Layered Lithium Insertion Material of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ for Lithium-Ion Batteries

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

(Received April 27, 2001; CL-010390)

Layered $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ was prepared by a solid state reaction at 1000 °C in air and examined in nonaqueous lithium cells. $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ showed a rechargeable capacity of 150 mAh g^{-1} in 3.5–4.2 V or 200 mAh g^{-1} in 3.5–5.0 V. Operating voltage of Li / $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ was by 0.2–0.25 V lower than that of a cell with $LiCoO_2$ or $LiMn_2O_4$ and by 0.15–0.3 V higher than that with $LiNiO_2$ or $LiCo_{1/2}Ni_{1/2}O_2$ due to a complex solid solution mechanism.

Over the past 10 years, there has been a growing interest in lithium insertion materials, largely because they potentially have a wide range of application for positive and/or negative electrodes in lithium-ion batteries. Many researchers including ourselves are going on to find new materials for advanced lithium batteries, as well as to get deeper understanding of insertion scheme. Lithium insertion materials, such as $LiCo_xNi_{1-x}O_2$($R\bar{3}m$) ($0 \le x \le 1$),[1–3] $Li[Li_xMn_{2-x}]O_4$($Fd\bar{3}m$) ($0 \le x \le 1/3$),[4–7] $Li[Li_{1/3}Ti_{5/3}]O_4$ ($Fd\bar{3}m$),[8] and so forth, are well known and some of them have already been used in the practical lithium-ion batteries. However, we need new materials to cover an expanding need for advanced batteries, so that a series of trials has been done to find strategy of material design on lithium insertion materials.

When we selected a model crystal of α-$NaFeO_2$ (space group $R\bar{3}m$) which is isostructural with $LiCoO_2$, $LiNiO_2$, or $LiCrO_2$ and we put three different transition metal elements into lattice sites to form [$\sqrt{3} \times \sqrt{3}$]R30° superlattice in a Wood notation for a basic net consisting of the 3(a) sites in a space group $R\bar{3}m$, we can expect layered materials which may show a new function in term of lithium insertion scheme. We examined possible combinations among the 3d-transition metal elements. After several trials we have succeeded to prepare $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ which is one of the target materials. In this paper, we report the synthesis of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ and its electrochemical reactivity in nonaqueous lithium cells.

$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ was prepared from $LiOH \cdot H_2O$, $CoCO_3$, and a nickel manganese hydroxide (MX-004-1, Ni : Mn = 1.02 : 0.98, 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 1000 °C for 15 h in air. The reaction product was ground into powders using a mortar and pestle, and stored in a desiccator over blue silica-gel before use. The samples were characterized by X-ray diffraction (XRD) using an X-ray diffractometer (XD-3A, Shimadzu Corp., Japan) with copper Kα radiation. The system was equipped with a diffracted graphite monochromator. Figure 1(b) shows the XRD pattern of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$. $LiCo_{1/2}Ni_{1/2}O_2$ and $LiMn_2O_4$ are also shown for comparison. As can be seen in Figure 1(b), a single phase of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ is obtained. The XRD pattern of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ is quite similar to that of $LiCo_{1/2}Ni_{1/2}O_2$

