Abs. 390, 206th Meeting, © 2004 The Electrochemical Society, Inc.

Thermal Stability of Lithium Magnesium Cobalt Oxides for High Safety Lithium-ion Batteries

Hiroshi Yoshizawa, Masatoshi Nagayama and Tooru Matsui

Matsushita Battery Industrial Co., Ltd.
Technology Development Center
1-1 Matsushita-cho, Moriguchi, Osaka 570-8511, Japan

Lithium cobalt oxides have been used as positive electrode materials in lithium-ion batteries during the last decades. Many reports on the oxides have been published in various fields of solid-state chemistry and electrochemistry [1-7]. During the electrochemical insertion and extraction of lithium ions for $LiCoO_2$ in non-aqueous solutions [4,6,7], the crystal structure of oxide changes from hexagonal phase to monoclinic phase at $Li_{0.45}CoO_2$. Ohzuku and Ueda showed that the electrochemical reaction of $Li_{1-x}CoO_2$ consists of one single-phase reaction (1/4<x<3/4) and two two-phase reactions (0<x<1/4 and 3/4<x<1) [4]. On the other hand, Mg doped $LiCoO_2$ remains as a single hexagonal phase [3,5]. We reported thermal stability of lithium cobalt oxides doped with several kinds of elements, such as Al, Ca, and Sr [8]. We also have investigated Mg doped $LiCoO_2$ materials from the viewpoint of both safety and electrochemical characters.

The Mg doped $LiCoO_2$ was prepared by heating the reaction mixture of Li_2CO_3 and Mg doped Co_3O_4 that was prepared by a co-precipitation method. We characterized the synthesized materials by XRD. BET surface area, tap density, and distribution of particle size were measured. Morphology of particles was observed with SEM. In order to collect electrochemical data on rechargeable capacity and operating voltage behavior, 2016 coin type cells were fabricated. Figure 1 compares Mg doped $LiCoO_2$ with $LiCoO_2$ on the electrochemical behaviors, such as charge-discharge curves and dQ/dE verses E curves. The voltage plateaus due to the crystal structure change of hexagonal to monoclinic were disappeared in the Mg doped $LiCoO_2$.

Figure 2 shows the XRD patterns of (a) $Li_{1-x}Mg_yCo_{1-y}O_2$ and (b) $Li_{1-x}CoO_2$ charged up to 4.7V. As seen in Fig.2, Mg doped $LiCoO_2$ remains up to the charge voltage of 4.7 V. It is suggested that Mg doped $LiCoO_2$ may improve the cycle life in a high voltage charge together with the thermal stability. We carried out accelerating rate calorimetry (ARC) to confirm the better thermal stability of charged Mg-doped $LiCoO_2$ as compared with $LiCoO_2$. Self-heating rate of charged Mg-doped $LiCoO_2$ was milder than that of $LiCoO_2$. We also measured high temperature XRD to investigate the crystal structure change of charged Mg doped $LiCoO_2$. From these results, we will discuss thermal stability of Mg-doped $LiCoO_2$ related with crystal structure change as well as implementation for high safety and large capacity lithium-ion batteries.

References:

[1] K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Googenough, *Solid State Ionics*, **3-4**, 171 (1981)
[2] K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, *Mater. Res. Bull.* **15**, 783 (1980)
[3] H. Tukamoto and A. R. West, *J. Electrochem. Soc.*, **144**, 3316 (1997)
[4] T. Ohzuku and A. Ueda, *J. Electrochem. Soc.*, **141**, 2972 (1994)
[5] S. Levasseur, M. Menetrier and C. Delmas, *J. Power Sources*, **112**, 419 (2002)
[6] J. N. Reimers and J. R. Dahn, *J. Electrochem. Soc.*, **139**, 2091 (1992)
[7] Y. Shao-Horn, S. Levasseur, F. Weil and C. Delmas, *J. Electrochem. Soc.*, **150**, A366 (2003)
[8] M. Nagayama, H. Yoshizawa, and H. Koshina, p. 273 in Extended Abstract for International Meeting on Power Sources for Consumer and Industrial Applications (Hawaii Battery Conference), 2001

