Electrochemical Properties of $LiNi_xMn_yCo_{1-x-y}O_2$ for Lithium Ion Secondary Batteries

Kazuhiro Kikuchi, Kouji Shima, Chisato Miura, Kenji Okahara
Mitsubishi Chemical Group Science and Technology Research Center, Inc.
1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan

Introduction

Recently, the research on alternative materials to $LiCoO_2$ for the cathode of lithium ion secondary batteries has been investigated. One of the candidates, a layered $Li(Ni_xCo_yAl_{1-x-y})O_2$ system has an advantage on capacity and disadvantages on thermal stability and irreversible capacity. On the other hand, a layered $Li(Ni_xMn_yCo_{1-x-y})O_2$ system, especially $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, has been attracting much attention because of its higher thermal stability and lower irreversible capacity [1-3]. However, its capacity is lower than that of the $Li(Ni_xCo_yAl_{1-x-y})O_2$ system. It is expected that Ni-rich compositions in $Li(Ni_xMn_yCo_{1-x-y})O_2$ system shows the good balance of capacity and thermal stability. In this study, we will report the electrochemical and thermal properties of $Li(Ni_{0.65}Mn_{0.15}Co_{0.20})O_2$ as a representative composition for Ni-rich $Li(Ni_xMn_yCo_{1-x-y})O_2$ in comparison with $Li(Ni_{0.80}Co_{0.15}Al_{0.05})O_2$.

Experimental

$LiNi_{0.65}Mn_{0.15}Co_{0.20}O_2$ (NMC65/15/20), $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC33/33/33), and $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA80/15/05) were prepared by calcining the stoichiometric mixtures of each starting raw material in air or oxygen atmosphere. The obtained products were examined by XRD for crystal structure, SEM for particle morphology, and DSC for thermal stability. 2032 type coin cells (vs. Li metal) and 18650 type cylindrical cells (vs. carbon anode) were used for initial charge and discharge capacities, and cycle life and impedance analyses, respectively. 1 M $LiPF_6$ in EC/DMC/EMC was used as an electrolyte.

Results and discussion

XRD results showed that the obtained products have the same crystal structure as the □-$NaFeO_2$ type (space group: R3-m). Fig. 1 presents the DSC profiles of these cathode samples charged at 4.2 V vs. Li/Li^+. NCA80/15/05 sample showed lower thermal stability with exothermic reactions around 200-250 °C, and NMC65/15/20 and NMC33/33/33 samples showed higher thermal stability with exothermic peak above 250 °C.

Cycling tests using 18650 cells showed that NMC65/15/20 revealed better retention in capacity than NCA80/15/05. In addition, the impedance of NCA80/15/05 increased drastically after cycling, while NMC65/15/20 showed little increase as shown in Fig. 2. More details of the properties and hypotheses will be presented in the symposium.

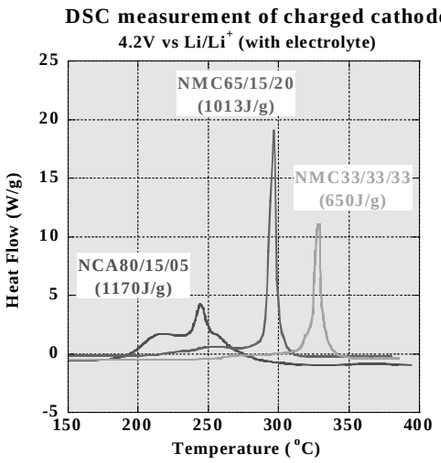

Fig. 1 DSC profiles of NMC65/15/20, NMC33/33/33 and NCA80/15/05.

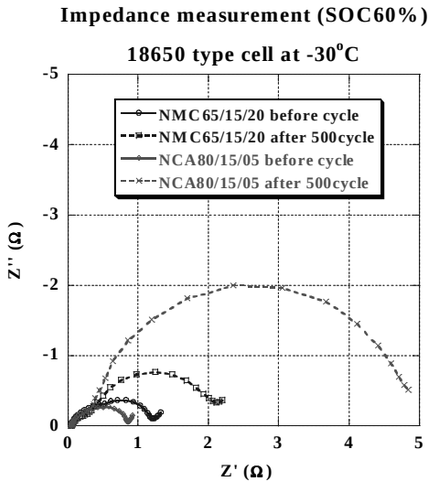

Fig. 2 Nyquist plots for NMC65/15/20 and NCA80/15/05.

References

[1] Z. Lu and J. R. Dahn, *J. Electrochem. Soc.*, **148**, A237 (2001).
[2] K. M. Shaju, G. V. Subba Rao, B. V. R. Chowdari, *Electrochim. Acta*, **48**, 145 (2002).
[3] N. Yabuuchi, T. Ohzuku, *J. Power Sources*, **119-121**, 171 (2003).