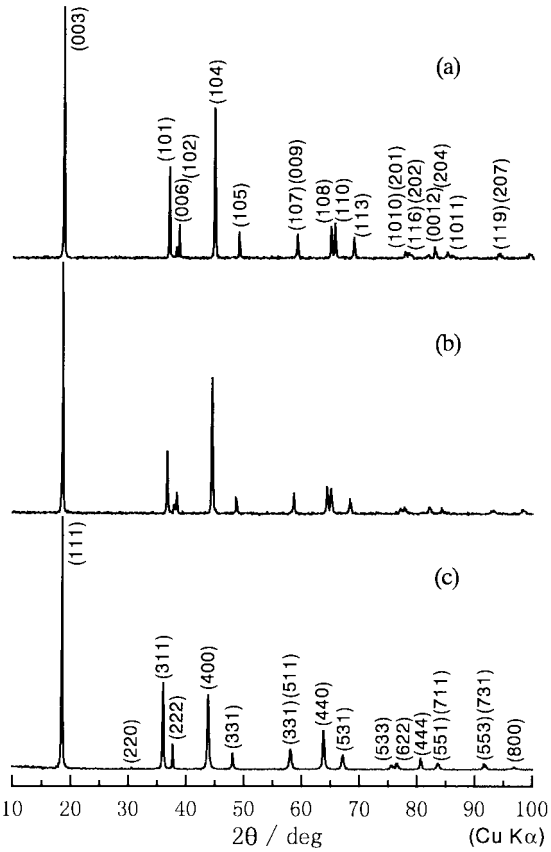

Figure 1. XRD patterns of (a) $LiCo_{1/2}Ni_{1/2}O_2$ ($R\bar{3}m$: a = 2.845 Å, c = 14.123 Å in hexagonal setting), (b) $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ (a = 2.867 Å, c = 14.246 Å in hexagonal setting), and (c) $LiMn_2O_4$($Fd\bar{3}m$: a = 8.242 Å).

($R\bar{3}m$) having a layer structure, not to that of $LiMn_2O_4$ ($Fd\bar{3}m$) having a spinel-framework structure. Lattice constant of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ is determined to be a = 2.867 Å and c = 14.246 Å in hexagonal setting by a least squares method using 15 diffraction lines.

Figure 2 shows the charge and discharge curves of a Li / $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cell from the 1st to 15th cycle for a cell operated at 0.17 mA cm^{-2} in voltages between 2.5 and 4.2 V. Electrochemical cells and data acquisition systems were the same as those described previously.[9] In preparing the electrode, polyvinylidene fluoride (PVdF) dissolved in *N*-methyl-2-pyrrolidone (NMP) solution was used as a binder. A black viscous slurry consisting of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, acetylene black, and PVdF was cast on an aluminum foil (15 × 20 mm^2) with blade. The composition of the electrode mix was 88 weight percent (wt%) $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, 6 wt% acetylene black, and

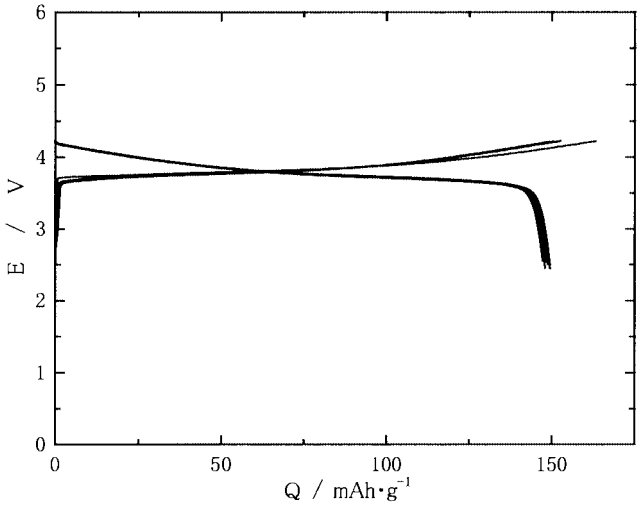

Figure 2. Charge and discharge curves of a Li / $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cell operated at a rate of 0.17 mA cm^{-2} in voltages between 2.5 and 4.2 V at 30 °C. The electrolyte used was 1M $LiPF_6$ dissolved in EC / DMC (3/7 by volume). Electrode consisted of 88 wt% $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, 6 wt% acetylene black, and 6 wt% PVdF.

6 wt% PVdF. The electrode was dried under vacuum at 150 °C for 12 h. A lithium electrode was prepared by pressing a lithium metal sheet onto a stainless steel plate (15×20 mm^2). Two sheets of porous polypropylene membrane (Celgard 2500) were used as a separator. The electrolyte used was 1M $LiPF_6$ dissolved in ethylene carbonate (EC) / dimethyl carbonate (DMC) (3/7 by volume) solution. Open-circuit voltages of the freshly fabricated cells were around 3.2 V. During charge at 0.17 mA cm^{-2}, the cell voltage rapidly increased to 3.7 V and then stayed at 3.7–3.75 V until the charge capacity reaches about 80 mAh g^{-1}. On further charging, the voltage increased monotonously to 4.2 V of charge-end voltage. The first charge capacity was ca. 165 mAh g^{-1} based on $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ sample weight, while the first discharge capacity was ca. 150 mAh g^{-1}. Irreversible capacity was ca. 15 mAh g^{-1} in this case. For subsequent cycles, the curves converged on a single charge or discharge curve, as seen in Figure 2. The rechargeable capacity was 150 mAh g^{-1} when the cell was operated in 2.5–4.2 V.

