

# Thermal stabilities of lithium magnesium cobalt oxides for high safety lithium-ion batteries

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Available online 22 June 2005

## Abstract

Lithium magnesium cobalt oxide (LMCO) was synthesized with heating a reaction mixture of dehydrated magnesium cobalt hydroxide and  $\text{Li}_2\text{CO}_3$  to stabilized crystal structure of  $\text{LiCoO}_2$ . The sample was characterized by XRD. All diffraction lines could be indexed by assuming a hexagonal lattice. Rietvelt analysis indicated that magnesium were located at cobalt site in the layered structure. The voltage plateau around 4.1 V (versus Li) for  $\text{LiCoO}_2$  was not observed for LMCO. The prismatic lithium-ion batteries of lithium magnesium cobalt oxide and graphite with  $\gamma$ -butyrolactone (GBL) were fabricated and examined in terms of rate capability, low temperature discharge characteristics, high-temperature storage, and safety inspection by so-called hot pot test of the positive electrolyte. Interesting phenomenon on thermal stability of the lithium magnesium cobalt oxide was reported.

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*Keywords:* Lithium magnesium cobalt oxide; Thermal stability; Lithium-ion batteries

## 1. Introduction

Lithium cobalt oxide has been widely used as a positive active material in lithium-ion batteries during the last decade. Many reports on lithium cobalt oxide have been published in various fields such as solid-state chemistry and electrochemistry [1–7]. Tukamoto and West [3] reported the conductivity of  $\text{LiCoO}_2$  doped some kinds of element and they concluded that the conduction in  $\text{LiCoO}_2$  was p-type and acceptor doping with Mg enhanced the conductivity. Crystal structure during the electrochemical charge and discharge changes from hexagonal to monoclinic phase near  $\text{Li}_{0.45}\text{CoO}_2$ . Ohzuku and Ueda showed that the electrochemical reaction of  $\text{Li}_x\text{CoO}_2$  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]. However, magnesium-doped  $\text{LiCoO}_2$  proceeds a topotactic reaction in one hexagonal phase [3,5]. The thermal behaviors of the materials have to be fully evaluated before the application to the lithium-ion batteries. We have investigated Mg-doped  $\text{LiCoO}_2$  materials from the viewpoints of both safety and

electrochemical characters. In this paper, we report the cell performance of prismatic lithium-ion battery consisting of lithium magnesium cobalt oxide and graphite with GBL-based electrolyte, and we discuss safety issue for lithium-ion batteries.

## 2. Experimental

Magnesium-doped  $\text{LiCoO}_2$  was prepared by heating the reaction mixture of  $\text{Li}_2\text{CO}_3$  and Mg-doped  $\text{Co}_3\text{O}_4$  that was prepared by a co-precipitation method. The prepared samples were characterized by XRD (X'Pert, Phillips), BET surface area, tap density, and distribution of particle size. Morphology of particles was observed by SEM (S-4500 Hitachi Co. Ltd., Japan). In order to collect electrochemical data, 2016 coin-hardware was used. Positive electrode for prismatic cell were prepared by blending LMCO, acetylene black, and polyvinylidene fluoride (PVdF) in weight ratio of 100:2:2, respectively, dispersed in *N*-methyl-2-pyrrolidone (NMP), coating on both side of an aluminum foil with a coater, and pressing to obtain an even thickness of desired

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value. The electrodes were heated at about 100 °C to remove NMP. The negative electrodes were prepared from graphite and acrylic rubber binder dispersed in water with CMC. After coating the mix on both sides of copper foil with a coater and heated at about 110 °C to remove water, the electrodes were pressed. The positive and negative electrodes were dried at 85 °C for 3 h under vacuum before use. Separator used was polyethylene micro porous membrane. To fabricate the prismatic lithium-ion batteries (850 mAh; 34 mm width, 50 mm height, and 5.2 mm thickness), the positive and negative electrodes were wound with separator to make an element, and then sealed in prismatic aluminum housing case. Hot pot tests were carried out with heating charged-positive electrode in nickel-plated steel can at heating rate of 5 °C min<sup>-1</sup>. Other sets of experimental conditions are given in Section 3.

