

Short communication

# Preparation and characterization of spinel $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$ by oxalate precipitation

Byeong Woo Lee\*

Department of Materials Engineering, Korea Maritime University, Pusan 606-791, South Korea

Received 4 September 2001; accepted 10 January 2002

## Abstract

$\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$  ( $x = 0, 1/9, 1/6$ ) powders have been synthesized by an oxalate precipitation method. Single phase spinel  $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$  is formed at temperatures as low as 450 °C. Fourier transform infrared analysis shows that the spinel powder prepared at 600 °C has better phase quality than the powder prepared at 750 °C by a conventional solid-state reaction. X-ray diffraction and thermal gravimetric-differential thermal analysis show phase transition and impurity phase formation at three temperatures. It is also found that spinel phase stability increases with increase in cobalt (Co) content. The effects of Co content on the spinel lattice constant, high temperature stability, transition temperature and capacity on cycling are investigated. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium-ion battery;  $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$ ; Oxalate precipitation; Low temperature synthesis; Phase stability; Cycle performance

## 1. Introduction

Lithium-ion rechargeable batteries find wide application in modern portable electronic devices.  $\text{LiCoO}_2$  is commonly used as the cathode material in commercial lithium-ion batteries [1]. Nevertheless, it has several drawbacks which include high cost and toxicity.  $\text{LiMn}_2\text{O}_4$  spinel is one of the alternative cathode materials for lithium-ion batteries due to its economical and environmental advantages. An important problem prohibiting it from wider use as a cathode material is capacity fading during cycling [2–4]. To overcome the problem, several research groups have studied the properties of transition metal doped spinels,  $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$  ( $M = \text{Ni}, \text{Fe}, \text{Co}, \text{Cr}$ ) [5–7]. The improvement in the cycle performance of the modified spinel can be explained by the lowered lattice constant by adding the dopants, which results in the smaller volume change and a stable spinel framework during cycling [8]. Furthermore, the enhanced stability of the spinel phase leads to lower cathode solubility in the electrolyte solution and easier lithium diffusion during cycling, which is also believed to give rise the improved cycle performance [7,9]. The proposed enhanced phase stability of the doped spinel has not been clearly shown.

In the present study, oxalate precipitation is used as a novel wet chemical process to prepare the series of spinel  $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$  fine powders. The effects of Co substitution for Mn on the spinel lattice constant, phase stability and cycle performance are investigated.

Spinel  $\text{LiMn}_2\text{O}_4$  is usually synthesized at high temperatures (750–850 °C) by solid-state reactions using raw materials of oxides and/or carbonates. At lower temperatures, some  $\text{Mn}_2\text{O}_3$  may be present as an impurity which only disappears at 750 °C. At temperatures above 850 °C, other impurity phases of  $\text{Li}_2\text{MnO}_3$  and  $\text{LiMnO}_2$  may appear [9,10]. Therefore, the synthesis temperature range is quite narrow. Wet chemical synthesis such as oxalate precipitation employed in this study, rather than a solid-state reaction, normally can reduce the synthesis temperature and extend the synthesis temperature range because of homogeneous mixing of the starting components.

The quality of  $\text{LiMn}_2\text{O}_4$ -based materials for application in lithium-ion batteries also depends on powder morphology and particle size. Electrode materials, which have smaller particle size and larger surface area, usually deliver a high capacity [11,12]. Wet chemical synthesis also makes it possible to improve the morphology and prepare the high surface-area product at a low heating temperature in a shorter time.

This study examines the effects of important processing parameters, such as synthesis temperature, composition and cooling condition, on spinel preparation for application in lithium-ion batteries.

\* Tel.: +82-51-410-4356; fax: +82-51-404-3986.

E-mail address: bwlee@kmaritime.ac.kr (B.W. Lee).