Figure 3 shows the charge and discharge curves of a Li / $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cell operated at 0.17 mA cm^{-2} in voltages between 2.5 and 5.0 V. The first charge capacity at 5.0 V of charge-end voltage was ca. 250 mAh g^{-1} and the first discharge capacity was ca. 220 mAh g^{-1}. Although a loss in capacity during charge and discharge was observed mainly due to electrolyte oxidation occurring in higher voltages than 4.5 V, rechargeable capacity more than 200 mAh g^{-1} was obtained with little capacity fading. As reported previously,[3,10,11] $LiCoO_2$ or $LiNiO_2$ was rapidly deteriorated when the sample was charged to higher voltages than 4.5 V against a lithium electrode. As shown in Figure 3, a Li / $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cell shows a better capacity retention than those of $LiCoO_2$ or $LiNi_{1/2}Co_{1/2}O_2$ in that voltage range. We believe that $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ with rechargeable capacity of 200 mAh g^{-1} will be used in lithium-ion batteries.

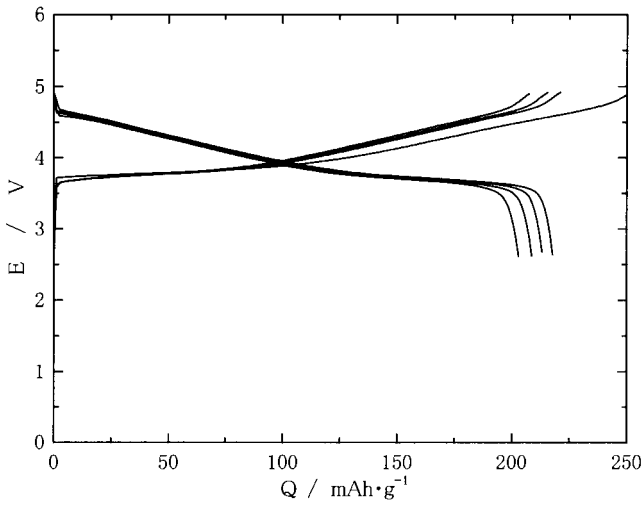

Figure 3. Charge and discharge curves of a Li / $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cell operated at a rate of 0.17 mA cm^{-2} in voltages between 2.5 and 5.0 V at 30 °C.

In conclusion $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ is a possible alternative to $LiCoO_2$ for lithium-ion batteries. In this letter we did not state the crystal structure of this sample. Its structure is close to $LiCoO_2$ or $LiNiO_2$, but something bothers us about a nature of complex solid solution mechanism. Structural refinements together with the optimization of synthetic processes are 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. This work is supported in part by a grant-in-aid for scientific research from Osaka City University Science Foundation.

References

1 K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, *Mater. Res. Bull.*, **25**, 783 (1980).
2 J. R. Dahn, U. von Sacken, and C. A. Michal, *Solid State Ionics*, **44**, 87 (1990).
3 T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakoshi, and H. Komori, *Electrochim. Acta*, **38**, 1159 (1993) and references therein.
4 J. C. Hunter, *J. Solid State Chem.*, **39**, 142 (1981).
5 M. M. Thackeray, W. I. F. David, P. G. Bruce, and J. B. Goodenough, *Mater. Res. Bull.*, **18**, 461 (1983).
6 T. Ohzuku, K. Sawai, and T. Hirai, *J. Electrochem. Soc.*, **137**, 3004 (1990).
7 T. Ohzuku, S. Kitano, M. Iwanaga, H. Matsuno, and A. Ueda, *J. Power Sources*, **68**, 646 (1997).
8 T. Ohzuku, A. Ueda, and N. Yamamoto, *J. Electrochem. Soc.*, **142**, 1431 (1995).
9 T. Ohzuku, K. Nakura, and T. Aoki, *Electrochim. Acta*, **45**, 151 (1999).
10 T. Ohzuku, A. Ueda, and M. Nagayama, *J. Electrochem. Soc.*, **140**, 1862 (1993).
11 T. Ohzuku and A. Ueda, *J. Electrochem. Soc.*, **141**, 2972 (1994).