

# Storage and cycling performance of Cr-modified spinel at elevated temperatures

Masaki Yoshio<sup>\*</sup>, Yongyao Xia<sup>1</sup>, Naoki Kumada, Shuhua Ma

*Department of Applied Chemistry, Saga University, Saga 840-8502, Japan*

Received 27 April 2000; received in revised form 5 January 2001; accepted 17 January 2001

## Abstract

The influences of partial substitution of Mn in  $\text{LiMn}_2\text{O}_4$  with  $\text{Cr}^{3+}$  and  $\text{Li}^+$  on their charge/discharge profiles were quite different:  $\text{Cr}^{3+}$  affected it only in the high-voltage region, while  $\text{Li}^+$  showed in the both high and low voltage regions. Either  $\text{Cr}^{3+}$  or  $\text{Li}^+$  doping significantly improved the storage and cycling performance of spinel  $\text{LiMn}_2\text{O}_4$  at the elevated temperature, specially both doped spinel.  $\text{Li}_{1.02}\text{Cr}_{0.1}\text{Mn}_2\text{O}_4$  shows very low rate of capacity retention, 0.1% per cycle, and maintained a steady discharge capacity of 114 mAh/g, 95% of the initial discharge capacity over 50 cycles at 50°C. The chemical analysis and X-ray diffraction measurement indicate that the capacity losses of  $\text{LiMn}_2\text{O}_4$  is mainly due to the dissolution of Mn into electrolyte, further transformation to lithium-rich spinel  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ . The improvements in their electrochemical profiles for the  $\text{Cr}^{3+}$  and  $\text{Li}^+$  modified spinel is attributed to that the partial substitution of Mn stabilize its structure, thus minimizing the dissolution of Mn into electrolyte, as well as maintaining its original morphologies. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium; Lithium-ion batteries; Spinel; Manganese oxides

## 1. Introduction

In the view of the economic and environmental advantages, there is no question that spinel  $\text{Li}_x\text{Mn}_2\text{O}_4$  will be used as a cathode material for lithium-ion batteries instead of  $\text{LiCoO}_2$  currently commercialized if the problem associated with the capacity fading on cycling at the elevated temperature would be solved. The major factors responsible for the capacity loss at the elevated temperature are ascribed to follows: (i) an electrochemical oxidation of the electrolyte at high-voltage [1–3]; (ii) a slow dissolution of the  $\text{LiMn}_2\text{O}_4$  electrode into the electrolyte solution according to the disproportion reaction:  $2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$  [1–3]; (iii) the transformation to a more stable structure defect spinel [2,4]; (iv) Jahn–Teller effect [5].

Apparently, all above the proposed mechanism are mainly associated with the crystal structure and morphologies. Accordingly, many researches have been devoted to these directions. Amatucci et al. [6,7] have done numerous works

to improve the elevated temperature performance by minimizing the  $\text{LiMn}_2\text{O}_4$ /electrolyte interface, including directly preparing spinel with small surface, partially substituting Mn with fluorine, and coating spinel with  $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ . On the other hand, many efforts have been devoted to stabilize its structure by doping the foreign metal ions, these introduce ion includes  $\text{Li}^+$  and  $\text{Co}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Ga}^{2+}$ , etc. Robertson et al. [8] did a detailed work on Cr-doped spinel, they showed the greater improvement in the capacity retention at room temperature, however show an increase in capacity fade rate on cycling at 55°C, relative to room temperature. We have found the elevated temperature performance was greatly increased in these both  $\text{Cr}^{3+}$  and  $\text{Li}^+$  doped spinel. The improvement in cycleability could be ascribed to that either lithium or metal ions presented in the 16d octahedral sites stabilized the structure, thereby allowing a homogenous lithium insertion and extraction over the entire 4 V intercalated region [9], as well as reduce of the dissolution of Mn into the electrolyte. Interestingly, the influence of  $\text{Li}^+$  and  $\text{Cr}^{3+}$  on the electrochemical profile was quite different:  $\text{Cr}^{3+}$  affected it only in the high-voltage region, while  $\text{Li}^+$  showed in both high and low voltage region. The present work aims to evaluate the elevated temperature performance of these  $\text{Cr}^{3+}$  and  $\text{Li}^+$  doped spinel, also to clarify the mechanism responsible for

<sup>\*</sup> Corresponding author. Tel.: +81-952-28-8673; fax: +81-952-28-8591. E-mail address: yoshio@ce.saga-u.ac.jp (M. Yoshio).

<sup>1</sup> Present address: Osaka National Research Institute, 1-8-31 Midorigaoka, Ikeda, Japan.

improvement performance compared to the stoichiometric spinel  $\text{LiMn}_2\text{O}_4$  by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), as well as chemical analysis.

## 2. Experimental

Stoichiometric spinel  $\text{LiMn}_2\text{O}_4$  was obtained from the reaction of a stoichiometric mixture of  $\text{LiOH}$  and  $\text{Mn}_3\text{O}_4$  ( $\text{Li}/\text{Mn} = 0.50$  in molar ratio). The mixture was preheated at  $470^\circ\text{C}$  for 5 h, with further heating at  $530^\circ\text{C}$  for 5 h under an  $\text{O}_2$  flow, and a final heating at  $800^\circ\text{C}$  for 20 h in air, then cooled in 3 h in air. The  $\text{Cr}^{3+}$ -doped spinel was obtained by the same process, and  $\text{Cr}(\text{NO}_3)_3$  was used as Cr source.

