Characteristic Features of Layered $\text{Li}[\text{M}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ ($\text{M} = \text{Co}$ and Ni) Positive Electrode Materials and Their Li-ion Batteries

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Layered lithium nickel manganese oxides described as $\text{Li}[\text{M}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ ($\text{M} = \text{Ni}$ and Co , $0 \leq x \leq 1/3$) were induced from superlattice layered $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$. XAS results suggested that $\text{Li}[\text{Ni}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ compounds contained $\text{Ni}^{2.3+}$ and Mn^{4+} , and that $\text{Li}[\text{Co}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ contained Co^{3+} , Ni^{2+} and Mn^{4+} . $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ showed almost the same reversible capacity as LiCoO_2 . From results on DSC of the electrode charged by 4.3 V versus Li metal, $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ exhibited higher thermal stability than LiCoO_2 . ARC measurements of the full-charged Li-ion batteries were carried out. The battery with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ exhibited lower self-heat rate for thermal runaway than that with LiCoO_2 , suggesting that the battery with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ was superior to that with LiCoO_2 in terms of thermal stability at full-charged state.

Key Words : Lithium-Ion Batteries, Positive Electrode, Layered Materials, Thermal Stability

1 Introduction

A commercial Li-ion battery typically consists of a carbon-based negative electrode, a porous polymer membrane separator, a LiCoO_2 positive electrode, and a flammable nonaqueous electrolyte. Energy density in Li-ion battery has increased since the commercialization. There is a trade-off relationship between energy density and thermal stability. The thermal reactions of individual components have been correlated with the thermal behavior of battery. Positive electrode material was an important factor to determine the performance and safety of Li-ion batteries. The development for a higher capacity and safer positive electrode material than LiCoO_2 and $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ is still ongoing task.¹⁻¹⁴⁾ Many researchers have tried to prepare a battery active layered LiMnO_2 , which is isostructural with LiCoO_2 . It, however, has not been discovered yet. Several battery active layered materials containing manganese ion were developed. $\text{Li}[\text{Li}_{0.2}\text{Cr}_{0.4}\text{Mn}_{0.4}]\text{O}_2$ showed a capacity of about 160 mAh/g at ambient temperature, was proposed by Amundsen *et al.*^{5, 6)} It was described to be a solid-solution between Li_2MnO_3 ($\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$) and LiCrO_2 , which contained a superlattice ordering of Li^+ and Mn^{4+} in the transition metal layer. The solid-solution materials $\text{Li}[\text{M}_{1-x}\text{Li}_{x/3}\text{Mn}_{2x/3}]\text{O}_2$ between Li_2MnO_3 and LiCoO_2 or between Li_2MnO_3 and LiNiO_2 were reported by Dahn *et al.*^{9, 11)} A series of $\text{Li}[\text{Ni}_{1-x}\text{Li}_{x/3}\text{Mn}_{2x/3}]\text{O}_2$ can be cycled with 160 mAh/g in the voltage range of 3 to 4.5 V.^{9, 10)} Ohzuku *et al.* proposed a series of superlattice layered compounds of $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ ^{12, 13)} and $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ ¹⁴⁾ showing excellent cycle property in the voltage range of 3 to 4.5 V with 180 mAh/g of reversible capacity. $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ was classified from $\text{Li}[\text{Ni}_{1-x}\text{Li}_{x/3}\text{Mn}_{2x/3}]\text{O}_2$ in terms of the ordering of Ni and Mn on two-dimensional triangular lattice.

Here, we characterized layered lithium nickel manganese oxides described as $\text{Li}[\text{M}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ ($\text{M} = \text{Ni}$ and Co ; $0 \leq x \leq 1/3$) by XRD, XAS and DSC. The material features were described in detail. Thermal properties of Li-ion batteries with lithium nickel manganese oxide were reported in comparison with those with LiCoO_2 and LiMn_2O_4 .

2 Experimental

$\text{Li}[\text{M}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ compounds ($\text{M} = \text{Ni}$ and Co ; $x = 0, 1/4$ and $1/3$) were prepared by calcining stoichiometric amounts of coprecipitated mixed hydroxides with $\text{Ni} : \text{Mn} = 1 : 1$,¹³⁾ $\text{LiOH} \cdot \text{H}_2\text{O}$ and nickel or cobalt hydroxide at 900°C for 12 hrs in air. The compounds were characterized by XRD and XAS. XRD measurements were carried out by RINT2500 (RIGAKU DENKI) equipped with $\text{CuK}\alpha$ source.

