A 3-Volt Lithium-Ion Cell with $Li[Ni_{1/2}Mn_{3/2}]O_4$ and $Li[Li_{1/3}Ti_{5/3}]O_4$: A Method to Prepare Stable Positive-Electrode Material of Highly Crystallized $Li[Ni_{1/2}Mn_{3/2}]O_4$

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

(Received August 29, 2001 ; CL-010846)

$Li[Ni_{1/2}Mn_{3/2}]O_4$ having a spinel-framework structure was prepared by a two-step solid state reaction, i.e., crystallization at 1000 °C followed by an oxidation at 700 °C in air, and examined in nonaqueous lithium cells. Thus prepared $Li[Ni_{1/2}Mn_{3/2}]O_4$ showed low polarization and stability against electrolyte oxidation with rechargeable capacity of about 110–130 mAh/g at 4.7 V with 10–30 mAh/g at 4.0 V vs Li. Capacity in region of ca. 4.0 V vs Li, which was usually observed for the samples prepared by the conventional method, can be minimized by the oxidation process at 700 °C. A 3-volt lithium-ion battery with two insertion materials based on lithiated transition metal oxides having spinel-framework structures is demonstrated therefrom.

Since 1994 lithium-ion cells become very popular as a power source for wireless telephones and other electronic devices. In lithium-ion cells carbon materials are normally used as negative electrodes because of relatively high volumetric capacity and low operating voltage compared with a metallic lithium electrode. Carbon materials on a copper current feeder, however, tend to decompose electrolyte and have a chance to deposit metallic lithium. Degree of expansion or shrinkage in volume is another problem for the current lithium-ion cells in terms of reliability and cycle life. At present the most reliable negative-electrode material is a so-called zero-strain insertion material of $Li[Li_{1/3}Ti_{5/3}]O_4$[1] or $Li[CrTi]O_4$[2] with which we can dramatically improve cycle life of lithium-ion battery. However, operating voltage of $Li[Li_{1/3}Ti_{5/3}]O_4$ is 1.55 V vs Li, so that the combination with the conventional lithium insertion materials, such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ and so-forth, only gives the operating voltages of 2.0–2.5 V. This is degeneration or draw-back in lithium battery history even if the cells show excellent cycle life. Therefore, we need to explore the 5-volt lithium insertion materials in order to keep the operating voltage comparable at least to the primary Li/MnO_2 cells for camera. Among possible candidate materials we have selected $Li[Ni_{1/2}Mn_{3/2}]O_4$. After improving the processing method to prepare $Li[Ni_{1/2}Mn_{3/2}]O_4$ we have successfully demonstrated a 3-volt lithium-ion cell without carbon negative electrode. In this paper we report its core structure of the results.

Figure 1 shows a thermogravimetric (TG) curve of $Li[Ni_{1/2}Mn_{3/2}]O_4$ ($Fd\bar{3}m$: a = 8.17 Å) prepared at 700 °C by a method reported by Dahn et al.[3] except a starting material as will be described later. The sample weight decreased from 25.50 to 23.93 mg in a temperature range of 600 to 1000 °C on heating, and increased reversibly from 23.93 to 25.34 mg on cooling from 1000 to 600 °C. Such a reversible change in weight remind us a case for $LiMn_2O_4$, which is associated with oxygen loss and gain together with crystallization of $LiMn_2O_4$ forming octahedral morphology with nonporous body in their primary particles.[4,5] To examine whether or not $Li[Ni_{1/2}Mn_{3/2}]O_4$ is crystallized at 1000 °C and oxidized at 700 °C, the samples were carefully prepared under the conditions described below. Our starting material is nickel manganese double hydroxide (MX-003-2, Ni:Mn = 1.01:2.99 in molar ratio, obtained from Tanaka Chemical Corp. Ltd.). A reaction mixture with lithium hydroxide was pressed into pellets (23-mm diam and ca. 5-mm thick), heated at a rate of ca. 7.5 °C/min to 1000 °C and then reacted for 12 h in air. One sample was cooled down directly to room temperature at ca. 4.5 °C/min in air, and another was subsequently heated at 700 °C for 24 h and then cooled down to room temperature at the same cooling rate as described above. The samples were characterized by XRD using an X-ray diffractometer (Type XD-3A, Shimadzu