The chemical composition of each examined compound was determined by chemical analysis [10]. X-ray diffraction was used to determine the structure of the compound and the changes in the structure before and after storage at  $50^\circ\text{C}$  with Fe  $\text{K}\alpha$  radiation on a Rigaku RINT 1000 X-ray diffractometer (Rigaku Ltd., Japan). The Brunauer, Emmett, and Teller (BET) method in which  $\text{N}_2$  gas adsorption was employed analyzed the specific surface area for each as-prepared compound in a Micromeritics Gemini 2375 (Rigaku Ltd., Japan). Each compound was heated to  $200^\circ\text{C}$  for 20 min to remove the adsorbed water before measurement. The scanning electron microscopy (SEM) picture was taken in a JSM-5300E Scanning Microscope (Japan Electron Ltd.).

The elevated temperature performance of spinel and Cr and Li-doped spinel studies were mainly done by two procedures: directly testing the cycle life of as-prepared compound in coin-typed cell at  $50^\circ\text{C}$ , and measuring the battery profile after storage at  $50^\circ\text{C}$ . Typical experiment consists in placing 100 mg of  $\text{LiMn}_2\text{O}_4$  or  $\text{Li}_{1+y}\text{Cr}_x\text{Mn}_{2-x}\text{O}_4$  powders in a polypropylene package, followed by immersing in 10 ml 1 M  $\text{LiPF}_6$ -ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:2 in volume) electrolyte solution in a plastic bottle, stored in a dry box at  $50^\circ\text{C}$  for 3 weeks. After soaking, the compounds were washed by DMC or water, and then SEM, XRD, and battery tests were carried out. If for the chemical analysis of the Mn and Li contents, the residual compounds were dissolved into ca. 0.02 M hydroxylamine solution. Mn content was determined by a complexometric titration method [10], and lithium content was analyzed by atomic adsorption spectrum.

The electrochemical cell we used was the same as that described previously [9]. The cathode consisted of 20 mg active material and 12 mg conducting binder (acetylene black–polytetrafluoroethylene composite). The electrolyte solution used here was 1 M  $\text{LiPF}_6$ -EC/DMC (1:2 in volume). The cycling tests for the  $\text{Li}/\text{LiMn}_2\text{O}_4$  cell were performed in a CR2032-type button cell. Cells were cycled between the voltages limits of 3.0 and 4.3 V; the typical charge and discharge current rate was  $C/3$  (40 mA/g), except where otherwise specified.

## 3. Results and discussion

It has been well recognized that the rechargeability of spinel can be improved by the addition of various metal ions, including  $\text{Li}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ga}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Al}^{3+}$ , and  $\text{Cr}^{3+}$ . These modifiers substitute for  $\text{Mn}^{3+}$  occupying the 16d octahedral sites in the spinel framework, thus stabilize the structure, thereby allowing a homogenous lithium insertion and extraction over the entire 4 V intercalated region. To our knowledge, among them, doping Li show the best improvement, e.g. the compound substituted with 2% (m/o)  $\text{Li}^+$ ,  $\text{Li}_{1.04}\text{Mn}_2\text{O}_4$  dropped the initial capacity to about 110 mAh/g, but kept 98% of initial capacity over 100 cycles at room temperature [9]. Briefly, the initial capacity can be estimated for the compound  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  by the following formula:  $C = 148(1 - (4 - Z)X)$  [11], where  $Z$  is the valance of the doped-ion, and  $X$  the molar fraction of the dopant. Apparently, for the same doped-level,  $\text{M}^{3+}$  show much higher initial capacity. Therefore, in the following studies, the influences on the electrochemical behaviour are investigated by varying either the amount of  $\text{Cr}^{3+}$  or  $\text{Li}^+$ .

All examined compounds are single-phase spinel as determined by powder X-ray diffraction, and are indexed to a cubic spinel, space group  $Fd\bar{3}m$ . The  $\text{Cr}^{3+}$  and  $\text{Li}^+$  doped spinel shows a little smaller lattice parameter than stoichiometric spinel. The effect of dopant  $\text{Cr}^{3+}$  was first examined in  $\text{Li}/\text{Li}_{1.04}\text{Cr}_x\text{Mn}_{2-x}\text{O}_4$  CR2032 coin-typed cells at  $50^\circ\text{C}$ . The cycle life was evaluated by varying the amount of doped Cr. The capacity loss rate, we defined it as the capacity of each cycle over the second discharge capacity, is plotted in Fig. 1 as a function of cycle number. The second discharge capacity of each compound is also given in the option of the figures. The results in figure reveals that the stoichiometric spinel  $\text{LiMn}_2\text{O}_4$  exhibited the 130 mAh/g of the initial capacity, and lost 20 mAh/g over the first 40 cycles, and the cycle efficiency ( $\eta$ , rate of capacity retention per cycle) is 99.57%. Here we defined  $\eta$  as follows: if the

