

# Cyclic voltammetric study on stoichiometric spinel $\text{LiMn}_2\text{O}_4$ electrode at elevated temperature

Shuhua Ma, Hideyuki Noguchi, Masaki Yoshio\*

*Department of Applied Chemistry, Saga University, Saga 840-0852, Japan*

Received 21 July 2000; received in revised form 14 December 2000; accepted 18 December 2000

## Abstract

The high-temperature electrochemical cell behavior of Li-stoichiometric Li–Mn–O spinel material,  $\text{LiMn}_2\text{O}_{4.014}$ , has been studied by cyclic voltammetry and coulometric titration curve measurement methods. A split of the reduction peak at  $x > 0.5$ , in  $\text{Li}_x\text{Mn}_2\text{O}_{4.014}$ , during  $\text{Li}^+$  insertion was found at 85°C. Correspondingly, three plateaus appeared in its coulometric titration curve, which manifest itself as three peaks in  $dQ/dV-V$  plot. The peak split phenomenon was also found for oxygen deficient spinel,  $\text{LiMn}_2\text{O}_{3.986}$ , prepared at 900°C in both reduction and oxidation branches at room and elevated temperatures using a lower scan rate of 0.02 mV/s. The disproportionation dissolution of stoichiometric spinel  $\text{LiMn}_2\text{O}_{4.014}$  intensified by the elevated temperature in slightly acidic electrolyte is considered responsible for the occurrence of the phenomenon. The finding gives a piece of evidence for oxygen deficient spinel  $\text{LiMn}_2\text{O}_{4-z}$  as the insoluble product of disproportionation dissolution. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Lithium ion cell; Cathode; Li–Mn–O spinel; High-temperature performance; Cyclic voltammetry; Peak split; Oxygen deficient spinel

## 1. Introduction

Spinel structure Li–Mn–O compounds are the most promising lithium ion insertion electrode materials for rechargeable lithium batteries. A problem which prevented these compounds from being commercialized is their capacity fading on extended cycling or over elevated temperature [1,2]. In view of the commonness of extended cycling and storage and cycling at elevated temperature for the consumer applications of lithium ion battery, quite a few research works have been conducted for the ascertainment of fading mechanism and the improvement of rechargeability [3–8]. The instability of spinel in electrolyte solution at elevated temperatures into  $\text{Mn}^{2+}$  according to the disproportionation reaction  $2\text{Mn}^{3+}$  (insoluble)  $\rightarrow$   $\text{Mn}^{4+}$  (insoluble) +  $\text{MnO}$  (soluble) [4] was considered as one of the most cardinal reasons responsible for the rapid deterioration of spinel electrode in elevated temperature operation. As a disproportionation decomposition product,  $\text{MnO}$  can be obviously detected by the red-purple color of electrolyte. Whereas, for insoluble phase, difficulty was encountered in the exact identification of the dissolution product. One work attributed it to the formation of  $\text{Li}_2\text{MnO}_3$  compounds containing  $\text{Mn}^{4+}$

ions [9] and another research group to defect spinel  $\text{Li}_2\text{Mn}_4\text{O}_9$  [10]. Meanwhile, Robertson et al. ascribed it to both of them [11]. In addition, as causes of cell deterioration, formations of other compounds were also demonstrated, such as  $\lambda\text{-MnO}_2$ ,  $\text{Li}_2\text{Mn}_2\text{O}_4$ , etc. [12–14].

In this paper, we report on a new phenomenon found in high-temperature cyclic voltammetry (CV) studies of stoichiometric spinel  $\text{LiMn}_2\text{O}_{4.014}$ , i.e. the split of the reduction peak at  $x > 0.5$ , in  $\text{Li}_x\text{Mn}_2\text{O}_{4.014}$ , during  $\text{Li}^+$  insertion. The coulometric titration curve survey further verified the occurrence of the split phenomenon. By means of studies for the split properties, oxygen deficient spinel  $\text{LiMn}_2\text{O}_{4-z}$  was suggested to be the main dissolution product, which exhibited split at both room and high temperatures. It was tentatively considered that phase separation of oxygen deficient spinel, derived from disproportionational dissolution of spinel electrode in slightly acidic electrolyte, promoted by oxygen defect and high temperature resulted in the occurrence of the CV peak splits.