## 2. Experimental

Metal (Li, Mn, and Co) acetates required for  $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$  ( $x = 0, 1/9, 1/6$ ) spinel preparation were dissolved in ethylene glycol. A mixed solution of 0.3 M was prepared. Metal oxalate precipitates were formed when the solution was added to a 0.9 M solution of oxalic acid dissolved in acetone. The system was controlled to keep a constant bath temperature of 80 °C during the reaction. The solution that contained the precipitates was slowly dried up to 150 °C at a heating rate of 5 °C per hour to form a solid precursor without a filtering and washing process. The powders so obtained were ground and fired in air at 200–1000 °C for 10 h. The powders were cooled to the room temperature at a cooling rate of 2 °C per minute or quenched by pouring the hot powders directly on to a stainless-steel plate. For comparison, some  $\text{LiMn}_2\text{O}_4$  powders were prepared by a solid-state reaction of  $\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$ . The properties of the prepared powders were characterized by thermal gravimetric-differential thermal analysis (TG-DTA, heating and cooling rate of 5 °C per minute), X-ray diffraction (XRD), atomic absorption (AA), and Fourier transform infrared spectroscopy (FTIR). The morphology of the prepared powders was examined by scanning electron microscopy (SEM).

Battery cycling tests were carried out for the prepared spinel powders at a constant current density of  $2 \text{ mA cm}^{-2}$  between cut-off potentials of 4.5 and 3.5 V. A mixture of spinel powder, carbon black and polytetrafluoroethylene (PTFE) binder was used as the positive electrode and a lithium metal foil was used as the negative electrode. The electrolyte was 1 M  $\text{LiClO}_4$ , ethylene carbonate/dimethyl carbonate (EC/DMC).

## 3. Results and discussion

### 3.1. Powder preparation

A normal oxalate precipitation method usually delivers compositional differences of metal ions between the initial solution and the final precipitates. For  $\text{LiMn}_2\text{O}_4$ , AA analysis showed that 0.6% of Li and 7.4% of Mn remained unreactive in the solution after precipitation. In order to control precisely the desired composition with exact values of  $x$ , a precipitation followed by an evaporation process was used. This evaporative decomposition process of the solution that contained precipitates provided a precise composition control. This was hardly obtainable in the normal oxalate precipitation method which involved a filtering and washing

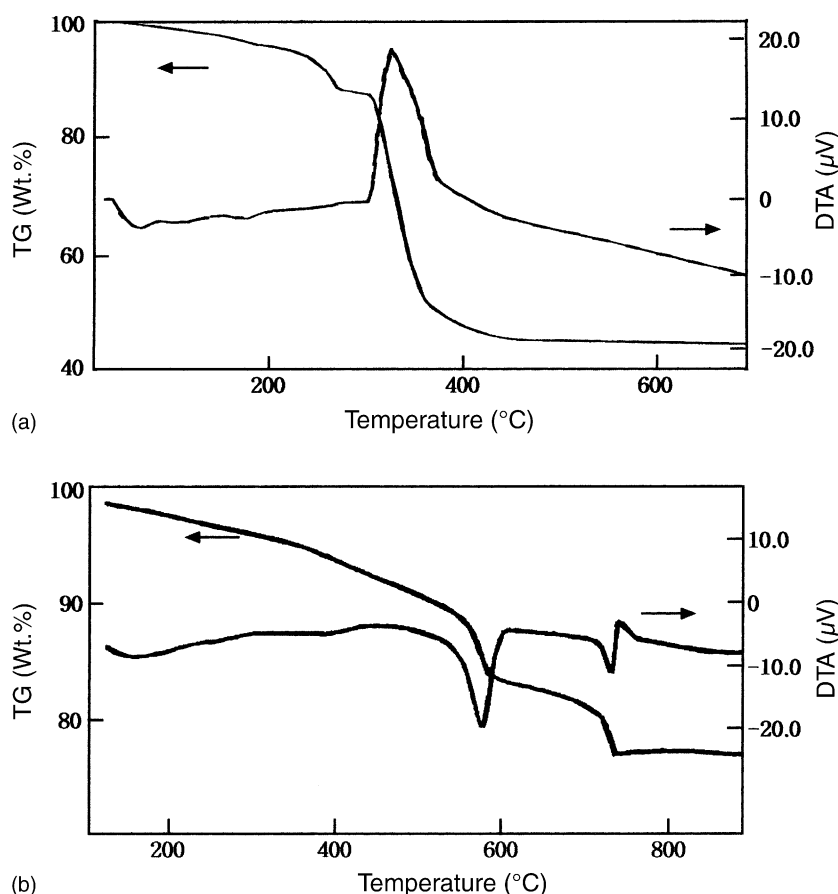


Fig. 1. TG-DTA curves of  $\text{LiMn}_2\text{O}_4$  powders prepared by (a) oxalate precipitation and (b) solid-state reaction.

process. In the evaporative decomposition process, the composition between the starting solution and the prepared powders determined by AA analysis was identical.