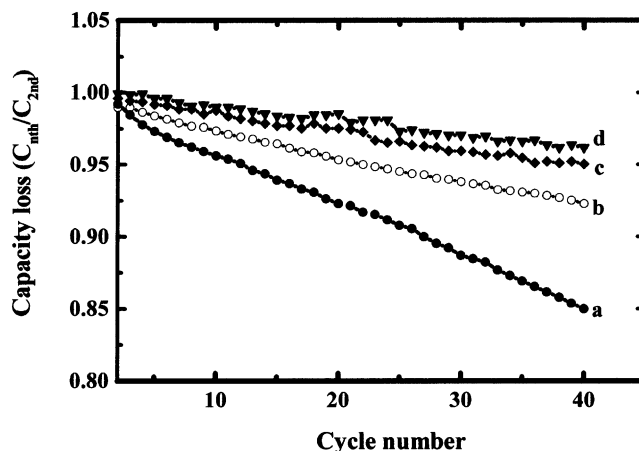


Fig. 1. Cycle life of  $\text{Li}_{1.04}\text{Cr}_x\text{Mn}_{2-x}\text{O}_4$  with various amounts of doped  $\text{Cr}^{3+}$  at  $50^\circ\text{C}$ . (a)  $\text{LiMn}_2\text{O}_4$  (130); (b)  $x = 0.025$  (123); (c) 0.05 (120), and (d) 0.1 (115). The value given in parentheses is the 2nd discharge capacity (mAh/g).

first discharge capacity is  $C_1$ , and the cycle efficiency  $\eta$  then the  $n$ th discharge capacity  $C_n = C_1 \eta^{(n-1)}$ , thereby  $\eta = [C_n/C_1]^{1/(n-1)}$ . The  $\text{Cr}^{3+}$  modified spinel  $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$  reduce the initial capacity from 127 to 121 mAh/g when the Cr-doped amount varies from 0.625 to 2.5% (Cr/O). As expected, it behaves the better cycleability. The cycle efficiency increases from 99.31 to 99.80%. The effect of  $\text{Li}^+$  was also investigated by varying the amount of doped  $\text{Li}^+$  at the fixed Cr doped-level. Fig. 2 gives the correction between the capacity loss rate and the amount of doped  $\text{Li}^+$ . The initial capacity decreased as the amount of  $\text{Li}^+$  was increased, but the cycleability was significantly increased, the cycle efficiency increases up to 99.96 when the amount of doped Li reaches to 2% (Cr/O).

The results in Figs. 1 and 2 are summarized in Table 1. It shows the cyclability was significantly increased with increase in the doped  $\text{Cr}^{3+}$  or  $\text{Li}^+$  contents. The cycling performance at the elevated temperature is found to be the best for the high dope-level compound, i.e.  $\text{Li}_{1.08}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ . However, as a practical cathode material, both the capacity and the cycleability are required, respectively. To further clarify the mechanism responsible for improvement, we herein selected two compounds  $\text{LiCr}_{0.025}\text{Mn}_{1.975}\text{O}_4$  (the top left compound in Table 1 and  $\text{Li}_{1.08}\text{Cr}_{0.1}\text{Cr}_{1.9}\text{MnO}_4$  (the right bottom in the Table 1) compared with the stoichiometric spinel  $\text{LiMn}_2\text{O}_4$ . Fig. 3 shows the second charge curves of the four compounds,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCr}_{0.025}\text{Mn}_{1.975}\text{O}_4$ ,  $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ , and  $\text{Li}_{1.08}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$  in the voltage range of 3.8–4.3 V. We interestingly found that the charge curve are quite different: the presence of  $\text{Cr}^{3+}$  changes only in the charge/discharge curves in the voltage region, while addition of  $\text{Li}^+$  affects it in the both low and high-voltage region. The exact definition of the “high and low voltage for spinel cathode” was given in our previous work [9]. In order to see the difference more clearly, linear sweep voltammetry (LSV) was performed from OCV to 4.5 V

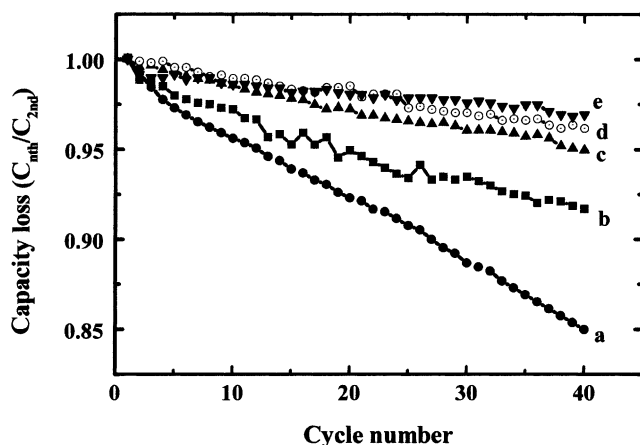


Fig. 2. Cycle life of  $\text{Li}_x\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$  with various amounts of doped  $\text{Li}^+$  at 50°C. (a)  $\text{LiMn}_2\text{O}_4$  (130); (b)  $y = 1.0$  (121); (c) 1.02 (119); (d) 1.04 (115), and (e) 1.08 (106). The value given in parentheses is the 2nd discharge capacity (mAh/g).