XAS measurements were carried out in Ritsumeikan University, Synchrotron Radiation Center, BL4 port (Compact SR source: AURORA, the beam energy of 575 MeV and the beam current of 300 mA). White X-rays were monochromatized by $\text{Ge}(220)$ double crystal. The energy calibrations were monitored using Ni and Mn foils. In measurement for Co and Ni K-edge spectra, the X-ray intensities were monitored using ionization chambers filled with a mixture of $\text{Ar}(50\%)/\text{N}_2(50\%)$ for the incident beam and a mixture of $\text{Ar}(50\%)/\text{N}_2(50\%)$ for the transmitted beam. In measurement for Mn K-edge spectra, the ionization chambers were filled with a mixture of $\text{Ar}(85\%)/\text{N}_2(15\%)$ for the incident beam and $\text{Ar}(50\%)/\text{N}_2(50\%)$ for the transmitted beam. The data obtained was analyzed by using a software of REX2000 (RIGAKU DENKI).

Electrochemical properties were evaluated by using Li cells. A mixture of 90 wt% active material, 5 wt% con-

ductive additive (KS6, LONZA), and 5 wt% PVdF binder (#1120, KUREHA) was coated on Al foil. It was dried at 100°C, and pressed with 2 ton/cm². The electrolyte used was 1.2 M LiPF₆ solved in EC/EMC(1/2) solution (TOMIYAMA PURE CHEMICALS). Electrochemical tests were carried out by an automatic cycle system (TOSCAT2500, TOYO SYSTEM). Trial 14500 size cylindrical Li-ion batteries with layered lithium nickel manganese oxide positive electrode were fabricated. The negative electrode used consisted of a MCMB type artificial graphite showing 320 mAh/g of 1st charge capacity and PVdF binder (#9306, KUREHA). The separator used was 25 µm thick polyethylene film (SETERA E 25 MME, TOHMEN CHEMICAL NASU). The battery capacity was designed to be 620 mAh.

Thermal properties of the materials were evaluated by DSC measurement (Pyris 1, PERKIN ELMER). A charged electrode was removed from a cell in Ar filled glove box. The electrode was soaked in DME. The sample (3.5 mmφ diameter electrode, about 1.6 mg active material) was sealed with 3 µl electrolyte in Au coated stainless steel cell. Thermal properties of the batteries were evaluated by Accelerating Rate Calorimeter (ARC) (Arther D. Little Co.). ARC measurements of full-charged batteries were carried out. ARC measurements with the heat-wait-search mode in adiabatic condition were needed to determine the thermal response (temperature versus time) and self-heat rates of full-charged batteries. Using ARC in heat mode, the sample/sample holder assembly was heated from 40°C with 5°C steps at 1°C/min. At the end of each heating step, twenty minutes of wait time was allowed for the ARC and the sample/sample holder assembly to reach equilibrium. In the following search mode of 10 min, the ARC searched for a sample/sample holder assembly temperature rose of 0.02°C/min or higher. If this self-heat rate was detected, the ARC switched to the adiabatic mode and recorded the exothermic activity of the sample. Otherwise, the ARC proceeded to the next heat-wait-search step.

3 Result and Discussion

3.1 XRD features of Li[M_xNi_{(1-x)/2}Mn_{(1-x)/2}]O₂ (M = Ni and Co; 0 ≤ x ≤ 1/3)

Figure 1 showed the XRD patterns of Li[M_xNi_{(1-x)/2}Mn_{(1-x)/2}]O₂ (M = Ni and Co; x = 1/3) in comparison with Li[Ni_{1/2}Mn_{1/2}]O₂ (a = 2.895 Å, c = 14.320 Å; density = 4.59 g/cm³). Li[M_xNi_{(1-x)/2}Mn_{(1-x)/2}]O₂ (M = Ni or Co; x = 1/3) were suggested to be isostructural with Li[Ni_{1/2}Mn_{1/2}]O₂ in terms of stacking formation of transition metal and lithium ion layer in cubic closed oxygen packing. All of diffraction lines was identified in hexagonal setting. The lattice parameters of Li[M_xNi_{(1-x)/2}Mn_{(1-x)/2}]O₂ (M = Ni and Co; x = 0, 1/4, 1/3) were summarized in Table 1. The lattice parameters were a = 2.893 Å, c = 14.294 Å; density = 4.63 g/cm³ for Li[Ni_{2/3}Mn_{1/3}]O₂ and a = 2.855 Å, c = 14.225 Å; density = 4.78 g/cm³ for Li[Co_{1/3}Ni_{1/3}Mn_{1/3}]O₂. The a and c-axis parameter for Li[Ni_xNi_{(1-x)/2}Mn_{(1-x)/2}]O₂ remained and shrunk, respectively, as a function of the amount of Ni. Both of a and c-axis parameter of