TG-DTA analysis of  $\text{LiMn}_2\text{O}_4$  powders prepared by oxalate precipitation is presented in Fig. 1(a). The reaction, which involves a weight loss from decomposition of organic precursors, is finished at around  $450^\circ\text{C}$ . This shows that the synthesis temperature is as low as  $450^\circ\text{C}$ . The corresponding analysis of solid-state reaction powders made from  $\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$  is shown in Fig. 1(b). The observed weight loss results from vaporization of  $\text{CO}_2$  and extra  $\text{O}_2$  in the spinel composition. There is spinel synthesis with an exothermic reaction at around  $750^\circ\text{C}$ . The TG-DTA results for the oxalate precipitates and the solid-state reaction products are identical, as are the results obtained by XRD analysis (Fig. 2) of powders heat-treated at different temperatures. For the oxalate precipitates (Fig. 2(a)), well-developed peaks of a single phase spinel are formed at  $600^\circ\text{C}$  from the complex metal-oxalate peaks for the

precipitates prepared at  $80^\circ\text{C}$ . A  $750^\circ\text{C}$  is the lowest synthesis temperature of single phase spinel from the powders by solid-state reaction (Fig. 2(b)). The precursors ( $\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$ ) shown at RT in Fig. 2(b) are basically amorphous. Below the synthesis temperatures for the single spinel phase, an intermediate impurity phase indexed as  $\text{Mn}_2\text{O}_3$  is formed in both methods.

The XRD results, however, do not disclose the degree of phase (crystal) quality of the synthesized spinel powders. The FTIR spectra of powders prepared at different heat-treatment temperatures for 10 h (oxalate precipitates) and 24 h (solid-state reaction product) are shown in Fig. 3. In the case of oxalate precipitates (Fig. 3(a)), the spinel peaks at  $613 (\times)$  and  $505 \text{ cm}^{-1} (\otimes)$  are more prominent at lower temperatures than those of solid-state reaction powders (Fig. 3(b)). This suggests that the spinel powder prepared at  $600^\circ\text{C}$  for 10 h has a high degree of phase quality compared with the spinel powder prepared by solid-state reaction at  $750^\circ\text{C}$  for 24 h.

