Layered Nickel Manganese Oxides ($LiNi_{1/2}Mn_{1/2}O_2$) Possible Alternative to $LiCoO_2$ for Lithium-ion Batteries ?

Tsutomu Ohzuku and Yoshinari Makimura

Electrochemistry and Inorganic Chemistry Laboratory, Department of Applied Chemistry, Graduate School of Engineering, Osaka City University (OCU), Osaka 558-8585, Japan

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-ion batteries, as well as to get a deeper understanding of insertion scheme. Although several candidate materials have been proposed so far, $LiCoO_2$ has still been used in practical lithium-ion batteries for several reasons. Some of the reasons are easiness to prepare the sample and to obtain reasonable reversible capacity and safety in spite of poor material economy for an expanding need of advanced lithium-ion batteries.

Material strategy in the first stage of our systematic study on lithium insertion materials are (1) the formation of solid solution of $LiNiO_2$(R3m) and $LiMnO_2$(R3m ; not stable in its pure form) and (2) the formation of solid solution of $LiNi_2O_4$(Fd3m ; not stable in its pure form) and $LiMn_2O_4$. The methods with the combination of each transition metal oxide with several lithium salts and the low temperature synthesis below 650 °C did not give good results. After several trials, we found a method to prepare a series of lithium nickel manganese oxides with or without a third transition metal.

Figure 1 shows XRD of (a) $LiNi_{1/2}Mn_{1/2}O_2$, (b) $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, and (c) $LiCo_{1/2}Ni_{1/2}O_2$. All diffraction lines can be indexed assuming a hexagonal lattice as shown in Fig. 1. Preliminary structural analysis for $LiNi_{1/2}Mn_{1/2}O_2$ indicated that a simple structural model based on $LiNiO_2$(R3m) did not illustrate a structural nature of these materials prepared from complex solid solution mechanism. Structural nature and chemical properties of $LiNi_{1/2}Mn_{1/2}O_2$ are somewhere between $LiNiO_2$(R3m) and $LiMn_2O_4$(Fd3m).

Figure 2 shows the charge and discharge curves of lithium cells with $LiNi_{1/2}Mn_{1/2}O_2$. Charge and discharge curves of lithium cells with $LiCoO_2$(R3m), $Li[Li_{0.1}Mn_{1.9}]O_4$(Fd3m), $LiCo_{1/2}Ni_{1/2}O_2$(R3m), and $Li[Li_{1/3}Ti_{5/3}]O_4$(Fd3m) are also shown for comparison. Reversible capacities of $LiNi_{1/2}Mn_{1/2}O_2$ are 150 to 170 mAh/g depending on the change-end voltage, and the capacity loss was hardly observed for the continuous 30 cycle tests. Operating voltage is in order : $Li[Li_{0.1}Mn_{1.9}]O_4$ > $LiCoO_2$ > $LiNi_{1/2}Mn_{1/2}O_2$ > $LiCo_{1/2}Ni_{1/2}O_2$, while reliable rechargeable capacity is reverse order in a present cell chemistry. XRD and DSC examinations of partially to fully oxidized $LiNi_{1/2}Mn_{1/2}O_2$, dilatometric examinations of the cells with $LiNi_{1/2}Mn_{1/2}O_2$ and graphite, and acoustic emission examinations were also carried out.

From these results we will discuss whether or not $LiNi_{1/2}Mn_{1/2}O_2$ is a possible alternative to $LiCoO_2$ for lithium-ion batteries with a graphite-negative electrode by comparing the results with $LiCoO_2$, $LiNiO_2$, and $Li[Li_xMn_{2-x}]O_4$. Some derivatives with cobalt, aluminum, and so forth, will also be given.