### 3. Results and discussion

LMCO (Mg/(Co + Mg) = 0.07) was characterized by XRD, BET surface area, and tap density. Crystal structure was identified as a layered structure having  $a = 2.825 \text{ \AA}$  and  $c = 14.097 \text{ \AA}$  (XRD density of  $4.88 \text{ g cm}^{-3}$ ) in a hexagonal setting. Surface area and tap density are, respectively,  $0.52 \text{ m}^2 \text{ g}^{-1}$  and  $2.50 \text{ g cm}^{-3}$ . Fig. 1 shows the results of Rietvelt analysis. As seen in Fig. 1, magnesium ions are located at cobalt sites. Morphology of particles observed by SEM is shown in Fig. 2. The particles were well crystallized and nonporous body with smooth crystal surface can be seen. Average diameter of secondary particles was about 6  $\mu\text{m}$ . In order to design lithium-ion batteries with graphite, we need to know reversible capacity, so that LMCO was preliminary examined in 2016 coin cells with lithium negative electrode under the same conditions as for the lithium-ion batteries except cell hardware and negative electrode. Fig. 3 shows the charge and discharge curves of Li/LiMg<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> cells operated in voltage of 3.0–4.2 V at constant current of 1/5C at 20 °C. The reversible capacity observed was  $139 \text{ mAh g}^{-1}$ . From these data, we have designed prismatic lithium-ion batteries of LMCO and graphite.

Fig. 4 shows the rate capability for thus designed prismatic lithium-ion batteries with GBL-based electrolyte. For rate capability tests, the cell was charged at 820 mA (1C rate) up to

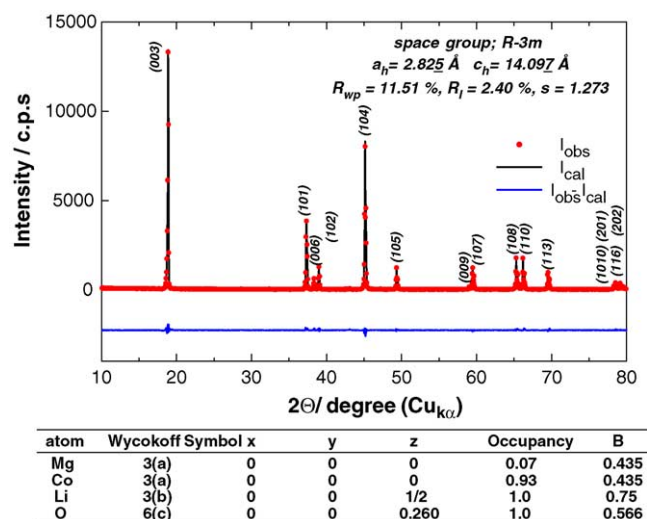


Fig. 1. Results on Rietvelt analysis by assuming a space group symmetry of  $R3m$  ( $a = 2.825 \text{ \AA}$  and  $c = 14.097 \text{ \AA}$  in hexagonal setting). Magnesium ions are located at cobalt sites, not lithium sites.

4.2 V followed by constant voltage until the current reduced to 1/20C mA. As seen in Fig. 4, 96 or 82% of nominal capacity is respectively delivered at 1 or 2C rate. Rate capability is acceptable. Even 2C rate, i.e., 1.7 A continuous discharge, this cell can deliver electricity for 30 min. The temperature on the cell surface increases about 10 °C when a battery is discharged at 2C rate.

Fig. 5 shows the preliminary cycle tests on prismatic lithium-ion battery of LMCO with graphite, operated in voltage of 3.1–4.2 V at 23 °C together with capacity examined at 0.2C rate every 100 cycles. For cycle tests, the lithium-ion batteries were charged at 1C mA until voltage reached 4.2 V at which constant-voltage charging was applied until current reduced to 1/10C mA. Ten minutes of relaxation were used after charging and discharging. As seen in Fig. 5, the battery delivers 600 mAh at 1C rate or 700 mAh at 0.2C rate even after 500 cycles. Serious increase in polarization by cycling cannot be seen in Fig. 5 for lithium-ion battery of LMCO and graphite with GBL-based electrolyte.

Fig. 6 shows the dependence of temperature upon discharge capacity when the cells were examined at 1C rate. As can be seen in this figure, the cell can be operated even at  $-20 \text{ }^\circ\text{C}$ . Discharged capacity observed at a rate of 1C rate

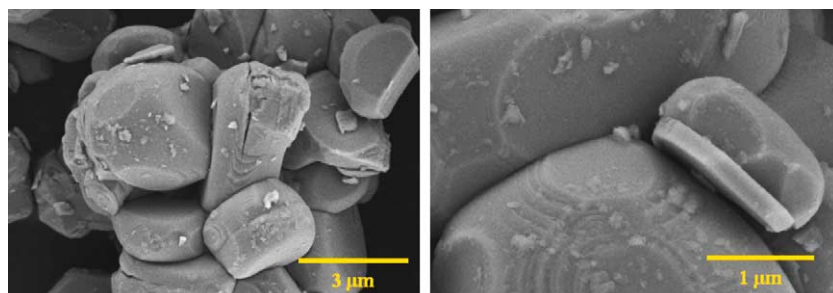


Fig. 2. SEM photographs of lithium magnesium cobalt oxide.