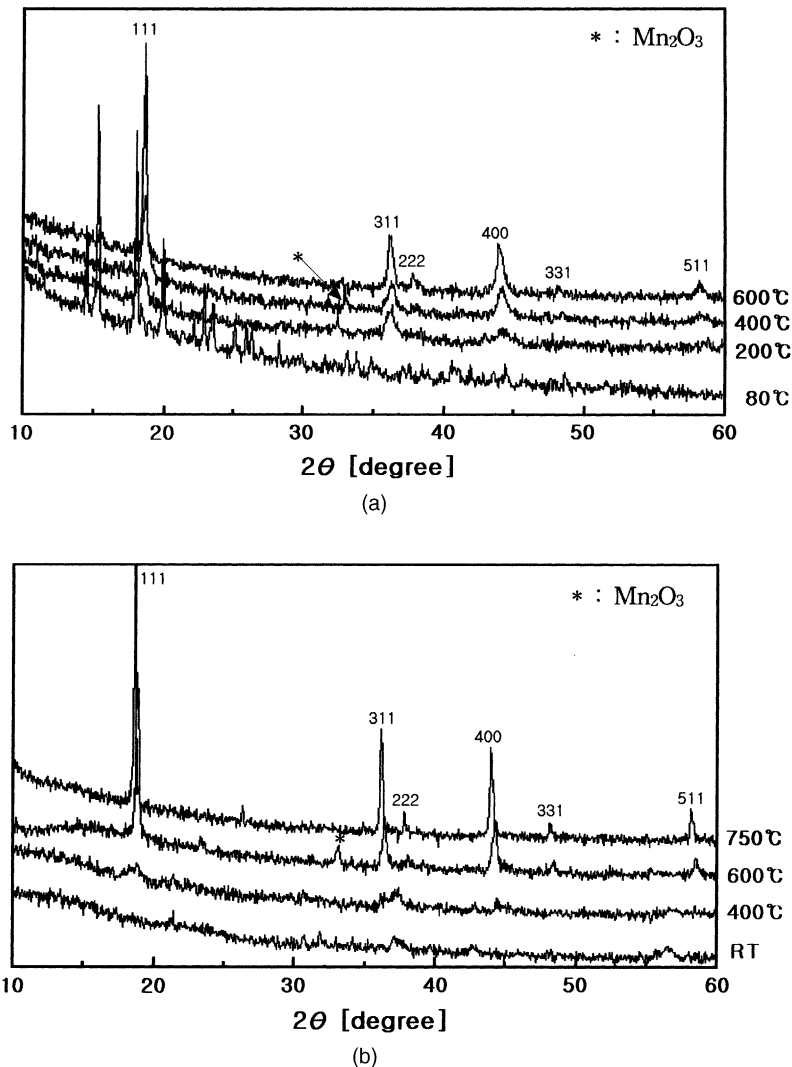


Fig. 2. XRD patterns of prepared  $\text{LiMn}_2\text{O}_4$  powders heat treated at various temperatures: (a) oxalate precipitation and (b) solid state reaction. Miller indices represent spinel phase.

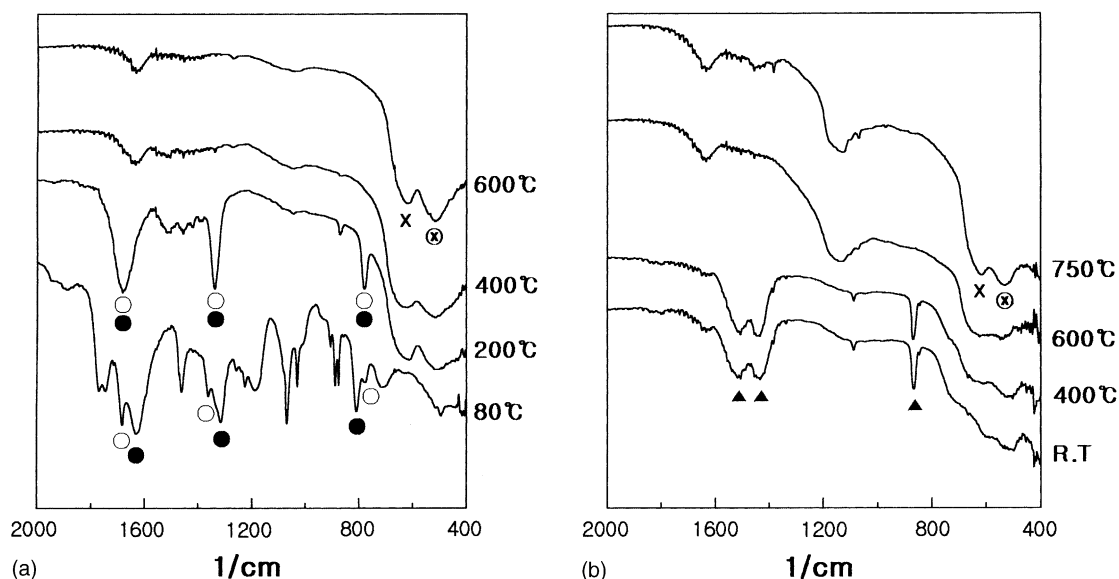


Fig. 3. FTIR spectrum of prepared  $\text{LiMn}_2\text{O}_4$  powders: (a) oxalate precipitation heat-treated for 10 h ((○) Li oxalate; (●) Mn oxalate; (×, ⊗) spinel) and (b) solid-state reaction for 24 h at different temperatures ((▲) Li carbonate; (×, ⊗) spinel).