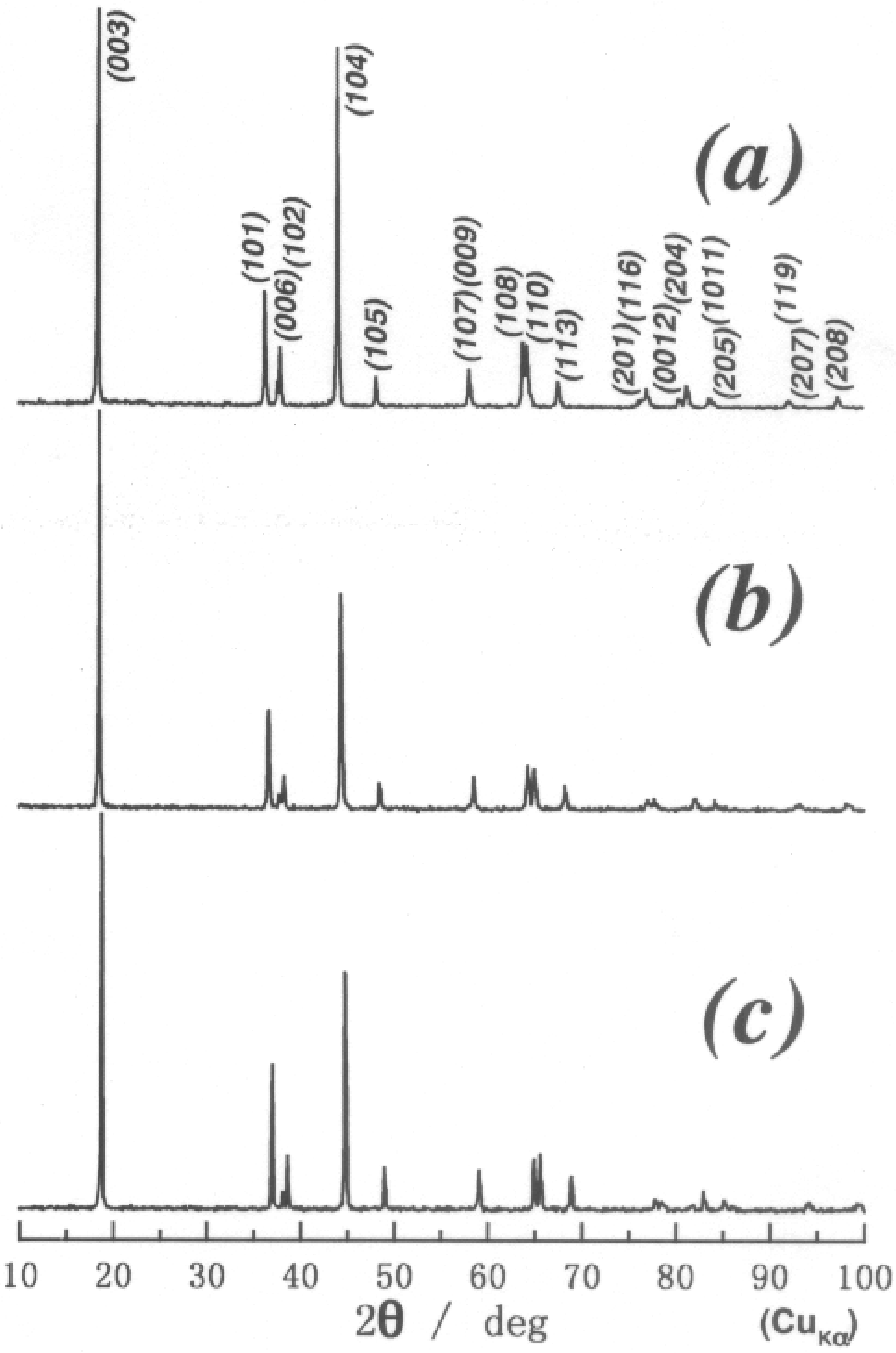

Fig. 1 XRD patterns of (a) $LiNi_{1/2}Mn_{1/2}O_2$, (b) $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, and (c) $LiCo_{1/2}Ni_{1/2}O_2$.

