

## LETTER TO THE EDITOR

Differences in Electrochemical Behavior of  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  as 4-V Li-Cell CathodesYongyao Xia, Hideyuki Noguchi, and Masaki Yoshio<sup>1</sup>*Department of Applied Chemistry, Saga University, 1 Honjo, Saga 840, Japan*

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Stoichiometric spinel  $\text{LiMn}_2\text{O}_4$  delivers a large initial capacity of 140 mA hr/g and has unstable rechargeability. The capacity fading of the cell on cycling occurs only in the higher charge voltage range of  $x < 0.45$  in  $\text{Li}_x\text{Mn}_2\text{O}_4$ . Nonstoichiometric spinel  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  has a slightly lower capacity of 110 mA hr/g and has an excellent cycling behavior. © 1995 Academic Press, Inc.

## INTRODUCTION

Spinel structure Li–Mn–O compounds are the most promising 4-V cathodes for “lithium ion” batteries because they are cheaper, less toxic, and easier to prepare than their alternatives. A problem which prevents these compounds from being applied on an industrial scale is their unstable rechargeability. Even though the rechargeability has been greatly improved by several research groups (1–3), capacity fading on cycling was also observable for those stoichiometric spinels. This was attributed to the fact that a  $\text{LiMn}_2\text{O}_4$  electrode dissolves slowly into the electrolyte solution (2). In this paper, we report on new phenomenon in which capacity fading on cycling for those stoichiometric spinels occurs only at a higher charge plateau, and the capacity loss was almost arrested for those nonstoichiometric spinels which were obtained by the melt-impregnation method.

## EXPERIMENTAL

All samples examined here were prepared by the melt-impregnation method (1). Stoichiometric spinel  $\text{LiMn}_2\text{O}_4$  (Sample A) was obtained from LiOH reacting with the chemically prepared manganese dioxide (International Common Sample, No. 12, Sedema, Belgium) (Li/Mn = 0.5) at 470°C for 12 hr in air, and 700°C for 24 hr under  $\text{N}_2$ . Nonstoichiometric spinel  $\text{Li}_{1.04}\text{Mn}_2\text{O}_4$  (Sample

B) was synthesized from LiOH and CMD (Li/Mn = 0.52) at 470°C for 12 hr and 700°C for 24 hr in air.

The composition of both samples was characterized by chemical analysis and atomic adsorption spectroscopy. X-ray diffraction was applied to determine the structure of the compounds and the changes in crystal structure at various charge depths of the resulting compounds with  $\text{FeK}\alpha$  radiation, monochromated by a graphite crystal on a Rigaku RINT1000 X-ray diffractometer (Rigaku Ltd., Japan). The composition of the cathode and the assembly of the cell were similar to those reported previously (1).

## RESULTS AND DISCUSSION

The results of powder X-ray diffraction experiments indicate that both samples characterize the signature of spinel. The chemical analysis values of both samples are  $\text{Li}_{1.0}\text{Mn}_{1.99}\text{O}_4$  for Sample A and  $\text{Li}_{1.04}\text{Mn}_{2.00}\text{O}_{4.14}$  for Sample B. If Sample B is represented as Thackeray's expression,  $\text{Li}_{1.04}\text{Mn}_{2.00}\text{Mn}_{0.14}\text{O}_{4.14}$  is defect spinel  $\text{Li}_{1.0}[\text{Mn}_{0.966}\text{Li}_{0.002}\square_{0.032}]_2\text{O}_4$  in which vacancies exist in 16d octahedral sites in the structure.

The typical charge and discharge profiles of the cell containing both samples at a current rate of  $C/3$  are presented in Fig. 1. The results show that Sample A has a voltage profile of a spinel electrode with the characteristic two-step process plateau at 4.05 and 4.16 V in the charge curve and delivers an initial charge capacity of about 140 mAh/g. Sample B provides a slightly lower capacity of about 110 mA hr/g with a quasi-one-step process.

The cycling test for cells Li/1 M  $\text{LiPF}_6$ -EC/DMC (1 : 2 in volume)/ $\text{LiMn}_2\text{O}_4$  containing Sample A and Sample B were examined in the button CR2032-type cells. Each cell was cycled at a current rate of  $C/3$  between 3.5 and 4.5 V. The capacities of both samples are plotted as a function of cycle number in Fig. 2. The capacity fading of Sample A is somewhat faster than that of Sample B. Sample A loses about 12% initial capacity, and Sample B preserves about 98% initial capacity for the first 100 cycles.

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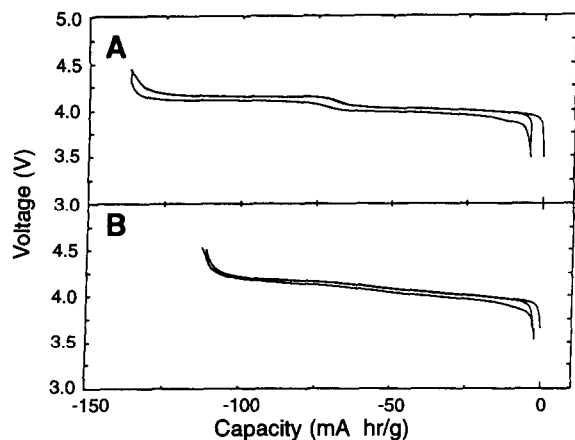


FIG. 1. Typical charge and discharge curves for (A) Sample A and (B) Sample B at a current rate of  $C/3$ .

We found that the capacity loss occurs only at a higher voltage plateau. To our knowledge, no information is known regarding this phenomenon. The 1st, 2nd, 25th, and 50th charge curves in the voltage range of 3.9 and 4.2 V are illustrated in Fig. 3.