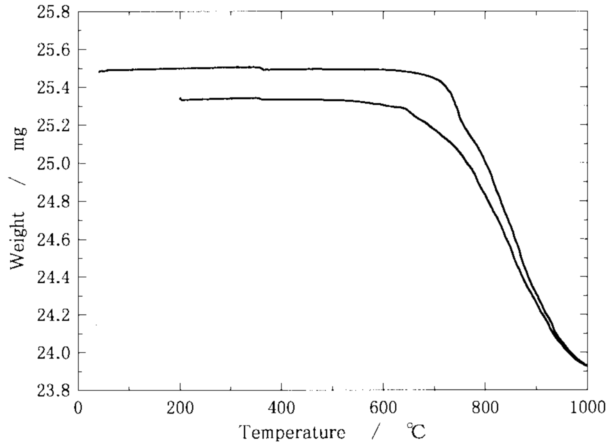

Figure 1. The thermogravimetric curve of $Li[Ni_{1/2}Mn_{3/2}]O_4$ prepared at 700 °C. The temperature was scanned at a rate of 5 °C/min under an air flow at 10 cm^3/min.

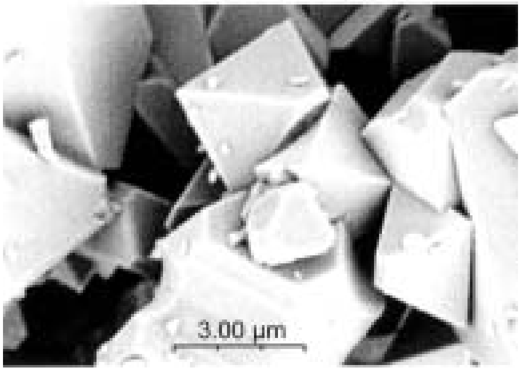

Figure 2. A SEM photograph of $Li[Ni_{1/2}Mn_{3/2}]O_4$ ($Fd\bar{3}m$: a = 8.17 Å) prepared by heating a reaction mixture at 1000 °C for 12 h and subsequently at 700 °C in air for 24 h. Nonporous body can be seen with octahedral morphology.

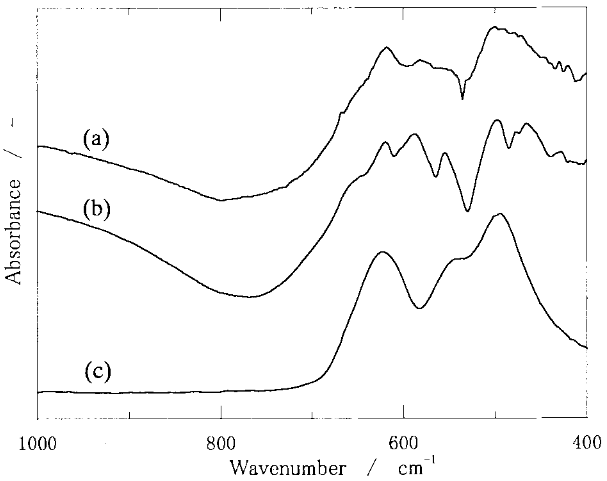

Figure 3. FT-IR spectra of Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$ prepared by heating a reaction mixture at 1000 °C for 12 h. Sample (a) was cooled down directly from 1000 °C to room temperature, and sample (b) was subsequently heated at 700 °C for 24 h and then cooled down to room temperature. LiMn$_2$O$_4$ ($Fd\bar{3}m$: $a = 8.24$ Å) was also shown in (c).

Corp.) with copper Kα radiation. All diffraction lines could be indexed assuming a cubic lattice for both samples. Lattice constant of sample cooled down directly from 1000 °C to room temperature was determined to be 8.19 Å while the sample oxidized at 700 °C was 8.17 Å by a least squares method using 14 diffraction lines.

Figure 2 shows the SEM image on the primary particles of Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$ prepared at 700 °C followed the heating at 1000 °C. Spherical morphology of the secondary particles is derived from a raw material (not shown). Octahedral shape characteristic of cubic spinel is observed when the samples were heated at higher temperatures than 850 °C regardless of the subsequent oxidation at 700 °C. To characterize the samples in addition to XRD and SEM, the FTIR measurements were carried out. The results are shown in Figure 3. The IR spectrum of LiMn$_2$O$_4$ is also shown in comparison. The spectra were obtained by a KBr method using a Fourier-transform infrared spectrometer (FTIR-8300, Shimadzu Corp.). Spectra in 1000–2000 cm^{-1} were featureless for all samples. The spectrum of LiMn$_2$O$_4$ exhibits two main absorption bands at 494 and 623 cm^{-1} with a weak band at 544 cm^{-1}. The sample oxidized at 700 °C shows fine structure around these absorption bands for a cubic spinel while the sample without the oxidation at 700 °C does not show such a well-defined fine structure. Although Gryffroy et al.[6] have already described the increase in the number of absorption bands in relation to a long-range 1:3 octahedral order for their Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$ samples prepared at about 800 °C, its origin of the fine structure is still unknown.