Table 1  
Cycle efficiencies of  $\text{Cr}^{3+}$  and  $\text{Li}^+$  doped  $\text{Li}_y\text{Cr}_x\text{Mn}_{2-x}\text{O}_4$  at 50°C

$\text{Li}_y\text{Cr}_x\text{Mn}_{2-x}\text{O}_4$	Capacity (mAh/g) and efficiency <sup>a</sup>	$x = 0.025$	$x = 0.05$	$x = 0.1$
$y = 1.00$	2nd cycle	127	127	121
	30 cycle	113	117	116
	$\eta$	99.31	99.72	99.80
$y = 1.02$	2nd cycle	127	123	119
	30 cycle	117	118	114
	$\eta$	99.65	99.79	99.90
$y = 1.04$	2nd cycle	123	120	115
	30 cycle	115	115	111
	$\eta$	99.81	99.88	99.91
$y = 1.08$	2nd cycle	118	112	106
	30 cycle	115	108	104
	$\eta$	99.90	99.92	99.96

$$^a \eta = 100 \times [C_n/C_{2nd}]^{1/(n-2)}$$

versus  $\text{Li}/\text{Li}^+$  and the results are given in Fig. 4. The decrease in the current intensity of both peaks was observable for the  $\text{Li}^+$  modified spinel, while decrease of the peak only in the high potential was detected on the  $\text{Cr}^{3+}$  modified one. Tarascon et al. proposed a model to explain the origin of these two peaks during lithium insertion/extraction process in spinel [12]: the splitting of the voltage plateau at 4.0 V was interpreted in terms of cation–cation interactions. Li can fill half tetrahedral sites without forming any nearest-neighbour Li–Li interactions. Then fill the other half tetrahedral site in which four such interactions are formed, and the energy of each interaction is 0.05 eV. Gao et al. [13] suggested a simple lattice–gas model to explain two peak for these lithium-rich compounds, the weakening of the peaks with increasing  $x$  is due to the presence of intercalated Li atoms pinned to the excess Li atoms which occupy the octahedral site instead of Mn. These pinned Li ions would

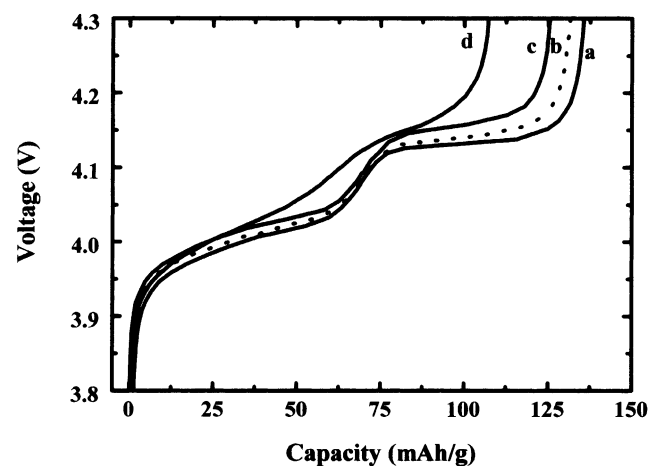


Fig. 3. Charge curves of (a)  $\text{LiMn}_2\text{O}_4$ , (b)  $\text{LiCr}_{0.025}\text{Mn}_{1.975}\text{O}_4$ , (c)  $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ , and (d)  $\text{Li}_{1.08}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$  between 3.8 and 4.3 V at a current rate of  $C/3$ .

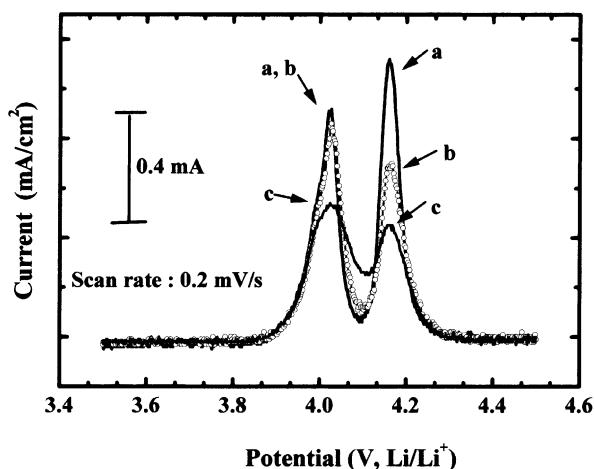


Fig. 4. Linear sweep voltammograms of (a)  $\text{LiMn}_2\text{O}_4$ , (b)  $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ , and (c)  $\text{Li}_{1.08}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ .

then make it difficult for Li ions to order in the 8a sites. The difference in potential depends on the binding energy between  $\text{Li}^+$  and its neighbours. We speculate that the difference in oxidation potential for the  $\text{Cr}^{3+}$  modified spinel is due to the removal of lithium ions from the different environments of the tetrahedral sites. It can easily be envisaged that removal of lithium ions from the tetrahedral sites which is close to the  $\text{Cr}^{3+}$  substituted octahedral sites require more energy since  $\text{Cr}^{3+}$  present in the octahedral sites will slightly affect bond force between O and Mn. However, the real original of this should be further clarified.