It is apparent that the capacity fading on cycling for a cell containing Sample A occurs only in region II, while the capacity at a lower voltage region (region I) always remains at 80 mA hr/g during cycling, corresponding to 0.55 molar  $\text{Li}^+$  insertion/extraction per unit. The shape of the charge curve in region II also gradually changes from an "L-shape" to an "S-shape," indicating that a two-phase structure has a tendency to be transformed to a one-phase structure in this region. Simultaneously, the voltage also shifts to a higher value for lithium removal. The main factor causing capacity loss for a stoichiometric spinel is proposed to be the removal/insertion of lithium from the spinel framework, which needs higher energy compared to the first cycle and does not simply cause the dissolution of Mn ions into solution. In concert with stoichiometric spinel, the excellent rechargeability of non-stoichiometric spinel  $\text{Li}_{1.0}\text{Mn}_{1.93}\text{O}_4$  results from a homoge-

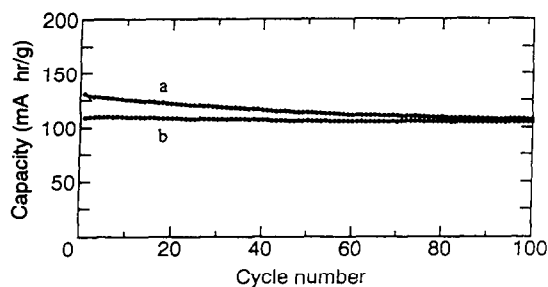


FIG. 2. Cycling tests for (a) Sample A and (b) Sample B at a current rate of  $C/3$  between 3.5 and 4.5 V.

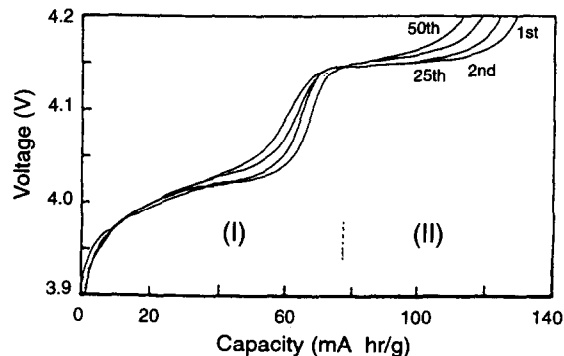


FIG. 3. The 1st, 2nd, 25th, and 50th charge curves for Sample A in the voltage range from 3.9 to 4.2 V.

neous insertion/extraction reaction proceeding over the entire intercalated region, in which more manganese vacancies are present in  $16d$  octahedral sites.

As described above, Sample A and Sample B have different battery performances; this should be attributed to their different crystal structures. To follow the changes in the crystal structure during the extraction of lithium ions from the spinel framework, XRD diffraction was used to investigate the structural changes at various charge depths for both samples, after the cells were equilibrated for 10 days. The XRD patterns show that extraction of lithium ions from the spinel results in a shift of the peaks to higher diffraction angles during the charge. The peaks for Sample A begin to split when being charged to  $x = 0.25$  in  $\text{Li}_x\text{Mn}_2\text{O}_4$ , whereas no split peaks were detected for Sample B over the entire examined region. The changes in the lattice parameter  $a_0$  as a function of lithium content  $x$  in  $\text{Li}_x\text{Mn}_2\text{O}_4$  for both samples are plotted in Fig.

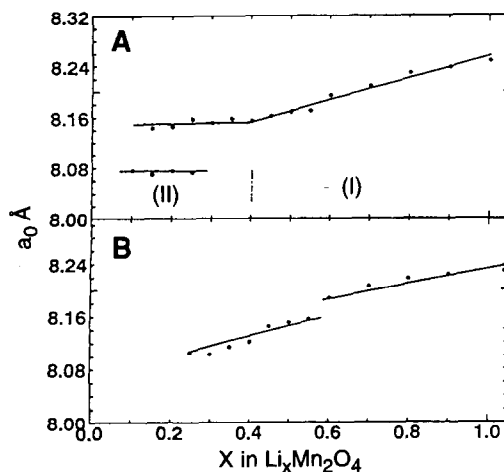


FIG. 4. Variation of cubic lattice parameter  $a_0$  as a function of the lithium content  $x$  in  $\text{Li}_x\text{Mn}_2\text{O}_4$  during the oxidation. (A) Sample A and (B) Sample B.

4. It is evident in Fig. 4A that a homogeneous phase reaction occurs in region I for  $0.4 < x < 1.0$  ( $a_0 = 8.247\text{--}8.155 \text{ \AA}$ ), and two cubic phases ( $a_0 = 8.150$  and  $8.027 \text{ \AA}$ ) coexist in region II for  $0.1 < x < 0.4$ , indicating that lithium ion insertion and extraction reactions proceed in the unstable two-phase region. In contrast, a homogeneous reaction occurring over the entire intercalated range ( $0.25 < x < 1.04$ ) was detected for Sample B, as described in Fig. 4B. The lattice parameter  $a_0$  decreases almost linearly from  $8.219$  to  $8.105 \text{ \AA}$  with two different slopes. These results strongly support the fact the capacity fading on cycling of Sample A occurring in the higher voltage region is due to the unstable two-phase region existing during lithium ion insertion and extraction from

the spinel framework, whereas a homogeneous structure for nonstoichiometric spinel  $\text{Li}_{1.0}\text{Mn}_{1.93}\text{O}_4$  will result in excellent rechargeability.

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