Hydrothermal Soft Chemical Synthesis of $Ni(OH)_2$–Birnessite Sandwich Layered Compound and Layered $LiNi_{1/3}Mn_{2/3}O_2$

Qi Feng,*# Yaohua Xu,## Koji Kajiyoshi, and Kazumichi Yanagisawa
Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780-8520

(Received July 2, 2001; CL-010624)

A layered lithium nickel manganese oxide, $Li_1Ni_{1/3}Mn_{2/3}O_2$, has been hydrothermally prepared from a sandwich nickel manganese hydroxide–oxide precursor, $Ni_7Mn_{14}O_{27}(OH)_{10}\cdot nH_2O$, which has been hydrothermally synthesized at 200 °C by intercalating $Ni(OH)_2$ into layered birnessite. In this precursor, MnO_2 layer and $Ni(OH)_2$ layer alternately pack together to form sandwich-like layered structure. The compounds were characterized by XRD and IR spectrum.

Layered oxide $LiCoO_2$ has been commercially used as cathodic material in secondary lithium battery,[1] but it is well known that the cobalt is expensive and toxic.[2] To overcome this drawback, many attempts for searching new excellent substitutes have been made.[3] Among these potential materials, manganese oxides are most attractive materials due to the low expense and high average redox potential of manganese.[4–6] In particular, the layered $LiMnO_2$ in orthorhombic (*Pmnm*) or monoclinic (*C2/m*) phase, is a promising material because of its high discharge capacity (Li/Mn= 1).[7–9] However, the orthorhombic $LiMnO_2$, which is usually prepared by solid-state reaction method,[10] is partly transformed into Li–Mn–O spinel phase during charge–discharge process resulting in the decrease of the discharge capacity. The monoclinic $LiMnO_2$, which was synthesized by ion-exchange or hydrothermal reactions,[9,11,12] shows high discharge capacity and higher stability than the orthorhombic phase, but it is still partly transformed into the spinel phase after charge–discharge process. Recently, two types of layered lithium transition metal oxides O3- and T2-$Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ (O = octahedral, T = tetrahedral) have been reported, and the T2 phase exhibits a large reversible capacity of 180 mA·h/g during cycling.[13,14] These materials were prepared by Li^+/Na^+ ion-exchange from P3- and P2-$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ (P = prismatic), respectively, which have an in-plane ordering of transition metal in the transition metal layer.[14] To our knowledge, there is no report on the synthesis of $LiNi_{1/3}Mn_{2/3}O_2$. This maybe due to that such materials are not easy to be prepared by a normal method.

Recently, we have prepared a $LiAl_2(OH)_6$–birnessite sandwich layered compound from a Na-birnessite (NaBir, $Na_4Mn_{14}O_{27}\cdot 9H_2O$) with a layered structure by using both intercalation and hydrothermal reactions, which is named hydrothermal soft chemical process.[15] We think such sandwich layered compound would be a useful precursor for the soft chemical synthesis of lithium transition metal oxides, such as Li–M–Mn–O (M = Ni, Co, Fe, etc.) compounds. Here we report preparation of a $Ni(OH)_2$–birnessite sandwich compound from NaBir by hydrothermal soft chemical process, and hydrothermal synthesis of $LiNi_{1/3}Mn_{2/3}O_2$ using the sandwich compound as precursor.

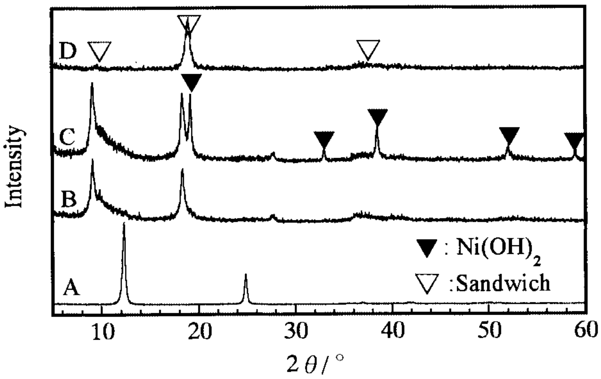

Figure 1. XRD patterns of the samples. (A) NaBir, (B) NiBir, (C) $Ni(OH)_2$+ NiBir, (D) Sample obtained by hydrothermal treatment of sample C (Ni/Mn = 1/2).