Fig. 1 XRD patterns of Li[Ni_{1/2}Mn_{1/2}]O₂ and Li[M_{1/3}Ni_{1/3}Mn_{1/3}]O₂ (M = Ni and Co).

Table 1 Lattice parameters of Li[M_xNi_{(1-x)/2}Mn_{(1-x)/2}]O₂ (M = Co, Ni; x = 0, 1/4, 1/3) in hexagonal setting.

Li[M _x Ni _{(1-x)/2} Mn _{(1-x)/2}]O ₂	a/Å	c/Å	Density/g cm ⁻³
Li[Ni _{1/2} Mn _{1/2}]O ₂	2.895	14.320	4.59
Li[Co _{1/4} Ni _{3/8} Mn _{3/8}]O ₂	2.874	14.277	4.70
Li[Co _{1/3} Ni _{1/3} Mn _{1/3}]O ₂	2.855	14.225	4.78
Li[Ni _{5/8} Mn _{3/8}]O ₂	2.894	14.305	4.62
Li[Ni _{2/3} Mn _{1/3}]O ₂	2.893	14.294	4.63

Li[Co_xNi_{(1-x)/2}Mn_{(1-x)/2}]O₂ shrunk with the amount of Co. From results on our continuous researches for Li[M_xNi_{(1-x)/2}Mn_{(1-x)/2}]O₂ (M = Ni, Co; x > 1/3), Li[Ni_xNi_{(1-x)/2}Mn_{(1-x)/2}]O₂ and Li[Co_xNi_{(1-x)/2}Mn_{(1-x)/2}]O₂ exhibited homogeneous phase and phase separation of LiCoO₂/Li[Co_{1/3}Ni_{1/3}Mn_{1/3}]O₂, respectively, above x = 1/3 in Li[M_xNi_{(1-x)/2}Mn_{(1-x)/2}]O₂. As can be seen in Fig. 1, there was a little difference in the intensity ratio of I(104)/I(003) between Li[Ni_{2/3}Mn_{1/3}]O₂ and Li[Co_{1/3}Ni_{1/3}Mn_{1/3}]O₂. Li[Ni_{2/3}Mn_{1/3}]O₂ and Li[Co_{1/3}Ni_{1/3}Mn_{1/3}]O₂ showed higher and lower intensity ratio, respectively, than Li[Ni_{1/2}Mn_{1/2}]O₂. According to earlier studies on crystal structure of LiNiO₂,¹⁸⁾ the intensity ratio of I(104)/I(003) was relevant to concentrated rock-salt domains in layered LiNiO₂. Li[Ni_{2/3}Mn_{1/3}]O₂ seemed to contain high concentrated rock-salt domains in comparison with Li[Ni_{1/2}Mn_{1/2}]O₂ and Li[Co_{1/3}Ni_{1/3}Mn_{1/3}]O₂.

3.2 XAS features of Li[M_xNi_{(1-x)/2}Mn_{(1-x)/2}]O₂ (M = Ni and Co; 0 ≤ x ≤ 1/3)

In order to estimate the formal valence state of Ni and Mn in Li[Ni_{1/2}Mn_{1/2}]O₂, the XANES spectrum for Li[Ni_{1/2}Mn_{1/2}]O₂ at Ni and Mn K-edge were compared with spectra for several Ni and Mn compounds, respec-

Fig. 2 K-edge features of Ni and Mn in $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ in comparison with several manganese oxides and nickel oxides, respectively.

tively.¹⁹⁾ As shown in Fig. 2, the energy of Ni and Mn K-edge for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ were similar to that for NiO and $\beta\text{-MnO}_2$, respectively, suggesting that $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ contained Ni^{2+} and Mn^{4+} ion. The formal valence state of Ni and Mn in $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ did not correspond to Ni^{3+} in $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and Mn^{3+} in LiMnO_2 , respectively. Above results didn't suggest that $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ was a solid-solution of $\text{LiMnO}_2\text{-LiNiO}_2$.

