Layered Lithium Insertion Material of $LiNi_{1/2}Mn_{1/2}O_2$: A Possible Alternative to $LiCoO_2$ for Advanced Lithium-Ion Batteries

Tsutomu Ohzuku* and Yoshinari Makimura
Department of Applied Chemistry, Graduate School of Engineering, Osaka City University (OCU), Osaka 558-8585

(Received May 7, 2001 ; CL-010410)

We have successfully prepared a layered nickel manganese oxide of $LiNi_{1/2}Mn_{1/2}O_2$ (a = 2.89 Å and c = 14.30 Å in hexagonal setting) and shown that this material may be a possible alternative to $LiCoO_2$ for advanced lithium batteries in terms of the operating voltage, rechargeable capacity, cycleability, safety, and materials economy.

Effective use of titanium, manganese, or iron is a key to develop materials science for advanced lithium batteries. Orthorhombic $LiMnO_2$[1,2] can be applied for this purpose, but the orthorhombic phase converted to a spinel-related phase during charge and discharge in nonaqueous lithium cells. Consequently, the voltage profile in discharge curves shows a two-step reaction at about 4 and 3 V while the rechargeable capacity is more than 150 mAh g^{-1}. Dahn et al.[3] have reported layered manganese oxides that do not convert to spinel. They prepared an interesting sample by ion-exchange technique to give so-called O2 stacking of oxygen ions. The voltage profile, however, is almost the same as that of orthorhombic $LiMnO_2$ in terms of operating voltage and its profile. Ammundsen et al.[4] have reported Al or Cr-doped monoclinic $LiMnO_2$ which showed sloping discharge curves from 4 to 2.5 V with rechargeable capacity of more than 150 mAh g^{-1}. Meanwhile $LiNiO_2$, iso-structural with $LiCoO_2$, has been of great interest as a possible alternative to $LiCoO_2$ because of high rechargeable capacity (more than 150 mAh g^{-1}) with moderately high operating voltage.[5] However, it cannot be used in its current form for several reasons, mainly safety issue and the rigorous limitation on the charge-end voltage.[6] $LiNiO_2$ is stable, but $LiMnO_2$ is not stable as the layered structure, i.e., Li_2MnO_3 ($Li[Li_{1/3}Mn_{2/3}]O_2$ in a layered formulation) or $Li[Li_xMn_{2-x}]O_4$ having a spinel-framework structure is stable. Therefore, we have intended to adjust structural and chemical mismatch among lithium insertion materials with different chemical species. After several trials we have coped with this problem as will be reported hereafter. In this paper we report well-crystallized $LiNi_{1/2}Mn_{1/2}O_2$ which is a one-to-one mixture of $LiNiO_2$ and $LiMnO_2$ in a solid state and its electrochemical reactivity in nonaqueous lithium cells.

$LiNi_{1/2}Mn_{1/2}O_2$ was prepared from $LiOH{\cdot}H_2O$ and a nickel manganese double hydroxide (MX-004-1, Ni : Mn = 1.02 : 0.98 in molar ratio) obtained from Tanaka Chemical Corp., Ltd. Spherical morphology of the particle agglomerates is characteristic for MX-004-1. The reaction mixture was pressed into pellets (23 mm diam and ca. 5 mm thick.) and heated at several temperatures with varying reaction time in air. The reaction product was ground into powder using a mortar and pestle, and stored in a desiccator before use. The samples were characterized by X-ray diffraction (XRD) using an X-ray diffractometer (XD-3A, Shimadzu Corp., Japan) with a diffracted graphite monochromator with copper Kα radiation.

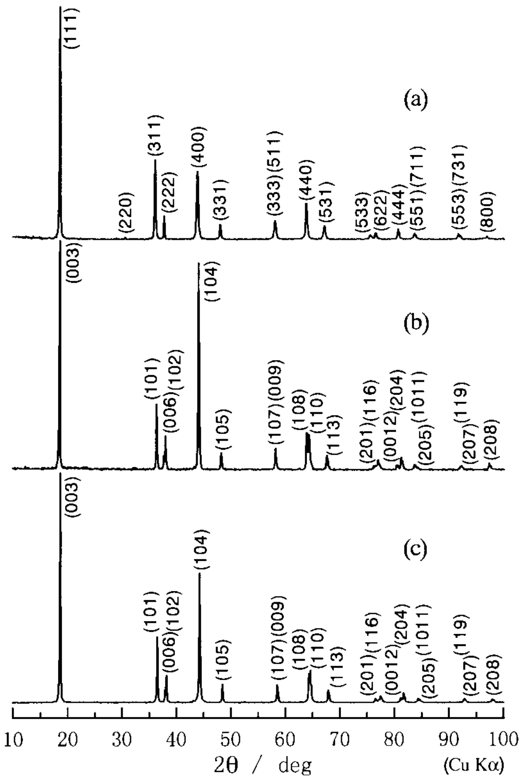

Figure 1. XRD patterns of (a) $LiMn_2O_4$ ($Fd\bar{3}m$: a = 8.24$\underline{2}$ Å), (b) $LiNi_{1/2}Mn_{1/2}O_2$ (a = 2.89$\underline{2}$ Å, c = 14.30$\underline{1}$ Å in hexagonal setting), and (c) $LiNiO_2$ ($R\bar{3}m$: a = 2.88$\underline{5}$ Å, c = 14.19$\underline{7}$ Å in hexagonal setting).