The $Ni(OH)_2$–birnessite sandwich layered compound was stepwise synthesized. The process is as follows. Firstly, NaBir was synthesized similarly as mentioned in the literature,[16] then Ni-birnessite (NiBir, $Ni_2Mn_{14}O_{27}\cdot nH_2O$) was prepared from NaBir by ion-exchange with $Ni(NO_3)_2$ solution (1 M). This NiBir (1.6 g) was mixed with a fresh $Ni(OH)_2$ (0.42 g), which resulted in the Ni/Mn molar ratio of the mixture corresponding to an ideal formula $Ni_7Mn_{14}O_{27}(OH)_{10}\cdot nH_2O$. The mixture with water (30 g) was put into a Teflon-lined autoclave, and heated at 200 °C for 3 days. Figure 1 shows the powder X-ray diffraction (XRD) patterns of the samples recorded on Rigaku RTP300 RC diffractometer with Cu Kα (λ = 1.5418 Å) radiation. The as-synthesized NaBir is a pure phase with a basal spacing of 7.2 Å (Figure 1A), which has layered structure with Na^+ and crystal water in the interlayer space.[15,17] NiBir remains the layered structure with a basal spacing of 9.7 Å after the ion-exchange (Figure 1B). Before the hydrothermal treatment, $Ni(OH)_2$ in the mixture of $Ni(OH)_2$ and NiBir is easy to be distinguished by XRD (Figure 1C). After the hydrothermal treatment, no $Ni(OH)_2$ can be detected in the product (Figure 1D), and the product is a pure phase with XRD profile similar to that of asbolane, a natural $Ni(OH)_2$–birnessite sandwich layered compound.[18] This result indicates that $Ni(OH)_2$ was intercalated into the interlayer space of NiBir under the hydrothermal conditions, and a sandwich-like compound was formed. In the compounds, $Ni(OH)_2$ layer and MnO_2 layer are alternately packed together, and the ideal formula is $Ni_7Mn_{14}O_{27}(OH)_{10}\cdot nH_2O$.

It has reported that NiBir can be transformed to todorokite with a (3 × 3) tunnel structure, or to both todorokite and asbolane by hydrothermal treatment in distilled water.[18–20] Since the todorokite and the asbolane show similar XRD patterns, it is difficult to confirm whether the product prepared here has a layered or a tunnel structure only from the XRD pattern. To clear this question, we prepared a $Ni(OH)_2$–birnessite

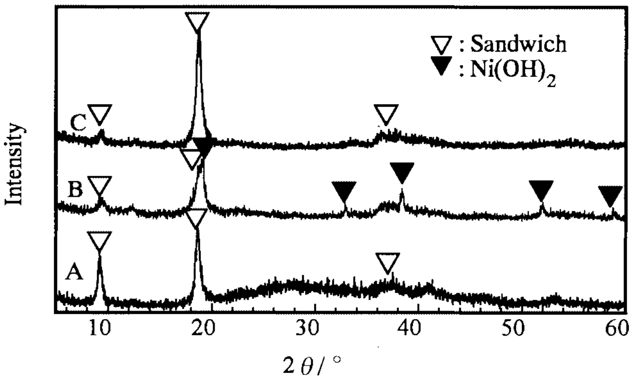

Figure 2. XRD patterns of (A) Sandwich compound (Ni/Mn = 1/7), (B) mixture of sample A and Ni(OH)$_2$, (C) hydrothermal reaction product of mixture B.

compound with less Ni(OH)$_2$ content (Ni/Mn = 1/7 in molar ratio) (Figure 2A) by the hydrothermal treatment of NiBir at 200 °C. Then this Ni(OH)$_2$–birnessite was mixed with Ni(OH)$_2$ and hydrothermally treated in distilled water at 200 °C. The final product is a pure phase with Ni/Mn = 2/7 in molar ratio (Figure 2C), implying that Ni(OH)$_2$ can be intercalated into the Ni(OH)$_2$–birnessite (Ni/Mn = 1/7 in molar ratio) compound. This result suggests that the Ni(OH)$_2$–birnessite sample would be a layered compound rather than a tunnel compound. If the compound was a tunnel compound, it would be difficult to intercalate further Ni(OH)$_2$, because there is no more space in the tunnel structure for accommodating more Ni(OH)$_2$. The Ni(OH)$_2$ intercalation can be also confirmed by IR, TG–DTA, and SEM analyses (no shown).

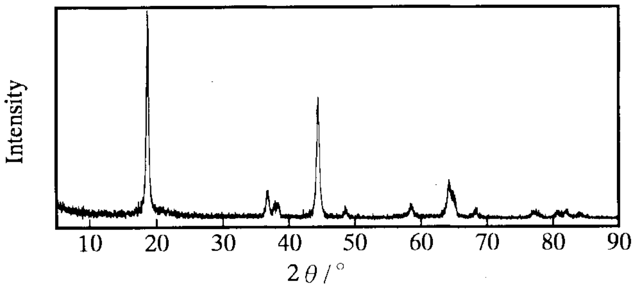

Figure 3. The XRD pattern of LiNi$_{1/3}$Mn$_{2/3}$O$_2$.