XANES spectra for $\text{Li}[\text{Ni}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ at Ni and Mn K-edge were shown in Fig. 3. The K-edge position of Ni was shifted toward high energy with the amount of Ni, meaning that $\text{Li}[\text{Ni}_{2/3}\text{Mn}_{1/3}]\text{O}_2$ contained a mixture of Ni^{3+} and Ni^{2+} . The energy of Mn K-edge for $\text{Li}[\text{Ni}_{2/3}\text{Mn}_{1/3}]\text{O}_2$ corresponded to that for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$, meaning that $\text{Li}[\text{Ni}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ contained Mn^{4+} . Figure 4 showed the XANES spectra for $\text{Li}[\text{Co}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ at Co, Ni, and Mn K-edge. The energy of Ni and Mn K-edge corresponded to that of Ni and Mn for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$, respectively. The energy of Co K-edge corresponded to that for LiCoO_2 . Thus, we suggested that $\text{Li}[\text{Co}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ contained Co^{3+} , Ni^{2+} and Mn^{4+} .

As described above, $\text{Li}[\text{M}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ ($\text{M} = \text{Ni}$ and Co) compounds were induced from $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ containing a superlattice ordering of Ni^{2+} and Mn^{4+} .

Fig. 3 K-edge features of Ni and Mn in $\text{Li}[\text{Ni}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$.

3.3 Electrochemical behaviors of $\text{Li}/\text{Li}[\text{M}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ ($\text{M} = \text{Ni}$ and Co) cells

It was difficult to prepare an electroactive $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ compound with reliability. Since $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ is an imperfect superlattice compound, the reversible capacity decreases with concentrated rock-salt domains, as suggested from the results on study of electroactive LiNiO_2 .¹⁸⁾ According to studies on $\text{Li}[\text{Ni}_{1-x}\text{Li}_{x/3}\text{Mn}_{2x/3}]\text{O}_2$,⁹⁻¹¹⁾ the reversible capacity decreases with the amount of excess Li ion, suggesting that the reversible capacity of $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ is also sensitive to the amount of Li ion. $\text{Li}/\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ cell showed about 160 mAh/g of 1st charge capacity by the upper limit voltage of 4.3 V and 145 mAh/g of discharge capacity by the lower limit voltage of 3.0 V, as shown in Fig. 5(A). Charge and discharge curves for $\text{Li}/\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cell were also shown in comparison. The 1st cycle efficiency for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ was about 85%, was similar to that for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. The working voltage for $\text{Li}/\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ cell was 3.75 V, which was almost the same value for $\text{Li}/\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cell, 3.70 V, as seen in Fig. 5(B). The cell exhibited excellent cycle properties with 145 mAh/g of reversible capacity in the voltage range from 3 to 4.3 V. From above electrochemical features, $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ was suggested to be induced from lithium nickel oxide.

Figure 6 showed discharge curves of $\text{Li}/\text{Li}[\text{M}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ ($\text{M} = \text{Ni}$ and Co) cells in the voltage range of 3 to 4.3 V. $\text{Li}/\text{Li}[\text{Ni}_{2/3}\text{Mn}_{1/3}]\text{O}_2$ cell showed smaller reversible capacity than $\text{Li}/\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ cell

Fig. 4 K-edge features of Ni, Mn, and Co in $\text{Li}[\text{Co}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$. K-edge feature of Co in LiCoO_2 was also shown in comparison.

due to concentrated rock-salt domains with the amount of Ni. Such a electrode feature was quite similar to that of LiNiO_2 containing rock-salt domains as was described previously.¹⁸⁾ The $\text{Li}/\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ cell exhibited higher reversible capacity than $\text{Li}/\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ cell, was resulted on reducing rock-salt domains with Co substitution.

As described above, it was suggested that electrochemical behaviors of $\text{Li}[\text{M}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ was dependent upon the concentrated rock-salt domains. $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ was the most promising positive electrode material for practical Li-ion batteries among them.

Fig. 5 (A) Initial charge and discharge curves and (B) the differential chronopotentiogram for discharge curve of $\text{Li}/\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ cell in comparison with $\text{Li}/\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cell.