The question is whether or not the single-phase reaction is directly responsible for the improvement in the electrochemical profile at the elevated temperature. In our previous work [2,9], we reported that the spinel, e.g. lithium-rich spinel with best cycling performance at room temperature to be found to have a one-phase insertion/extraction. Further, we demonstrated that the major factors responsible for the capacity loss at the elevated temperature are ascribed to follows: (i) the transformation of unstable two-phase on the high-voltage region to a more stable one-phase structure, accompanying by the loss of  $\text{MnO}_3$ ; (ii) direct dissolution of  $\text{Mn}_2\text{O}_3$  in the electrolyte solution; and (iii) the decomposition of electrolyte solution on the electrode. Those works suggested that the single-phase reaction is still a major factor, but not only factor to affect the elevated performance. In other world, the spinel having an excellent elevated temperature performance must show a one-phase insertion/extraction. However, spinel, in some extent, directly loses  $\text{Mn}_2\text{O}_3$  into the electrolyte solution despite of its structure, these spinel sharing with a single-phase reaction could lose capacity at the elevated temperature, even it shows an improved behaviour. Having a one-phase insertion/extraction is the indispensable condition for an excellent cycleability, but not a sufficient condition. We speculate that either doping  $\text{Cr}^{3+}$  or  $\text{Li}^+$  stabilize the crystal structure, thereby allowing a homogenous lithium insertion and

extraction over the entire 4 V intercalated region, thus improve its elevated temperature performance.

The storage performance at the elevated temperature was also evaluated for the  $\text{Cr}^{3+}$  and  $\text{Li}^+$  doped spinel in comparison with stoichiometric spinel  $\text{LiMn}_2\text{O}_4$ . Attempt was performed to test the battery performance after storage at  $50^\circ\text{C}$  for 3 weeks. Typical charge/discharge curves for these compounds after storage are shown in Fig. 5. Stoichiometric spinel  $\text{LiMn}_2\text{O}_4$  loses capacity of 42 mAh/g,  $\text{LiCr}_{0.025}\text{Mn}_{1.975}\text{O}_4$  of 26 mAh/g, and 7 mAh/g of  $\text{Li}_{1.08}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ . It is clear the storage performance was also significantly improved in these Cr-doped, specially both  $\text{Cr}^{3+}$  and  $\text{Li}^+$  doped spinels. Carefully observing the shape charge/discharge curves, it shifts to higher voltage. However, the electrode polarization increase after storage was not observed. It is thereby high possibility that, in our case, the stoichiometric spinel  $\text{LiMn}_2\text{O}_4$  transform to the defect spinel, e.g. lithium-rich spinel.

There is no general consensus as to the chemical composition about the spinel after storage or cycling at the elevated temperature. It could be of (i)  $\text{LiMn}_2\text{O}_4$  with a second phase such as  $\text{Li}_2\text{MnO}_3$  and defect spinel [8,14]; (ii) lithium-rich spinel  $\text{LiMn}_{2-x}\text{O}_{4-y}$  [2,9]; and protonated  $\lambda\text{-Mn}_{2-y}\text{O}_4$  phase [15]. Such major differences most likely result from the different experimental conditions. The Mn dissolution process are quite complex, it is critically dependent on the crystal structure of electrode, electrolyte, temperature and time of storage, as well as the cycled voltage region and

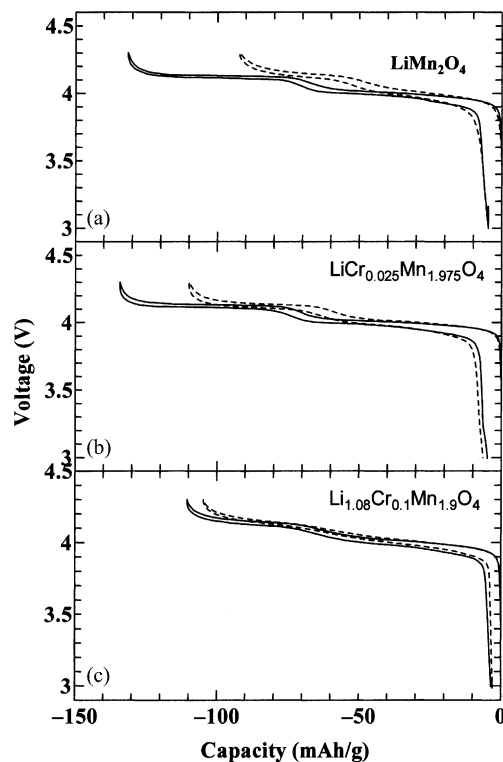


Fig. 5. Comparison of charge/discharge curves of spinel before (solid line) and after (dash line) storage at  $50^\circ\text{C}$  for 3 weeks: (a)  $\text{LiMn}_2\text{O}_4$ , (b)  $\text{LiCr}_{0.025}\text{Mn}_{1.975}\text{O}_4$ , and (c)  $\text{Li}_{1.08}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ .