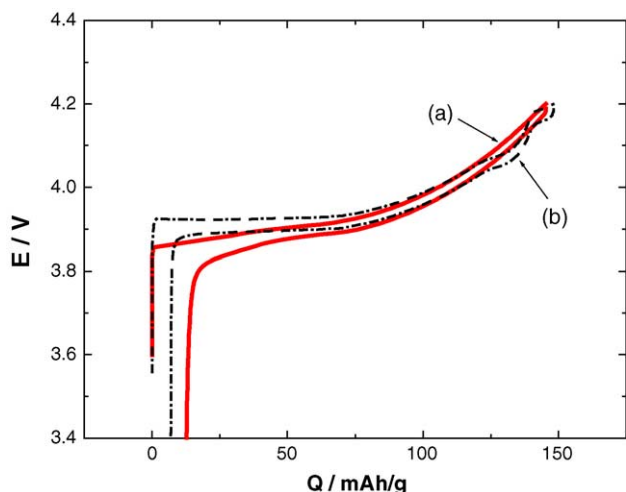


Fig. 3. Charge and discharge curves of (a) Li/LMCO and (b) Li/LiCoO<sub>2</sub> cells operated in voltage of 3.0–4.2 V at 1/5C rate at 20 °C.

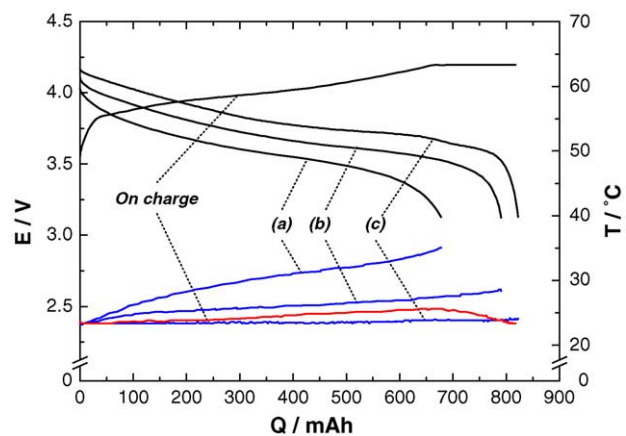


Fig. 4. Rate capability tests on the prismatic lithium-ion battery of LMCO with graphite negative electrode. Nominal capacity is 850 mAh. The cell was discharged at (a) 2C, (b) 1C and (c) 0.2C rate at 23 °C.

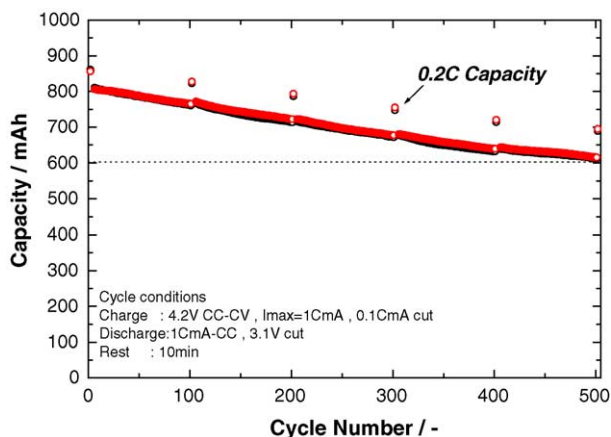


Fig. 5. Cycle tests on the prismatic lithium-ion battery of LMCO with graphite negative electrode. The battery was cycled in voltages of 3.1–4.2 V at 1C rate at 23 °C.