Fig. 6 Discharge curves of $\text{Li}/\text{Li}[\text{M}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ ($\text{M} = \text{Ni}$ and Co) cells at a rate of $0.5 \text{ mA}/\text{cm}^2$ in comparison with that of $\text{Li}/\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ cell.

3. 4 Ex-situ XAS result for Lithium extraction from $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$

Li ion extraction from $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ was characterized by *ex-situ* XRD and XAS measurements.¹⁵⁻¹⁷⁾ Li ions are extracted from $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ electrochemically by using Li cells; $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2 \rightarrow \delta\text{Li}^+ + \delta\text{e}^- + \text{Li}_{1-\delta}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$. The theoretical capacity is determined to be 279.9 mAh/g .

Changes in the lattice parameters of $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ for Li ion extraction were shown in Fig. 7. The *a*- and *c*-axis length shrunk and elongated, respectively from $\delta = 0$ to $1/2$ in $\text{Li}_{1-\delta}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$. At more than $\delta = 1/2$, the *a*- and *c*-axis length elongated and shrunk, respectively. The changes in lattice parameters of

Fig. 7 Changes in the *a* and *c* parameter of $\text{Li}_{1-\delta}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ for charge.

$\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ were much similar to those of $\text{Li}[\text{Co}_{1/2}\text{Ni}_{1/2}]\text{O}_2$.²⁰⁾

Figure 8 showed changes in the energy of Ni and Mn K-edge for $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ during Li ion extraction. The energy of Ni K-edge shifted toward higher energy from $\delta = 0$ to $1/2$ in $\text{Li}_{1-\delta}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$, but remained at more than $\delta = 1/2$. Redox centers were suggested to be Ni^{2+} ions for lithium ion extraction from $\delta = 0$ to $1/2$ in $\text{Li}_{1-\delta}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$. The energy of Mn K-edge remained in an entire region, meaning that the valence state of Mn remained tetravalent during Li ion extraction from $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$. According to XAS study on Li ion extraction from $\text{Li}[\text{Co}_{1/2}\text{Ni}_{1/2}]\text{O}_2$,²¹⁾ the formal valence state of both Ni^{3+} and Co^{3+} ion increased with the number of Li ion extracted. In Li ion insertion/extraction into/from (Li)-M-O ternary phase (M=transition metals), change in the number of d-electrons for transition metals corresponds to the number of Li ion inserted/extracted. Therefore, Li ion insertion/extraction has been characterized as a solid-state redox reaction of the transition metal, M. The cell potential for Li ion insertion/extraction is relevant to the d-level energy of specific transition metal.²²⁾ From $\delta = 0$ to $1/2$ in $\text{Li}_{1-\delta}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$, the change in the d-level energy of Ni ion was observed, meaning that the solid-state redox reaction was specified by Ni ion. The cell potential of $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ is quietly similar to that of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ in spite of the difference in the valence state of Ni ion, will be in future discussion. At more than $\delta = 1/2$ in $\text{Li}_{1-\delta}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$, the valence state of both Ni and Mn ion remained with the number of Li ion extracted, meaning that transition metals were not redox centers in the solid-state redox reaction. As suggested in earlier studies on Li doped NiO materials,²³⁾ it was possible for the oxygen 2p holes to provide a charge neutralization in the system. Therefore, we believe that the formal valence state of oxygen ion decrease at more than $\delta = 1/2$ in $\text{Li}_{1-\delta}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ in an assumption of charge neutralization. Consequently, $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ was similar to LiNiO_2 in terms of the electrochemical features in the voltage range of 3 to 4.3 V versus Li/Li^+ . The specific electrochemical features of Mn ion in $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ were not observed.

Fig. 8 Changes in K-edge feature of Ni and Mn in $\text{Li}_{1-\delta}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ for charge.