The particle size of  $\text{LiMn}_2\text{O}_4$  powders prepared by oxalate precipitation at  $750\text{ °C}$  for 10 h is smaller than  $0.3\text{ }\mu\text{m}$  (Fig. 4), and the specific surface-area determined by Brunauer, Emmett, and Teller (BET) analysis is  $6.93\text{ m}^2\text{ g}^{-1}$ . The surface-area is about three times as large as that ( $2.07\text{ m}^2\text{ g}^{-1}$ ) of the solid-state reaction powders prepared at  $750\text{ °C}$  for 24 h.

### 3.2. Phase transition and structural stability of spinel $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$

The results of TG-DTA analysis of spinel  $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$  ( $x = 1/6$ ) powders prepared by oxalate precipitation are presented in Fig. 5. There are discontinuities in the curves at temperatures  $T_1$  ( $720\text{ °C}$ ) and  $T_2$  ( $940\text{ °C}$ ) during heating,

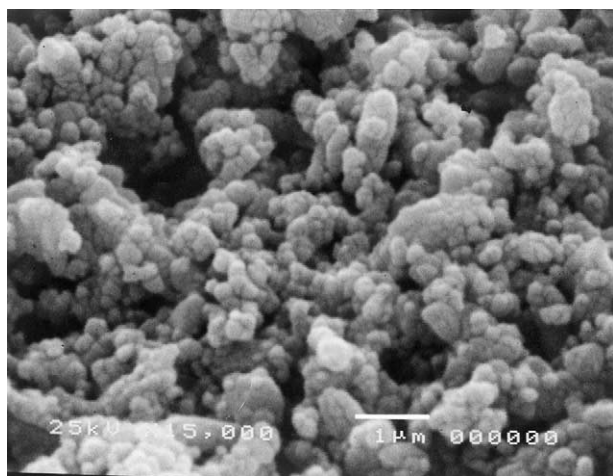


Fig. 4. Scanning electron micrograph of oxalate precipitated  $\text{LiMn}_2\text{O}_4$  powder showing fine particle morphology.

and  $T_2'$  ( $930\text{ °C}$ ) during cooling. The temperatures are associated with phase transitions. The DTA analysis shows that the transition at  $T_1$  denotes a continuous decomposition (endothermic) reaction, while those at  $T_2$  and  $T_2'$  are related to an additional endothermic and an exothermic reaction, respectively. The weight loss above  $T_1$  is attributed to the extraction of oxygen from the structure, and to the formation of oxygen-deficient spinel and  $\text{Li}_2\text{MnO}_3$  phases. The results are the same as those reported by Gao and Dahn [9,13]. Unlike the transition at  $T_1$ , TG-DTA analysis suggests that  $T_2$  and  $T_2'$  are superheating and supercooling temperatures of a transition. They are slow because the transitions require extra energy to nucleate and grow another phase. XRD measurements of quenched samples show that the main impurity phase formed above  $T_2$  is  $\text{LiMnO}_2$ . The XRD patterns of  $\text{LiMn}_2\text{O}_4$  powders quenched from  $1000\text{ °C}$  are presented in Fig. 6. A considerable amount of impurity phase, mainly  $\text{LiMnO}_2$ , is detected in the quenched  $\text{LiMn}_2\text{O}_4$  powder ( $x = 0$ ) prepared by solid-state reaction (denoted as SSR), while reduced impurity content is shown in the spinel powder ( $x = 0$ ) obtained by oxalate precipitation. No noticeable impurity phases are found in the Co-doped spinel powder ( $x = 1/6$ ) prepared by oxalate precipitation. This suggests that the spinel structure in Co-doped spinel, especially in powders prepared by oxalate precipitation, is stable and the impurity phases formed above  $T_2$  are transformed to spinel easily during quenching. It is assumed that the poor phase homogeneity due to the mechanical mixing in powders prepared by solid-state reaction results in the presence of impurity phases in quenched powders. If samples are heated above  $T_1$  or  $T_2$ , they must be cooled slowly to permit the impurity phases to convert back to the spinel phase because the transition requires thermally activated oxygen diffusion and/or nucleation and growth of the spinel phase. Therefore,