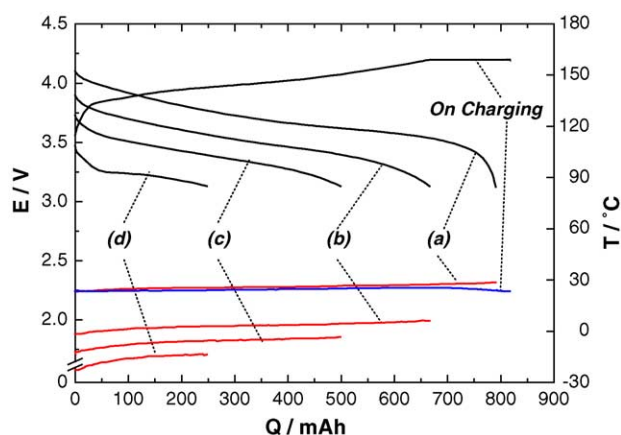


Fig. 6. Effect of temperature on the discharge capacity of the lithium-ion battery of LMCO with graphite. The cell was discharged at 1C rate at (a) 23°, (b) 0°, (c) -10°, and (d) -20 °C. The temperature on the cell surface is also shown.

at 0, -10, or -20 °C was, respectively, 84, 63, or 33% with respect to that examined at 23 °C.

Fig. 7 shows the results of high-temperature storage tests. The fully charged cells were stored at 100 °C for 5 h. About 95% of capacity was observed even after 5 h-storage at 100 °C.

For safety inspection, we have conducted so-called hot pot tests of charged-positive electrodes. Fig. 8 shows the results on hot pot tests for positive electrodes in various charged states. There is no signal due to heat generation until temperature reaches about 180 °C for all samples. As is clearly seen in Fig. 8, thermal stability increases with increasing charge capacity, and the heat generation becomes milder with higher charging voltage.

From these results, LMCO is superior to LiCoO<sub>2</sub> as a positive electrode for high safety advanced lithium-ion batteries. We have already reported the thermal behaviors of

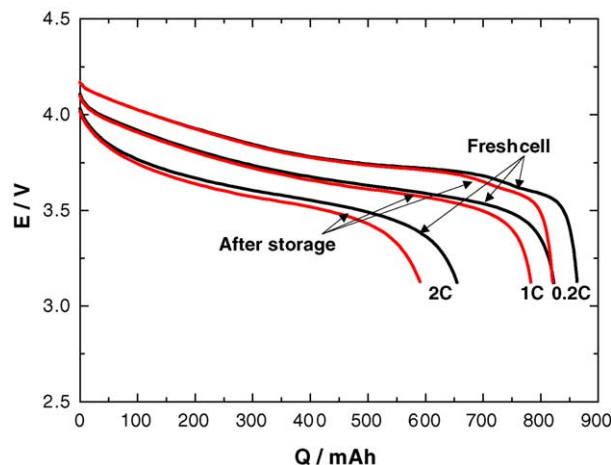


Fig. 7. Charge and discharge curves of the prismatic lithium-ion battery of LMCO and graphite. The broken-in batteries were stored in fully charged state at 100 °C for 5 h. Charge and discharge curves before and after storage were compared.

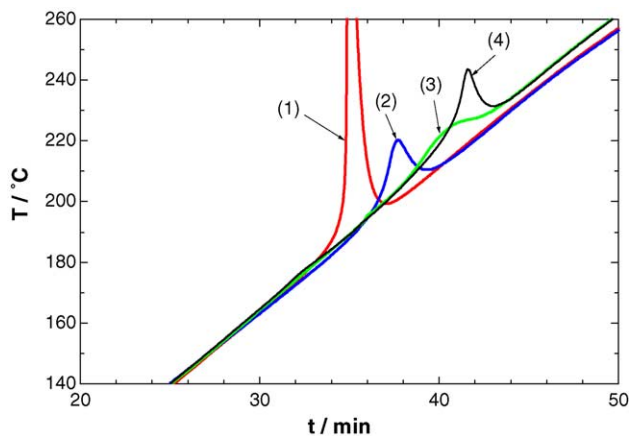


Fig. 8. Results on hot pot tests for LMCO-positive electrodes in various charged states prepared at (1) 4.25 V, (2) 4.4 V, (3) 4.6 V or (4) 4.8 V of charge-end voltage.

$\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  [8,9]. According to high-temperature XRD examinations [9] on the charged  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  ( $[\ ]_{0.67}\text{Li}_{0.33}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ) prepared at 4.45 V in lithium-ion batteries, we observed phase change from a layered to spinel-framework structure by heating, which seemed to be a key to reduce active oxygen reacting with organic and then to reduce heat generation. In the same manner, observations by hot pot tests with EGA/MS, ARC, high-temperature

XRD, and DSC will give more insights into the mechanism of less heat generation of LMCO than that of  $\text{LiCoO}_2$  which will be discussed in future paper in due course.

### Acknowledgement

One of us (H.Y.) wishes to thank professor Tsutomu Ohzuku, Osaka City University, for his help on preparing the manuscript.

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