## 2. Experimental

The sample, stoichiometric spinel  $\text{LiMn}_2\text{O}_{4.014}$  was gotten from Tohso Co. Ltd. and used as obtained. It features a  $\text{Fd}\bar{3}m$  space group with cubic symmetry, gives a lattice

\* Corresponding author. Tel.: +81-952-28-8675; fax: +81-952-28-8591.  
E-mail address: yoshio@ccs.ce.saga-u.ac.jp (M. Yoshio).

constant of 8.2346 Å. Oxygen deficient spinel was prepared by treating at 900°C in air for 20 h with a slow cooling of 20 h to room temperature. The exact compositions of the two samples were determined by ICP and chemical titration methods, which are  $\text{LiMn}_2\text{O}_{4.014}$  and  $\text{LiMn}_2\text{O}_{3.986}$ , respectively. The high-temperature CV and coulometric titration curve measurements were carried out in a self-made hot box with oscillation range of  $\pm 2^\circ\text{C}$ . For CV measurements, a three-electrode glass cell of flooded electrolyte was used, with a gas-tight spigot of high compression strength. Discharge coulometric titration curve test was conducted using coin cell of CR2032 type after potentiostatically charged to 4.5 V with an ending current limit of 0.01 mA. The measurement was done repeatedly by the regulation of discharging the cell for 1 h at 0.05 mA/cm<sup>2</sup>, following it, recorded the potential as closed circuit voltage (CCV) and then leaving it up in the air for a 10-h relaxation, afterwards logged the potential as open circuit voltage (OCV).

### 3. Results and discussion

Fig. 1 shows the CV behaviors of stoichiometric spinel  $\text{LiMn}_2\text{O}_{4.014}$  electrode in 1 M  $\text{LiPF}_6$  EC/DMC 1:2 (in volume) electrolyte at room temperature and 85°C. The room temperature CV curve gives two pairs of well-separated reversible redox peaks at near 3.99 and 4.12 V, which is typical of a stoichiometric spinel phase. The peaks are attributed to the insertion/extraction of  $\text{Li}^+$  into/from spinel tetrahedral sites. The two-step process is associated with an ordering of the  $\text{Li}^+$  ions on half of the tetrahedral 8a sites. On the contrary, at 85°C, a split of the second insertion peak of  $\text{Li}^+$  in normal spinel was found. With the increase of cycle number, the split peaks were more clearly separated.

The split phenomenon can also be seen in a slow discharge operation from the discharge coulometric titration

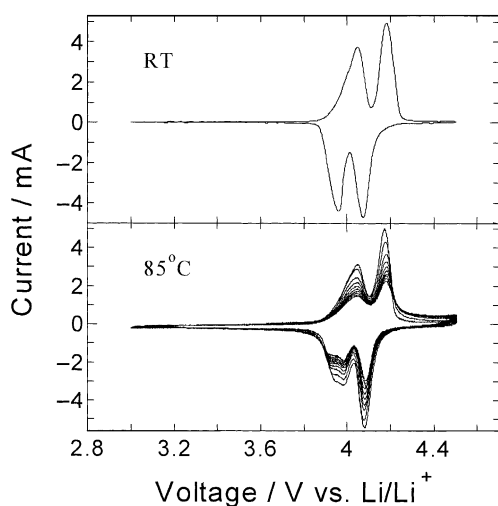


Fig. 1. Cyclic voltammograms of  $\text{LiMn}_2\text{O}_{4.014}$  at room temperature and 85°C in the electrolyte of 1 M  $\text{LiPF}_6$  EC/DMC 1:2 (in volume). Scan rate = 0.2 mV/s, scan range = 3–4.5 V vs.  $\text{Li/Li}^+$ .