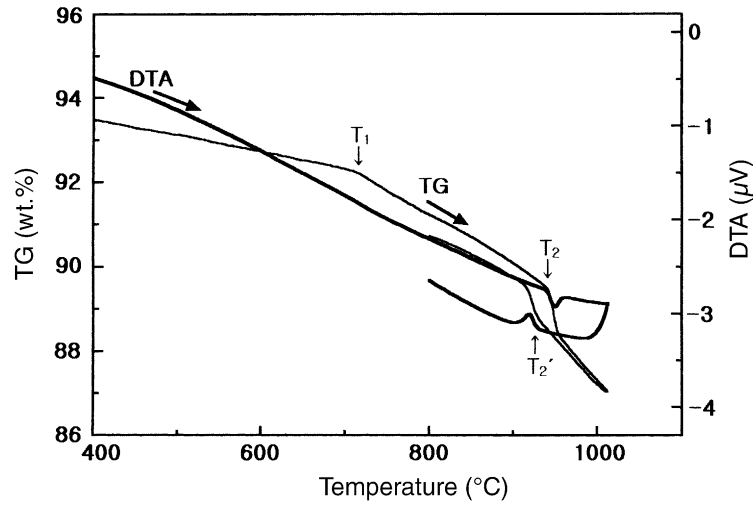


Fig. 5. TG-DTA curves of oxalate precipitated  $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$  ( $x = 1/6$ ) powder. Before analysis, the powder has been heat-treated at  $600^\circ\text{C}$  for 10 h.

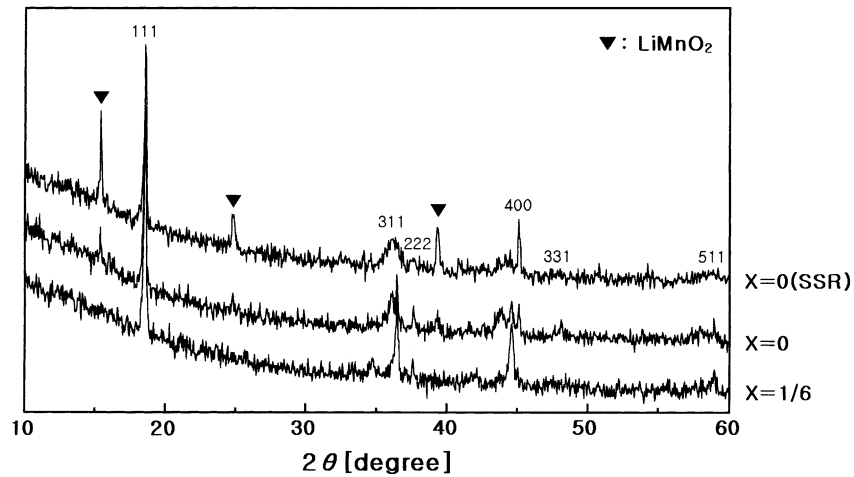


Fig. 6. XRD patterns of quenched  $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$  powders from  $1000^\circ\text{C}$  (SSR for solid-state reaction product and others for oxalate precipitation). Miller indices represent spinel phase.

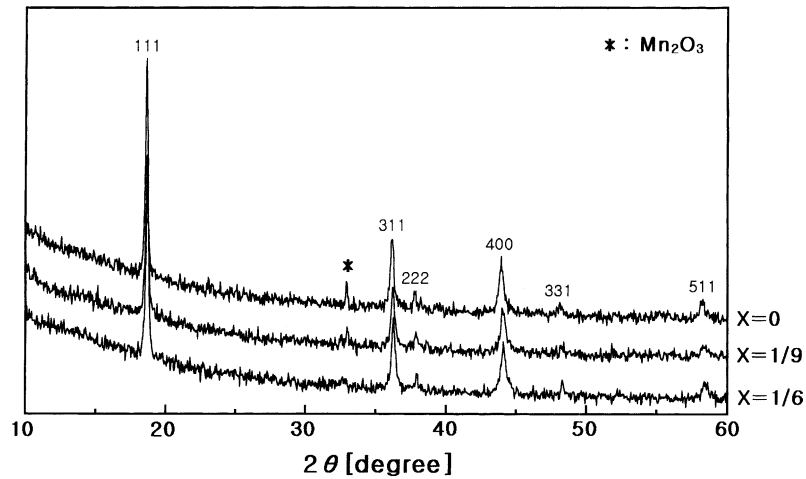


Fig. 7. XRD patterns of Li-deficient  $\text{Li}_{1-0.2}\text{Co}_x\text{Mn}_{2-x}\text{O}_4$  powders prepared by oxalate precipitation at  $700^\circ\text{C}$  for 10 h. Miller indices represent spinel phase.