3.5 DSC features of $\text{Li}[\text{Co}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ ($x = 0, 1/3$)

Thermal stability of positive electrode material may have a close relationship to oxygen releasing for thermal decomposition.^{7,24)} Lithium manganese oxide consisting 100% Mn has been expected to be high thermal stability. For example, spinel LiMn_2O_4 electrode is charged by the following reaction; $\text{LiMn}_2\text{O}_4 \rightarrow 2\text{MnO}_2 + \text{Li}^+ + \text{e}^-$. The full-charged material of MnO_2 exhibits high thermal stability. In addition, thermal stability of lithium manganese oxide is independent upon the state of charge; the amount of Li. In a case of LiCoO_2 , the full-charged material of CoO_2 decomposes into $1/3\text{Co}_3\text{O}_4 + 1/3\text{O}_2$. In assuming that $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ electrode is fully charged by the following reaction; $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2 \rightarrow [\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2 + \text{Li}^+ + \text{e}^-$, the full-charged material of $[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ may decompose into $1/2\text{MnO}_2$, $1/4\text{Ni}_2\text{O}_3$, and $1/8\text{O}_2$. In comparison with LiCoO_2 , $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ is expected to exhibit more thermal stable in terms of the amount of oxygen releasing from the full-charged state. Above considerations, thermal property of $\text{Li}[\text{M}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ is suggested to be highly dependent upon both the amount of manganese and the state of charge. Figure 9 showed results on DSC measurement of $\text{Li}[\text{Co}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ ($x = 0, 1/3$) electrodes charged by 4.3 V versus Li metal. DSC features for LiCoO_2 and LiMn_2O_4 electrode were shown in comparison. Thermal stability of the material was evaluated in terms of an onset temperature of main exothermic

Fig. 9 DSC properties of $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}\text{O}_2]$ and $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2]$ electrode charged by 4.3 V versus Li metal. The properties of LiCoO_2 and LiMn_2O_4 electrode charged by 4.3 V were shown in comparison.

peak. $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}\text{O}_2]$, $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2]$, LiCoO_2 and LiMn_2O_4 exhibited about 200, 200, 180 and 220°C of the onset temperature, respectively. LiMn_2O_4 showed the highest thermal stability among them. Both $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}\text{O}_2]$ and $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2]$ was superior to LiCoO_2 in terms of thermal stability on DSC features.

3.6 Properties of trial Li-ion batteries with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2]$

Trial 14500 size cylindrical Li-ion batteries consisted of $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2]$ positive electrode, polyethylene separator, and MCMC type artificial graphite negative electrode. The capacity was designed to be 620 mAh. $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2]$ powder used was supplied by SE-IMI Chemical Ltd. The battery contained 4.0 g of positive electrode material and 2.1 g of negative electrode material. The electrolyte used was 1.7 ml of 1.2 M LiPF_6 solved in EC/EMC(1/2) solution. Figure 10(A) showed discharge curves of Li-ion batteries with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2]$, LiCoO_2 , and LiMn_2O_4 at a current rate of 1 C in the voltage range of 3 to 4.2 V at ambient temperature. The trial batteries with LiCoO_2 and LiMn_2O_4 exhibited 620 mAh and 500 mAh of discharge capacity, respectively. All of battery components used was the same that of Li-ion battery with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2]$. The battery with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2]$ showed lower working voltage and almost the same capacity in comparison with that with LiCoO_2 . The battery with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2]$ exhibited excellent cycle property, as can be seen in Fig. 10(B). The trial battery showed enough rate and cycle capability for practical use. Thermal stabilities of the batteries were described in the following section.

3.7 Thermal properties of trial Li-ion batteries with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2]$ by ARC

Thermal behaviors of Li-ion battery have been characterized as a sequence of thermal reaction and /or decomposition in each battery component by using Accelerating Rate Calorimeter(ARC).^{25, 26)} The reactions of individual components have been correlated with the thermal behavior of batteries. First, the SEI layer on carbon negative electrode consisting of Li_2O , LiOH , Li_2CO_3 , LiCO_2R

Fig. 10 (A) Discharge curve of 14500 size cylindrical Li-ion batteries with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2]$ positive electrode. (B) Cycle properties of the battery at a rate of 1C in the voltage range of 3 to 4.2 V. Discharge curves and cycle features of the batteries with LiCoO_2 and LiMn_2O_4 were shown in comparison, respectively.

and LiF or LiCl breaks down and allows further thermal reactions of the negative electrode with the LiPF_6 salt electrolyte at 100 to 150°C. Second, thermal decomposition of the positive electrode and the reaction with the electrolyte occurs above 150°C. Finally, the Li_xC_6 reacts with the PVdF binder at temperature above 250°C. These reactions are quite complex and are highly dependent on the specific materials and the state of charge in the cell. In real batteries, further complications arise due to interdependencies among these reactions, generation of by-products, and the presence of venting mechanisms and meltdown separators. Since the positive electrode material is major component of the Li-ion batteries, the thermal stability studies have become a common test in characterizing new positive electrode materials by using DSC.