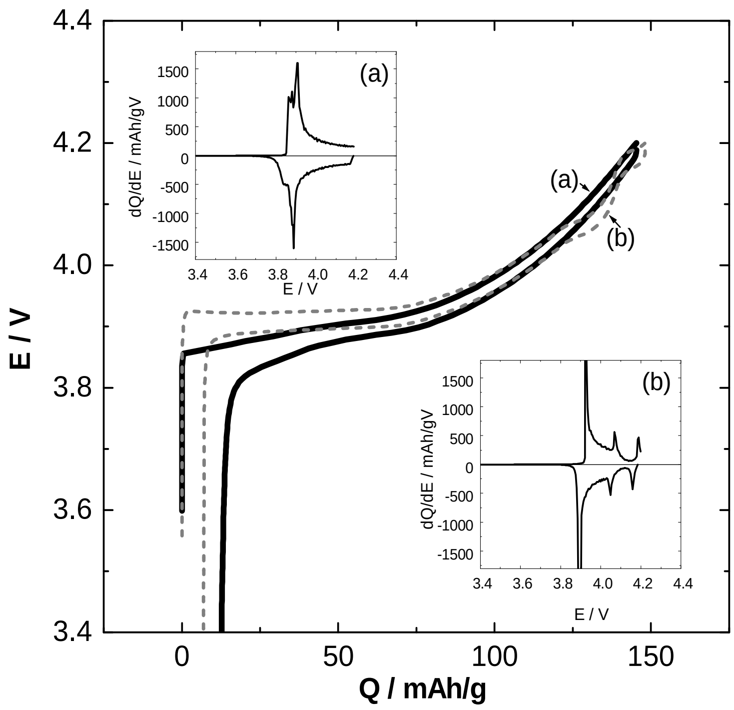

Fig. 1 Charge and discharge curves of (a) $Li/LiMg_yCo_{1-y}O_2$ and (b) $Li/LiCoO_2$ cells operated in voltages of 3.0-4.2 V at 20°C together with the dQ/dE. Difference is clearly seen in dQ/dE.

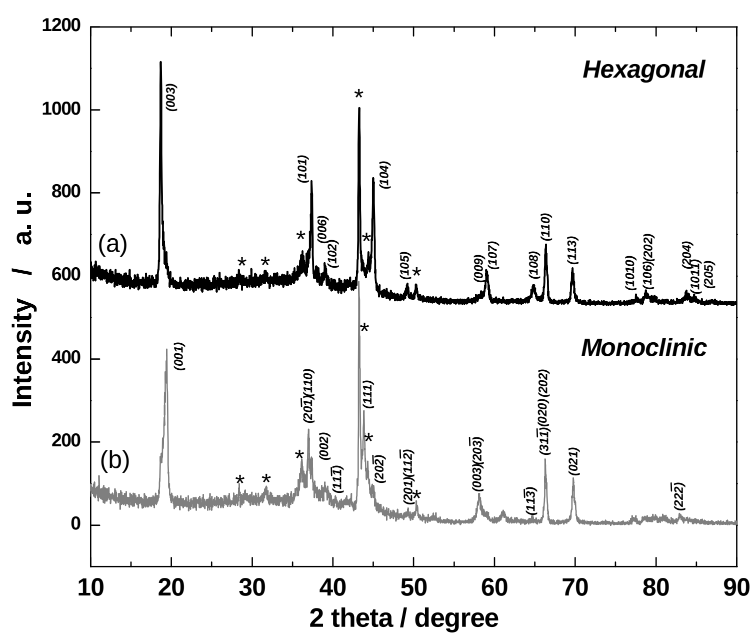

Fig. 2 XRD patterns of (a) $Li_{1-x}Mg_yCo_{1-y}O_2$ and (b) $Li_{1-x}CoO_2$ charged to 4.7V. (*Sample holder peak)