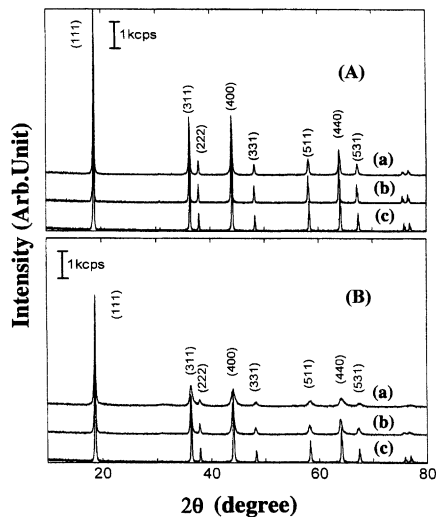


Fig. 6. XRD patterns of spinel before (A) and after (B) storage at 50°C for 3 weeks: (a)  $\text{LiMn}_2\text{O}_4$ , (b)  $\text{LiCr}_{0.025}\text{Mn}_{1.975}\text{O}_4$ , and (c)  $\text{Li}_{1.08}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ .

current rate. The detail work about the effect of the storage temperature and time on the electrochemical profile will be reported elsewhere [16]. X-ray diffraction patterns of  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCr}_{0.025}\text{Mn}_{1.975}\text{O}_4$ , and  $\text{Li}_{1.08}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$  before and after storage are shown in Fig. 6. XRD patterns reveal that no additional peaks resulted from  $\text{Li}_2\text{MnO}_3$  and defect spinel was observed.  $\text{LiMn}_2\text{O}_4$  shows a great reduce in XRD intensity and broad peak, and the peaks shift to higher diffraction angles after storage, while  $\text{Li}_{1.08}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$  still kept its intensity with a sharp peak. To more clearly see this phenomena, we used the diffraction and shape of (331) and (440) as a probe. The full-width at half maximum (FWHM) of both peaks before and after storage is given in Fig. 7. The lattice parameter calculated from XRD patterns in Fig. 6 are summarized in Table 2. The evidence of a broad peak and a smaller lattice parameter also supported that the stoichiometric spinel has been changed to a defect spinel.

To clarify whether or not the structure stability will affect the dissolution of Mn, the amount of dissolved Mn in the solution, the Mn and Li in the residual compounds were analyzed. The analysis results in Table 2 indicate that Cr or Li doped spinel have lowest manganese dissolution whereas the stoichiometric spinel exhibit largest manganese dissolution. Dissolved Mn and Cr ion were found to be 75.9 ppm for  $\text{LiMn}_2\text{O}_4$ , 46.3 and 0.7 ppm for  $\text{LiCr}_{0.025}\text{Mn}_{1.975}\text{O}_4$ ,

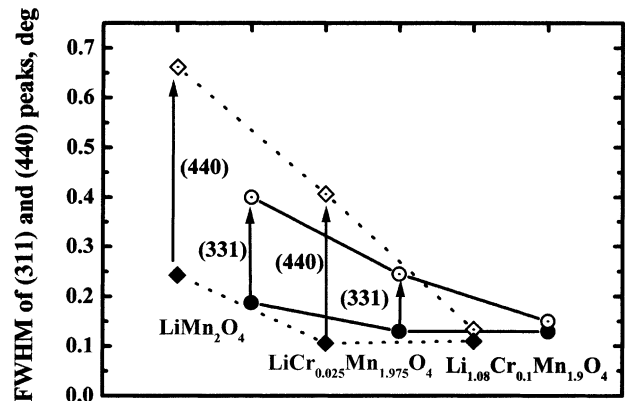


Fig. 7. Changes in the full-width at half maximum of peaks (440) and (311) of spinel before and after storage at 50°C for 3 weeks.

and 26.2 and 1.5 ppm for  $\text{Li}_{1.08}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ , respectively. The amount of dissolved total metal ion is decreased with the increase in dopants of Li and Cr. The amount of the dissolved Mn in three compounds are in the order:  $\text{LiMn}_2\text{O}_4 > \text{LiCr}_{0.025}\text{Mn}_{1.975}\text{O}_4 > \text{Li}_{1.08}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ . It has been well recognized that, beside the crystal structure stability, Mn dissolution at the elevated temperature also critically depends on its surface area and the content of HF in the electrolyte generated by reactions of fluorinated anions with water impurities present in the electrode and electrolyte, oxidation of the solvent, and instability of  $\text{LiPF}_6$ . The BET measurement indicated that the above three compounds have almost the same surface area, ca.  $3 \text{ m}^2/\text{g}$ , which is in good agreement with that reported by Howard's group for the  $\text{Cr}^{3+}$  modified spinel [8]. Therefore, the difference in the dissolved Mn in the solution could be mainly ascribed to their structure stability. Both  $\text{Cr}^{3+}$  and  $\text{Li}^+$  doping stabilize its structure, thereby minimizing the dissolution of Mn. Carefully analyzing the chemical composition of the stoichiometric  $\text{LiMn}_2\text{O}_4$  after storage at 60°C for 2 weeks, it showed the stoichiometric spinel  $\text{Li}_{1.006}\text{Mn}_{0.996}^{3+}\text{Mn}_{1.005}^{4+}\text{O}_{4.006}$  was transformed to a little oxygen-deficient lithium-rich spinel  $\text{Li}_{1.05}\text{Mn}_{0.943}^{3+}\text{Mn}_{1.048}^{4+}\text{O}_{3.97}$ . It is highly possible that spinel loses Mn accompanied by loss of oxygen (e.g.  $\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$ ), as we demonstrated previously [2].