Well-crystallized $LiNi_{1/2}Mn_{1/2}O_2$ is prepared by heating the reaction mixture typically at 1000 °C in air for 15 h. Chemical analysis of the sample prepared at 1000 °C indicated that a target composition of $LiNi_{1/2}Mn_{1/2}O_2$ was correctly prepared even at high temperature synthesis of lithium insertion materials, i.e., $Li_{1.01}Ni_{0.51}Mn_{0.49}O_{2.01}$. Figure 1 shows the XRD pattern of thus prepared $LiNi_{1/2}Mn_{1/2}O_2$ together with those of $LiMn_2O_4$($Fd\bar{3}m$) and $LiNiO_2$($R\bar{3}m$). The samples prepared at temperatures below 800 °C do not give good results in terms of XRD and electrochemical reactivity. As seen in Figure 1(b), all diffraction lines can be indexed by assuming a hexagonal lattice, indicating a single phase of $LiNi_{1/2}Mn_{1/2}O_2$. Lattice constant of $LiNi_{1/2}Mn_{1/2}O_2$ was determined to be a = 2.89$\underline{2}$ Å and c = 14.30$\underline{1}$ Å in hexagonal setting by a least squares method using 15 diffraction lines. The c-axis dimension is the largest value among the layered $LiMeO_2$ (Me : transition metal ions) as far as we know[7]. Although the XRD pattern of $LiNi_{1/2}Mn_{1/2}O_2$ is related closely to $LiNiO_2$ having

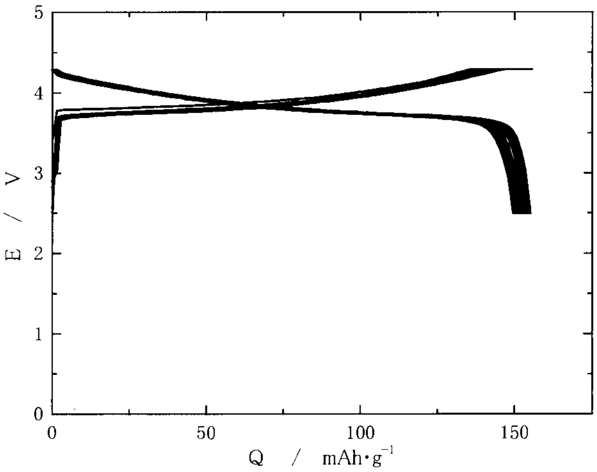

Figure 2. Charge and discharge curves of a Li / $LiNi_{1/2}Mn_{1/2}O_2$ cell operated at a rate of 0.1 mA cm^{-2} in voltages of 2.5 – 4.3 V for 30 cycles. The electrolyte used was 1M $LiPF_6$ dissolved in EC / DMC (3/7 by volume). The electrode mix consisted of 88 wt% $LiNi_{1/2}Mn_{1/2}O_2$, 6 wt% acetylene black, and 6 wt% PVDF.

a layer structure, not to $LiMn_2O_4$ having a spinel-framework structure, we cannot specifically illustrate the crystal structure of $LiNi_{1/2}Mn_{1/2}O_2$ at present. The integrated intensity ratio of (003) to (104), $I_{(003)}$ / $I_{(104)}$, is 0.84 for $LiNi_{1/2}Mn_{1/2}O_2$ while 1.35 for battery-active $LiNiO_2$. Since the value of $I_{(003)}$ / $I_{(104)}$ depended on the degree of the displacement between ions located at the 3(a) and 3(b) sites in a space group of ($R\bar{3}m$), this value was a measure to estimate reactivity of lithium insertion materials for a series of $LiNiO_2$ families. A low value of $I_{(003)}$ / $I_{(104)}$ was normally indicative of poor electrochemical reactivity due to high concentration of inactive rock-salt domains in a layered solid matrix, and consequently the (108) and (110) lines for a hexagonal lattice were usually merged to the (440) line for a cubic lattice, but this is not the case for $LiNi_{1/2}Mn_{1/2}O_2$.

