn_2O_4$	$Ni_xMn_{2-x}O_4$
NMO-1/2	NMO	NMO	$NiMnO_3$		γ-Mn_2O_3 $NiMnO_3$ $NiMn_2O_4$	γ-Mn_2O_3 $NiMnO_3$ $NiMn_2O_4$		$NiMn_2O_4$

γ-Mn_2O_3 and the release of O_2. The weight loss of 1.4% between 750 and 850 °C with an endothermal peak at 804 °C is attributed to the formation of $NiMn_2O_4$ and the evolution of O_2. The weight loss of 2.0% with an endothermal peak at 880 °C is referred to the formation of $Ni_xMn_{2-x}O_4$ and the release of O_2.

Figure 10 shows the XRD patterns of NMO-1/2 after heating at different temperatures. The crystallinity of NMO-1/2 became low at 400 °C, and it was transformed to $NiMnO_3$ phase at 540 °C. At 680 °C, it was transformed to γ-Mn_2O_3 phase, $NiMnO_3$ phase, and $NiMn_2O_4$ spinel phases, and at 1000 °C, the product was in the $NiMn_2O_4$ spinel phase. In the TG and DTA curves for NMO-1/2 (Figures 8D and 9D), the weight loss below 250 °C is very small, and a large and sharp endothermal peak at 375 °C with a large and sharp weight loss between 250 and 500 °C was observed. This behavior is similar to that of lithiophorite with the mixed layered structure of $LiAl_2(OH)_6$−manganese oxide,[13] while different from todorokite, which shows a broad endothermal peak at around 300 °C with a continual weight loss from room temperature to 350 °C by dehydration of the crystal water in tunnel.[6] The endothermal peak at 375 °C can be attributed to dehydrations of $Ni(OH)_2$ in the mixed layered structure. An exothermal peak without weight loss was observed at 535 °C. It can be attributed to the transformation of the layered phase to $NiMnO_3$ phase. The TG-DTA results are also in agreement with the result that the NMO compounds have a mixed layered structure, rather than a tunnel structure.

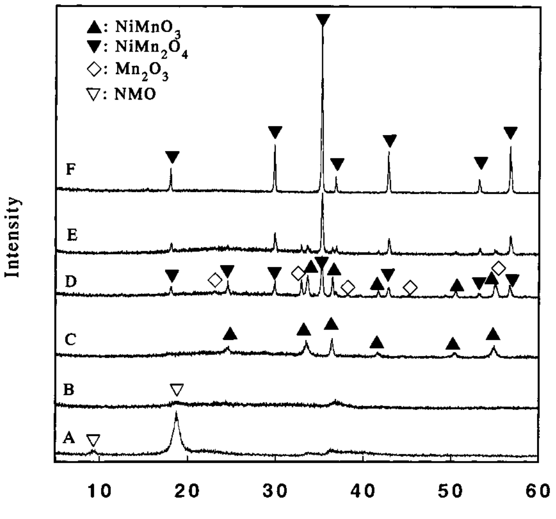

Figure 10. XRD patterns of (A) NMO-1/2, heat-treated NMO-1/2 at (B) 400 °C, (C) 540 °C, (D) 680 °C, (E) 720 °C, and (F) 1000 °C, respectively.

NMO-3/8 and NMO-1/7 also show a endothermal peak at 375 °C with a weight loss similar to NMO-1/2, which is attributed to dehydrations of $Ni(OH)_2$, and the weight loss decreases with decreasing the Ni content in the NMO samples (Figures 8 and 9). The intensity of exothermal peak around 535 °C, which corresponds to the transformation of the layered phase to $NiMnO_3$ phase, decreases with decrease of the Ni content in the NMO samples. An endothermal peak at around 570 °C with a weight loss was observed in NMO samples with low Ni content. This peak can be ascribed to the formation of γ-Mn_2O_3 and the release of O_2. The above results indicate that the NMO samples with different Ni content show similar TG-DTA behavior patterns below the temperature of 500 °C, while different behavior patterns occur over the temperature of 500 °C.

Conclusions

In the weak basic solution, $Ni(OH)_2$ is preferentially formed in the interlayer space of birnessite rather than as free $Ni(OH)_2$ from Ni^{2+} containing solution. The hydrothermal treatment is an useful method for the topotactic intercalation of $Ni(OH)_2$ into the layered manganese oxides. The intercalated product has a mixed layered $Ni(OH)_2$−manganese oxide structure. The amount of Ni inserted in the compound prepared by this method is limited in about Ni/Mn = 1/2. The amount of $Ni(OH)_2$ inserted in the compound is much less than the theoretical value, i.e., Ni/Mn = 1 mol; it is expected that there are some irregular lacunar sites in the $Ni(OH)_2$ layers.

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