The Ni(OH)$_2$–birnessite sandwich layered compound can be used as a precursor for synthesis of LiNi$_{1/3}$Mn$_{2/3}$O$_2$. Figure 3 shows XRD pattern of a product obtained by hydrothermal treatment of Ni(OH)$_2$–birnessite sandwich layered compound with Ni/Mn = 0.5 in a LiOH solution with LiOH·H$_2$O/H$_2$O = 1/2 in mass ratio at 200 °C for 3 days. The XRD profile corresponds to O3-Li$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ with a layered hexagonal structure.[14] A chemical composition analysis indicates the LiNi$_{1/3}$Mn$_{2/3}$O$_2$ product with molar ratios of Li/Mn = 1.4 and Ni/Mn = 0.47. Above facts reveal that Ni(OH)$_2$–birnessite sandwich compound is easily transformed to O3-LiNi$_{1/3}$Mn$_{2/3}$O$_2$ layered compound under the hydrothermal conditions in LiOH solution. The interlayer space of the sandwich compound presents a pathway for Li$^+$ diffusion into the bulk crystal in the transformation reaction. Furthermore, a series of layered Li–Ni–Mn–O compounds can be prepared by adjusting Ni content and Ni valence in the sandwich layered precursor. More detailed discussion about this will be published elsewhere.

References and Notes

[#] Present address: Department of Advanced Materials Science, Faculty of Engineering, Kagawa University, 2217-20 Hayashi-cho, Takamatsu 761-0396, Japan. e-mail: feng@eng.kagawa-u.ac.jp.
[##] Permanent Address: Department of Chemistry, Jilin University, Changchun 130023, P. R. China.
1 Sony lithium ion battery performance summary, *JEC Batt. Newsletter*, **2**, 31 (1994).
2 P. Arora, B. V. Popov, and R. E. White, *J. Electrochem. Soc.* **145**(3), 807 (1998).
3 R. Koksbang, J. Barker, H. Shi, and M. Y. Saidi, *Solid State Ionics*, **84**, 1 (1996).
4 F. Leroux and L. F. Nazar, *Solid State Ionics*, **100**, 103 (1997).
5 J. Kim and A. Manthiram, *Nature*, **390**(20), 265 (1997).
6 M. M. Thackeray, W. I. F. David, P. G. Bruce, and J. B. Goodenough, *Mater. Res. Bull.*, **18**, 461 (1983).
7 M. M. Thackeray, *J. Electrochem. Soc.*, **142**, 2558 (1995).
8 F. Leroux, D. Guyomard, and Y. Piffard, *Solid State Ionics*, **80**, 307 (1995).
9 A. R. Armstrong and P. G. Bruce, *Nature*, **381**, 499 (1996).
10 W. D. Johnston and R. R. Heike, *J. Am. Chem. Soc.*, **78**, 3255 (1956).
11 F. Capitaine, P. Graverau, and C. Delmas, *Solid State Ionics*, **89**, 197 (1996).
12 M. Tabuchi, K. Ado, H. Kobayashi, H. Kageyama, C. Masquelier, A. Kondo, and R. Kanno, *J. Electrochem. Soc.*, **145**, L49 (1998).
13 J. M. Paulsen, C. L. Thomas, and J. R. Dahn, *J. Electrochem. Soc.*, **147**, 861 (2000).
14 Z. Lu, R. A. Donaberger, and J. R. Dahn, *Chem. Mater.*, **12**, 3583 (2000).
15 Q. Feng, C. Honbu, K. Yanagisawa, and N. Yamasaki, *Chem. Mater.*, **11**, 2444 (1999).
16 Q. Feng, H. Kanoh, Y. Miyai, and K. Ooi, *Chem. Mater.*, **7**, 1722 (1995).
17 Q. Feng, H. Kanoh, and K. Ooi, *J. Mater. Chem.*, **9**, 319 (1999).
18 S. Turner and P. Buseck, *Science*, **212**, 1024 (1981).
19 D. C. Golden, C. C. Chen, and J. B. Dixon, *Science*, **1986**, **231**, 717 (1986). D. C. Golden, C. C. Chen, and J. B. Dixon, *Clays Clay Miner.*, **35**(4), 271 (1987).
20 Y.-F. Shen, S. L. Suib, and C.-L. O'Young, *J. Am. Chem. Soc.*, **116**, 11020 (1994).