to obtain the spinel single phase, a controlled combination of the processing parameters such as synthesis temperature, cooling rate and composition is essential.

The transition temperature,  $T_1$ , shows no noticeable change with Co content, while  $T_2$  and  $T_2'$  change drastically with Co content. For example, the transition temperatures change from 935 °C ( $T_2$ ) and 900 °C ( $T_2'$ ) for  $\text{LiMn}_2\text{O}_4$  to 940 °C ( $T_2$ ) and 930 °C ( $T_2'$ ) for  $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$  ( $x = 1/6$ ). The transition at  $T_2$  and  $T_2'$  is considered to be a first-order transition, which is accompanied by latent heat of nucleation and growth that gives rise to a temperature difference ( $\Delta T = T_2 - T_2'$ ) during heating and cooling [14]. In this study, the  $\Delta T$  of  $\text{LiMnO}_2$  and Co-doped ( $y = 1/6$ ) spinel was 35 and 10 °C, respectively. The lower  $\Delta T$  in Co-doped spinel means a lower energy barrier for the transition: spinel  $\leftrightarrow$   $\text{LiMnO}_2$ . This makes the transition easier, because  $T_2$  and  $T_2'$  were superheating and supercooling temperatures of the transition, respectively. The lower  $\Delta T$  demonstrates the increased spinel phase stability in Co-doped spinel shown in Fig. 6. Since  $T_2$  and  $T_2'$  are the transition temperatures for spinel  $\leftrightarrow$   $\text{LiMnO}_2$ , and  $\text{LiMnO}_2$  is the high temperature form, the higher values of both  $T_2$  and  $T_2'$  in Co-doped spinel also suggest that Co-doping causes an enhancement in spinel phase stability.

The XRD patterns for Li-deficient spinel prepared at 750 °C are shown in Fig. 7. Lithium deficiency in  $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$  spinel give rise because of Mn/Co-oxide phase formation. As expected,  $\text{Mn}_2\text{O}_3$  was formed in  $\text{Li}_{1-0.2}\text{Mn}_2\text{O}_4$  ( $x = 0$ ), while, for the case of Co-doped  $\text{Li}_{1-0.2}\text{Co}_x\text{Mn}_{2-x}\text{O}_4$  ( $x = 1/6$ ) spinel, no noticeable amount of the impurity phase was formed. This is further evidence of the increased spinel phase stability in Co-doped spinel.

The cubic (spinel) lattice constant,  $a$ , decreases with increase in Co content, namely, from 8.24 Å for the spinel  $\text{LiMn}_2\text{O}_4$  ( $x = 0$ ) to 8.19 Å for the spinel with  $x = 1/6$ .

### 3.3. Cell performance

The discharge characteristics of the oxalate precipitation-derived spinel ( $x = 0, 1/9$  and  $1/6$ ) prepared at 700 °C for 10 h are shown in Fig. 8. As a rapid and severe test to show that the Co content effects the battery cycling performance, the test was carried out for just seven cycles at a relatively high current density of 2 mA  $\text{cm}^{-2}$ . Reduced capacity fading is found for the Co-doped spinel, although the material gives a lower initial capacity. The capacity fade of the spinels with  $x = 0, 1/9$  and  $1/6$  was 21, 15 and 4% for first seven cycles, respectively. On the other hand, the initial capacity decreased from 128 mAh  $\text{g}^{-1}$  for the spinel with  $x = 0$  to 123 and 87 mAh  $\text{g}^{-1}$  for the spinels with  $x = 1/9$  and  $1/6$ , respectively. The improved cycling performance, but with sacrifice in initial capacity, can be attributed to a lower lattice constant and increased phase stability in the Co-doped spinel, as described.