$\text{LiCr}_{0.025}\text{Mn}_{1.975}\text{O}_4$  exhibited an improved cyclability compared with the stoichiometric spinel  $\text{LiMn}_2\text{O}_4$ , however showed a faster capacity retention than  $\text{Li}_{1.08}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ .

Table 2

The lattice parameter and chemical analysis results (dissolved Mn and Cr) of spinel before and after storage at 50°C for 3 weeks

Compound	$\text{LiMn}_2\text{O}_4$	$\text{LiCr}_{0.025}\text{Mn}_{1.975}\text{O}_4$	$\text{Li}_{1.08}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$
Lattice parameter (Å)			
Before soak	8.246	8.235	8.218
After soak	8.208	8.220	8.216
Dissolved Mn and Cr in solution (ppm)			
Mn	75	46.3	26.2
Cr	0	0.7	1.5

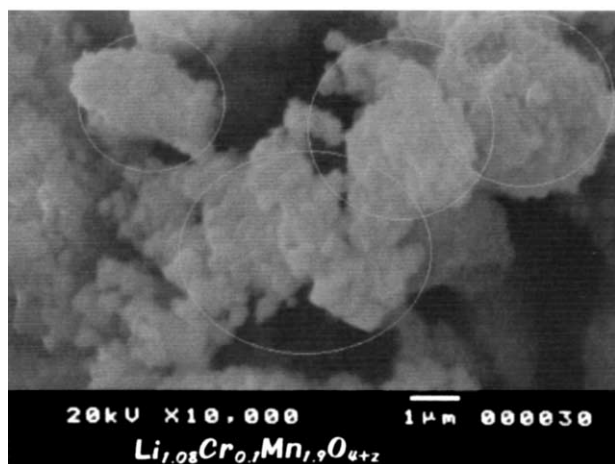
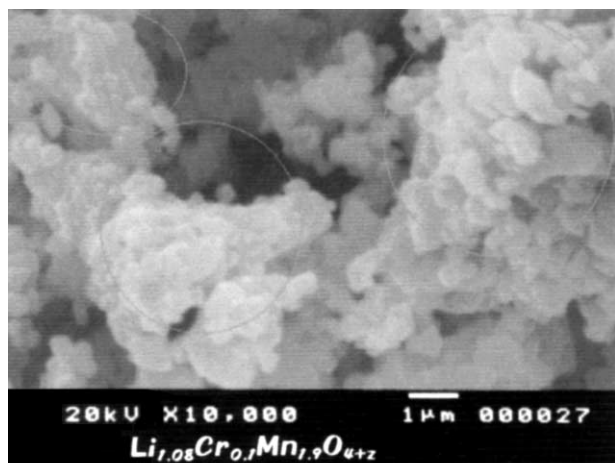


Fig. 8. SEM pictures of  $\text{Li}_{1.08}\text{Cr}_{0.1}\text{Mn}_{1.9}\text{O}_4$  before (top) and after (bottom) storage at  $50^\circ\text{C}$  for 3 weeks.

The change in morphology of both compounds before and after storage at  $50^\circ\text{C}$  are compared, and SEM pictures are showed in Figs. 8 and 9. The results revealed that no morphological changes had occurred for the Cr and Li modified spinel before and after storage at  $50^\circ\text{C}$  for 3 weeks. It maintains its smooth, well-developed, aggregated crystals, corresponding to still having sharp peaks in XRD patterns after storage.

However, for the  $\text{LiCr}_{0.025}\text{Mn}_{1.975}\text{O}_4$ , the aggregated crystals become to dispersed crystal with much smaller particles. In the XRD patterns, it shows the broad peaks. We speculate that crystallinity was destroyed due to Mn dissolution.

#### 4. Conclusion

The influences of partial substitution of Mn with  $\text{Cr}^{3+}$  and  $\text{Li}^+$  on their charge/discharge profile were quite different:  $\text{Cr}^{3+}$  only affect the high-voltage region, while  $\text{Li}^+$  showed in the both high and low voltage region. However, either