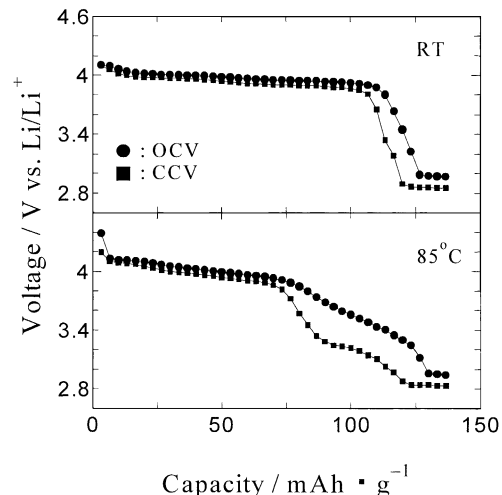


Fig. 2. Coulometric titration curve of  $\text{LiMn}_2\text{O}_{4.014}$  electrode at room temperature and 85°C, by discharging the cell for 1 h at 0.05 mA/cm<sup>2</sup> as CCV and then leaving it up for a 10 h relaxation, as OCV.

curve result in Fig. 2 at 85°C. Three plateaus can be discerned near 4 V as opposed to the two distinct plateaus in the case of room temperature. From its differential curves,  $dQ/dV$ - $V$  plot in Fig. 3, the observation of three plateaus can be confirmed, with three peaks at 85°C for both of CCV and OCV. It should be noted that the electrode has become oxygen deficient by disproportionational dissolution reaction after a long duration of nearly 20 days at 85°C. A plateau or peak at more than 3.2 V can be observed, which have been suggested to come from oxygen defect in  $\text{Li-Mn-O}$  spinel [15–17]. Obviously, the split behavior is related to the high experimental temperature and long duration. In this extreme operation condition, a serious dissolution can be expected.

In order to ascertain the origin of the split peak, we treated the stoichiometric  $\text{LiMn}_2\text{O}_{4.014}$  sample by heating

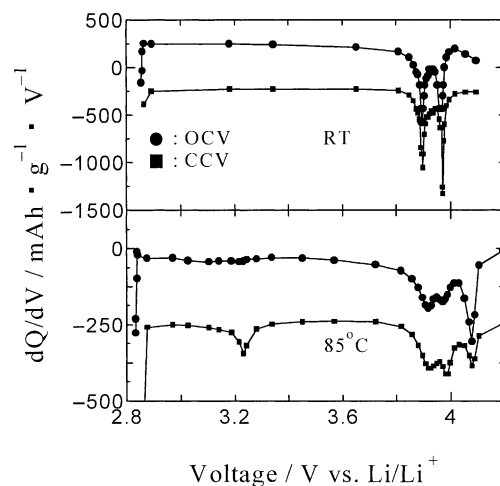


Fig. 3. Differential capacity–voltage relationship from coulometric titration curve of  $\text{LiMn}_2\text{O}_{4.014}$  electrode at room temperature and 85°C.

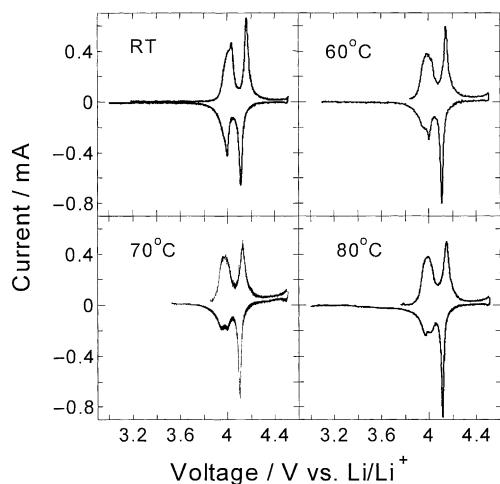


Fig. 4. Cyclic voltammograms of oxygen deficient spinel  $\text{LiMn}_2\text{O}_{3.986}$  prepared at  $900^\circ\text{C}$  in various experimental temperatures in the electrolyte of 1 M  $\text{LiPF}_6$  EC/DMC 1:2 (in volume). Scan rate = 0.02 mV/s, scan range = 3.0–4.5 V vs.  $\text{Li/Li}^+$ .