Extensive studies for the optimum composition and preparation conditions for improved electrochemical properties,

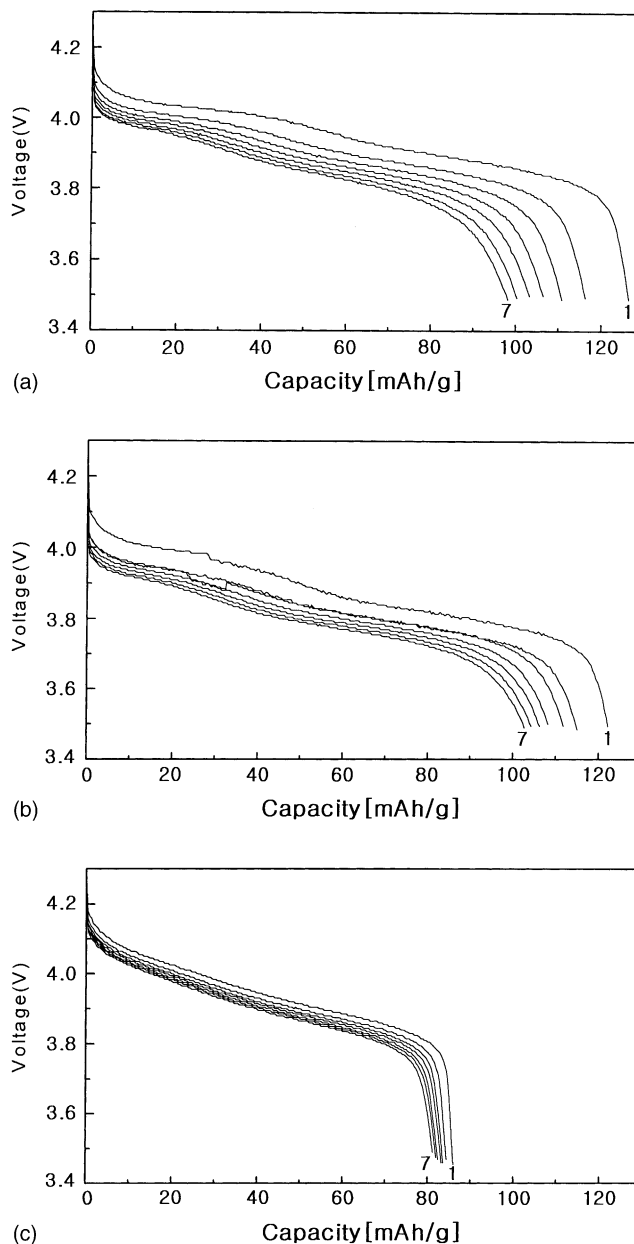


Fig. 8. Discharge characteristics of first seven cycles of oxalate precipitated  $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$ : (a)  $x = 0$ ; (b)  $x = 1/9$ ; and (c)  $x = 1/6$ .

including high initial capacity and cycling performance, are underway.

## 4. Conclusions

$\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$  ( $x = 0, 1/9, 1/6$ ) spinel was prepared by oxalate precipitation which involved evaporative decomposition. Phase stability is studied with respect to the effect of Co content.

The spinel is synthesized at low temperatures and yields a product with high surface-area. Detailed TG-DTA and XRD analyses of the prepared and quenched samples have shown

phase transitions at three temperatures and enhanced phase stability in Co-doped spinel. In the case of the powders prepared above the transition temperatures, undesirable phases are formed. To lessen the impurity phases, the powders must be cooled slowly to permit the phases to convert back to the spinel phase. The cubic lattice constant, which may affect cycling behavior, decreases with increase in Co content.

Improved phase stability and cycling behavior are obtained for the Co-doped cathode. The Co-doped phases are more tolerant to repeated lithium extraction and insertion than the undoped  $\text{LiMn}_2\text{O}_4$  phase, but at the expense of lower initial capacity. Capacity fading is suppressed by increasing the Co content.

### Acknowledgements

This work was supported by Grant No. KOSEF 97-0300-05-01-3 from the Korea Science and Engineering Foundation.

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