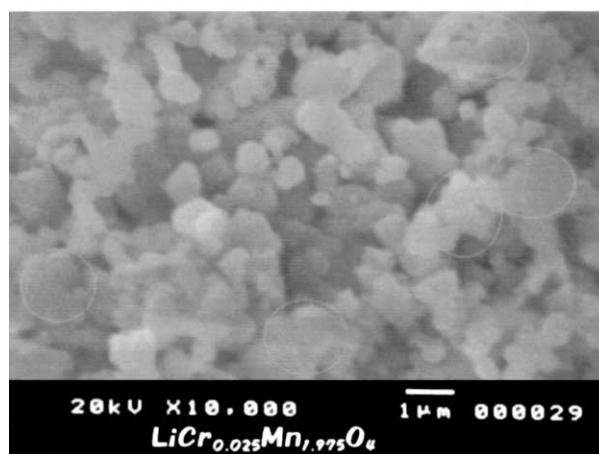
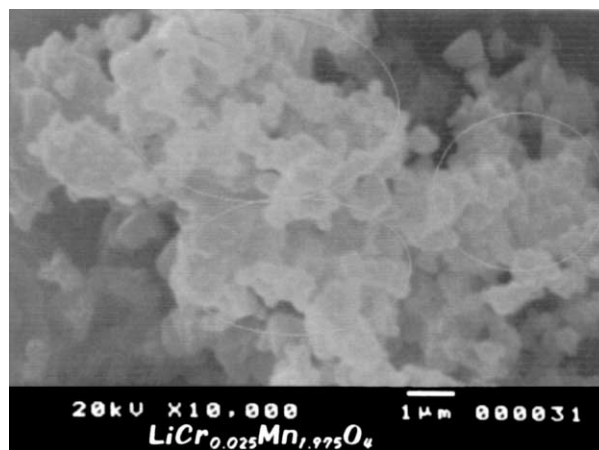


Fig. 9. SEM pictures of  $\text{LiCr}_{0.025}\text{Mn}_{1.975}\text{O}_4$  before (top) and after (bottom) storage at  $50^\circ\text{C}$  for 3 weeks.

$\text{Cr}^{3+}$  or  $\text{Li}^+$  doping significantly improved the storage and cycling performance of spinel  $\text{LiMn}_2\text{O}_4$  at the elevated temperature. The cycling performance at the elevated temperature was found to be the best for the both  $\text{Cr}^{3+}$  and  $\text{Li}^+$  modified spinel.

The chemical analysis and X-ray diffraction measurement indicate that the capacity losses of  $\text{LiMn}_2\text{O}_4$  is mainly due to the dissolution of Mn into electrolyte, further transformation to a little oxygen-deficient lithium-rich spinel  $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_{4-z}$ . The improvements in their electrochemical profiles for these  $\text{Cr}^{3+}$  and  $\text{Li}^+$  modified spinel was attributed to that the partial substitution of Mn stabilize its structure, thus minimizing the dissolution of Mn into electrolyte, and maintaining its original morphologies.

#### References

- [1] D.H. Jang, J. Shin, S.M. Oh, J. Electrochem. Soc. 143 (1997) 2592.
- [2] Y. Xia, Y. Zhou, M. Yoshio, J. Electrochem. Soc. 144 (1997) 2593.

- [3] G.G. Amatucci, C.N. Schmutz, A. Blyr, C. Sigala, A.S. Godzd, D. Larcher, J.J.M. Tarascon, *J. Power Sources* 69 (1997) 11.
- [4] S.J. Wen, T.J. Richardson, L. Ma, K.A. Striebel, P.N. Ross Jr., E.J. Cairins, *J. Electrochem. Soc.* 143 (1996) L136.
- [5] R.J. Gummow, A. de Kock, M.M. Thackeray, *Solid State Ionics* 69 (1994) 59.
- [6] G.G. Amatucci, C.N. Schmutz, A. Blyr, C. Sigala, A.S. Godzd, D. Larcher, J.M. Tarascon, *J. Power Sources* 69 (1997) 11.
- [7] G.G. Amatucci, A. Blyr, C. Sigala, P. Alfone, J.M. Tarascon, *Solid State Ionics* 104 (1997) 13.
- [8] A.D. Robertson, S.H. Lu, W.F. Averill, W.F. Howard Jr., *J. Electrochem. Soc.* 144 (1997) 3500.
- [9] Y. Xia, M. Yoshio, *J. Electrochem. Soc.* 143 (1996) 4186.
- [10] H. Kurimoto, K. Suzuoka, T. Murakami, Y. Xia, H. Nakamura, M. Yoshio, *J. Electrochem. Soc.* 142 (1995) 2178.
- [11] Y. Xia, M. Okada, M. Nagano, M. Yoshio, Batteries for portable applications and electric vehicles processing, in: C.F. Holmes, A.R. Landgrebe (Eds.), PV97-18, P494, The Electrochemical Society Proceeding Series, Pennington, NJ, 1997.
- [12] J.M. Tarascon, W.R. McKinnon, F. Coowar, N.T. Bowner, G.G. Amatucci, D. Guyomard, *J. Electrochem. Soc.* 141 (1994) 1421.
- [13] Y. Gao, K. Myrtle, M. Zheng, J.N. Reimers, J. Dahn, *Phys. Rev. B* 54 (1996) 3878.
- [14] G.G. Amatucci, D. Larcher, A.S. Gozda, F.K. Shokoohi, J.M. Tarascon, The Electrochemical Society Meeting Abstracts, Vol. 96-2, San Antonio, TX, 6–11 October 1996.
- [15] A. Du Pasquier, A. Blyr, P. Courjal, D. Larcher, G. Amatucci, B. Gerand, J.M. Tarascon, *J. Electrochem. Soc.* 146 (1999) 428.
- [16] X. Wang, Y. Yagi, Y.S. Lee, M. Yoshio, Y. Xia, T. Sakai, *J. Power Sources* 97–98 (2001) 427–429.