Figure 4 shows the charge and discharge curves of lithium cells with thus prepared samples. As seen in Figure 4, the effect of the oxidation at 700 °C after heating at 1000 °C on the rechargeable capacity is remarkable. By adjusting reaction time for oxidation at 700 °C we can control the rechargeable capacity. It should be noted here that staying period at about 4 V, which is adjustable, is good signal by which we notice the time to recharge. When we select thus prepared Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$ and so-called zero-strain insertion material of Li[Li$_{1/3}$Ti$_{5/3}$]O$_4$, we can provide a 3-volt lithium-ion cell which is compatible with two Zn/Ag$_2$O cells connecting in series as is shown in Figure 4(c). The negative-electrode material can be replaced by Li[CrTi]O$_4$[2] with 50 mV of voltage gain.

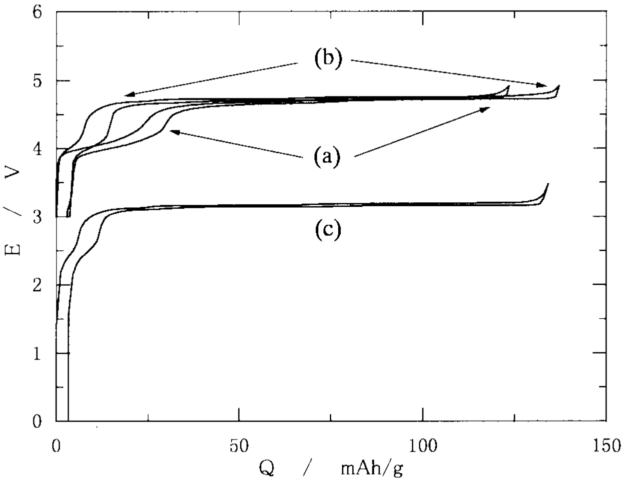

Figure 4. Charge and discharge curves of lithium cells with (a) Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$ directly cooled from 1000 °C to room temperature and (b) after oxidized at 700 °C for 24 h. A 3-volt lithium-ion cell with Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$ (the same sample as shown in (b)) and Li[Li$_{1/3}$Ti$_{5/3}$]O$_4$ is shown in (c). Electrolyte used was 1M LiPF$_6$ dissolved in ethylene carbonate (EC) / dimethyl carbonate (DMC) (3/7 by volume) solution. Cells were operated at a rate of 0.17 mA/cm^2 at 30 °C.

In summary, a 3-volt lithium-ion cell with Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$ and Li[Li$_{1/3}$Ti$_{5/3}$]O$_4$ can be fabricated by improving a method to prepare Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$. Since Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$ and Li[Li$_{1/3}$Ti$_{5/3}$]O$_4$ (or Li[CrTi]O$_4$) have the same spinel-framework structure with small change in lattice dimension during charge and discharge, i.e., a = 8.16–8.20 Å for Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$ and a = 8.36 Å for Li[Li$_{1/3}$Ti$_{5/3}$]O$_4$, it is not necessary to use organic or inorganic liquid electrolytes. Trials toward the implementation of 3-volt solid-state lithium-ion cells with these materials 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 nickel manganese double hydroxides.

References

1 T. Ohzuku, A. Ueda, and N. Yamamoto, *J. Electrochem. Soc.*, **142**, 1431 (1995).
2 T. Ohzuku, K. Tatsumi, N. Matoba, and K. Sawai, *J. Electrochem. Soc.*, **147**, 3592 (2000).
3 Q. Zhong, A. Banakdorpour, M. Zhang, Y. Gao, and J. R. Dahn, *J. Electrochem. Soc.*, **144**, 205 (1997).
4 A. Ueda, K. Furukawa, and T. Ohzuku, 34th Battery Symposium, Hiroshima, November 1993; Abstract No. 2A02.
5 J. M. Tarascon, W. R. McKinnon, F. Coowar, T. N. Bowmer, G. Amatucci, and D. Guyomard, *J. Electrochem. Soc.*, **141**, 1421 (1994).
6 D. Gryffroy and R. E. Vandenberghe, *J. Phys. Chem. Solids*, **53**, 777 (1992).