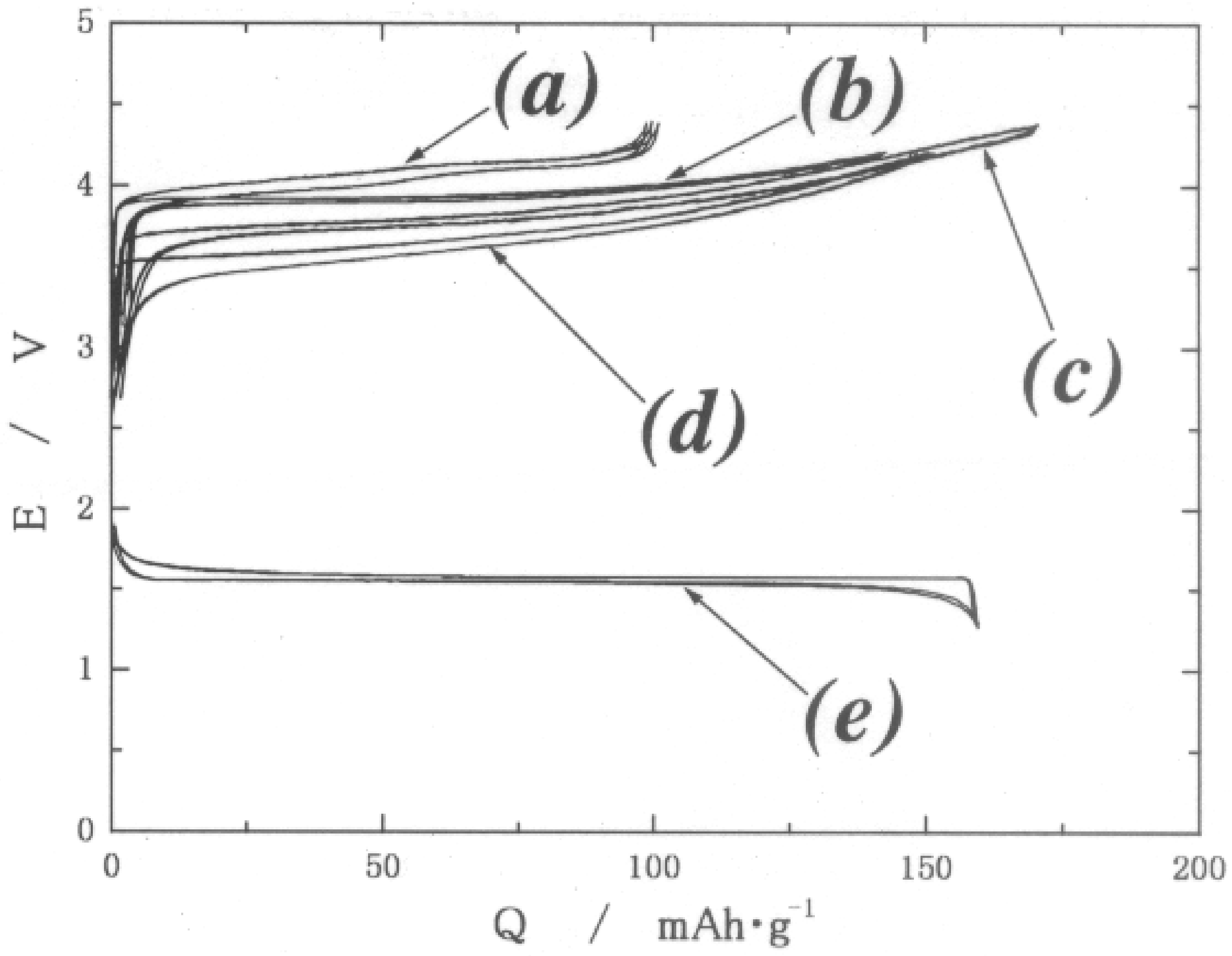

Fig. 2 Charge and discharge curves of the lithium cells with (a) $Li[Li_{0.1}Mn_{1.9}]O_4$(Fd3m), (b) $LiCoO_2$(R3m), (c) $LiNi_{1/2}Mn_{1/2}O_2$, (d) $LiCo_{1/2}Ni_{1/2}O_2$(R3m), and (e) $Li[Li_{1/3}Ti_{5/3}]O_4$(Fd3m). $LiNi_{1/2}Mn_{1/2}O_2$ was prepared by a usual ceramic method with (Ni, Mn)$(OH)_2$ and LiOH heating at 1000 °C for 12 h in air.

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