ARC measurement of cylindrical Li-ion battery with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2]$ charged by 4.3 V was carried out. Figure 11 showed the temperature profile against collecting time. The ARC features consisted of a heat-wait-search period and a self-heat generation period. A heat-wait-search mode had been continued from room temperature to 80°C for about 600 min. The self-heat generation started at 80°C of onset temperature. The temperature on surface of battery increased almost linearly by about 125°C. Open circuit voltage of the batteries remained 4.2 V from ambient temperature to about 125°C. The open-circuit voltage dropped to 0 V above 125°C due to separator meltdown. By following, the safety vent

Fig. 11 ARC features of 14500 size cylindrical Li-ion batteries with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ positive electrode, which was charged by 4.3 V.

opened due to gassing. Finally, the temperature of battery rose up over 200°C , indicating that the sample was burn up. The period for self-heat generation was about 1400 min.

In order to evaluate thermal stability of Li-ion battery with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, comparative studies with those with LiCoO_2 ²⁷⁾ and LiMn_2O_4 were carried out. As can be seen in Fig.12(A), Li-ion batteries with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ exhibited almost the same onset temperature as that of Li-ion batteries with LiCoO_2 and LiMn_2O_4 , meaning that the onset temperature for self-heat generation mode was not relevant to thermal stability of specific positive electrode material. Li-ion battery with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ showed almost the same period of self-heat generation as that with LiMn_2O_4 . Li-ion battery with LiCoO_2 , however, exhibited a rapid rising in temperature of battery for the period of self-heat generation. Consequently, the period was only 300 min, which was quite short that for Li-ion battery with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$. The period of self-heat generation is highly dependent upon thermal stability of the specific positive electrode material. Figure 12(B) showed the detail features in self-heat generation of Li-ion batteries. A heat-rate is an effective parameter in evaluation for thermal stability of Li-ion battery. Li-ion batteries with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, LiMn_2O_4 and LiCoO_2 exhibited 0.05, <0.02 and $1.0^\circ\text{C}/\text{min}$ of the heat rate at 125°C , respectively. Among them, Li-ion battery with LiMn_2O_4 showed the highest thermal stability. It was suggested that Li-ion battery with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ exhibited higher thermal stability than that with LiCoO_2 in terms of the rate of self-heat generation.

As described above, Li-ion battery with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ exhibited higher thermal stability than that with LiCoO_2 .

4 Conclusions

In this paper, we described the material features for $\text{Li}[\text{M}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$, and discussed thermal stability of the Li-ion batteries in comparison with those with LiCoO_2 or LiMn_2O_4 . From results on XRD measurement, $\text{Li}[\text{M}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ ($\text{M}=\text{Ni}$ and Co ; $0 < x \leq 1/3$)

Fig. 12 (A) ARC features of 14500 size cylindrical Li-ion batteries with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, LiCoO_2 , and LiMn_2O_4 positive electrode, whose capacities were 620, 620, and 500 mAh, respectively. (B) Plot of self-heat rate against temperature for each battery. Dotted line for Li-ion battery with LiMn_2O_4 means the heat-rates are under the setup value of $0.02^\circ\text{C}/\text{min}$ for thermal runaway mode.

exhibited homogeneous phase. XAS results suggested that $\text{Li}[\text{Ni}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ contained Ni^{2+} , Ni^{3+} and Mn^{4+} , and that $\text{Li}[\text{Co}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ contained Co^{3+} , Ni^{2+} , and Mn^{4+} . $\text{Li}[\text{M}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ compounds were suggested to induce from $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ containing a superlattice ordering of Ni and Mn. Li cells with $\text{Li}[\text{Ni}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ containing concentrated rock-salt domains exhibited small reversible capacity. Li cells with $\text{Li}[\text{Co}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ showed higher reversible capacity than that with $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{1/2}]\text{O}_2$. Trial Li-ion battery of MCMB carbon/ $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ exhibited almost the same capacities as that with LiCoO_2 in the voltage range from 3 to 4.2 V. From results on ARC evaluations, Li-ion battery with $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ showed low self-heat generation in comparison with that with LiCoO_2 . Thermal safety characteristics of Li-ion battery with $\text{Li}[\text{Co}_x\text{Ni}_{(1-x)/2}\text{Mn}_{(1-x)/2}]\text{O}_2$ were better than LiCoO_2 .

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