In order to examine electrochemical reactivity and stability in a high voltage region, a Li / $LiNi_{1/2}Mn_{1/2}O_2$ cell was charged at 0.1 mA cm^{-2} to 4.3 V and then held at a voltage of 4.30 V for 15 h, so-called a CCCV-charging mode. After charging, the cell was discharged at 0.1 mA cm^{-2} to 2.5 V, and the operation was repeated for 30 cycles. Results are shown in Figure 2. $LiNi_{1/2}Mn_{1/2}O_2$ shows the rechargeable capacity of 150 mAh g^{-1} even under such a severe operating condition, i.e., constant-voltage charge at 4.30 V with low-rate charge and discharge at 0.1 mA cm^{-2}. Figures 1 and 2 clearly show that the structural and electrochemical properties of $LiNi_{1/2}Mn_{1/2}O_2$ are different from those of $LiNiO_2$($R\bar{3}m$),[5] $LiCo_xNi_{1-x}O_2$($R\bar{3}m$),[8] $Li[Li_xMn_{2-x}]O_4$($Fd\bar{3}m$), monoclinic $LiMnO_2$,[4] or Dahn's O2–lithium manganese oxides[3] with respect to operating voltage, voltage profile, rechargeable capacity, stability at high voltage, and structural property.

Figure 3 shows the charge and discharge curves of a Li / $LiNi_{1/2}Mn_{1/2}O_2$ cell compared with those of a Li / $LiCoO_2$ cell. $LiCoO_2$ is widely used as a positive-electrode material and its cell performance is good if the negative-electrode material is properly selected. Preliminary test results on the DSC measurements for partially or fully charged $LiNi_{1/2}Mn_{1/2}O_2$ with the electrolyte indicate that exothermic reaction leading to thermal runaway is milder than that of $LiCoO_2$. The dilatometric examinations for dimensional change of electrode assembles also suggest that $LiNi_{1/2}Mn_{1/2}O_2$ is seemingly well fit in with graphite-negative electrodes. This may cover the voltage disadvantage compared with $LiCoO_2$ in Figure 3 due to a characteristic lithium-ion technology.

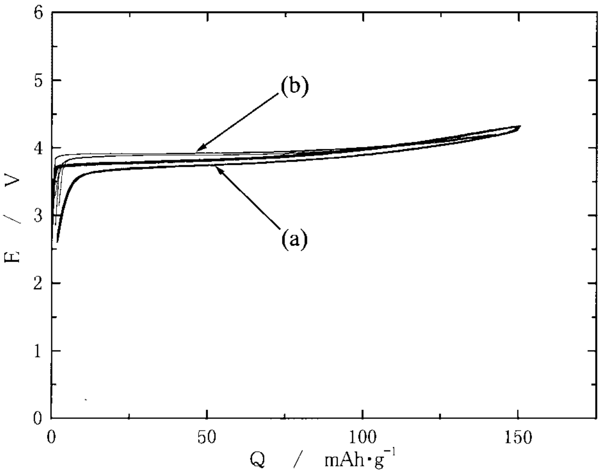

Figure 3. Charge and discharge curves of (a) Li / $LiNi_{1/2}Mn_{1/2}O_2$ and (b) Li / $LiCoO_2$ cells operated at a rate of 0.17 mA cm^{-2} at 30 °C.

In summary, a layered lithium insertion material of $LiNi_{1/2}Mn_{1/2}O_2$ (a = 2.89 Å and c = 14.30 Å in hexagonal setting) can be used as a possible alternative to $LiCoO_2$ in response to an expanding need for the advanced lithium-ion batteries. The combination of nickel and manganese may give an advantage in terms of materials economy. A structural refinement of $LiNi_{1/2}Mn_{1/2}O_2$ together with the optimization of synthetic processes is now in progress in our laboratory.

The authors wish to thank Mr. Hiroyuki Ito of Tanaka Chemical Corp. for his help on the preparation of a series of nickel manganese hydroxides and also to Dr. Keijiro Sawai of OCU for his help in preparing the manuscript. This work is supported in part by a grant-in-aid for scientific research from Osaka City University Science Foundation.

References

1 T. Ohzuku, A. Ueda, and T. Hirai, *Chemistry Express*, **7**, 193 (1992).
2 I. Koetschau, M. N. Richard, J. R. Dahn, J. B. Soupart, and J. C. Rousche, *J. Electrochem. Soc.*, **142**, 2906 (1995).
3 J. M. Paulsen, C. L. Thomas, and J. R. Dahn, *J. Electrochem. Soc.*, **147**, 861 (2000).
4 B. Ammundsen, J. Desilvestro, R. Steiner, and P. Pickering, the 10th International Meeting on Lithium Batteries, Como, May 2000, Abstr., No. 17.
5 T. Ohzuku, A. Ueda, and M. Nagayama, *J. Electrochem. Soc.*, **140**, 1862 (1993).
6 T. Ohzuku, A. Ueda, and M. Kouguchi, *J. Electrochem. Soc.*, **142**, 4033 (1995).
7 T. Ohzuku and A. Ueda, *Solid State Ionics*, **56**, 201 (1994).
8 T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakoshi, and H. Komori, *Electrochim. Acta*, **38**, 1159 (1993).