20 h in air at  $900^\circ\text{C}$ . Its CV behaviors are shown in Fig. 4. In a smaller scan rate of 0.02 mV/s, a split of the pair of redox peaks at lower voltage,  $x > 0.5$  for  $\text{Li}_x\text{Mn}_2\text{O}_{3.986}$ , in both room and high temperatures can be observed. From Fig. 4, at room temperature, a split of the oxidation peak at lower voltage can be found, whereas the reduction-branched peak's split is not obvious. With increases of the operation temperature, the oxidation peak became diffused and the split was confused by the normal oxidation peak; meanwhile the reduction peak became more separated, its split can be clearly observed. The higher the experimental temperature, the stronger the new split reduction peak at lower voltage. The results indicates that the splits of the oxidation branch in room temperature and the reduction branch in high temperatures maybe come from different sources.

As for the oxidation peak split in room temperature, it have been observed by Palacin et al. using incremental capacity voltammogram and attributed to a structural rearrangement of cubic spinel to double hexagonal phase by migration of Mn ions from 16d to 16c positions [18]. However, no corresponding reduction peak at about 3.2 V was found by CV studies in Fig. 4, although the 3.2 V plateau could be detected clearly in galvanostatic discharge curve [17]. The results remained the same even in an extensive range of scan rates. The kinetically controlled electrochemistry of the 3.2 V-reduction process supports Palacin's phase transformation model.

The results showed oxygen defect in spinel resulted in the split of the pair of redox peaks at lower voltage. The fact that split phase was intensified by elevated operation temperature demonstrated the importance of the temperature for phase separation of oxygen deficient spinel. It should be stated that no heavy red-purple color was observed in  $85^\circ\text{C}$  for oxygen deficient spinel electrode cell, with a smaller surface area of

$1.34 \text{ m}^2/\text{g}$ , as for stoichiometric spinel  $\text{LiMn}_2\text{O}_{4.014}$ ,  $5.26 \text{ m}^2/\text{g}$ , after CV experiment.

Above results indicate that a serious disproportionational dissolution occurred at  $85^\circ\text{C}$  for stoichiometric spinel  $\text{LiMn}_2\text{O}_{4.014}$  with a larger surface area. The disproportionational decomposition in slight acidic electrolyte, due to the reaction product (hydrofluoric acid) of  $\text{LiPF}_6$  with residual water impurity in solvents by the reaction  $\text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{LiF} + \text{POF}_3 + 2\text{HF}$ , as proposed by Aurbach and co-workers [19,20], was intensified by the high temperature of  $85^\circ\text{C}$ . The insoluble product, oxygen deficient spinel  $\text{LiMn}_2\text{O}_{4-z}$ , was left on the electrode and resulted in the split of the second reduction peak of the stoichiometric spinel electrode.

#### 4. Conclusions

A split of the reduction peak at  $x > 0.5$ , in  $\text{Li}_x\text{Mn}_2\text{O}_{4.014}$ , during  $\text{Li}^+$  insertion was found in high-temperature CV studies of stoichiometric spinel  $\text{LiMn}_2\text{O}_{4.014}$ . The coulometric titration curve measurements further verified the existence of the split phase. Oxygen deficient spinel  $\text{LiMn}_2\text{O}_{4-z}$  was identified with the split phase as an insoluble disproportionational decomposition product of  $\text{LiMn}_2\text{O}_4$ . The result highlighted the importance of disproportionational dissolution as a source of capacity fading, especially at elevated temperature.

#### Acknowledgements

The authors are grateful to the grants-in-aid for Scientific Research from the Japanese Ministry of Education for financial support of this research.

#### References

- [1] D. Guyomard, J.M. Tarascon, J. Electrochem. Soc. 139 (1991) 937.
- [2] A. Momchilov, V. Manev, A. Nassalevska, J. Power Sources 41 (1993) 305.
- [3] D. Guyomard, J.M. Tarascon, J. Power Sources 54 (1995) 92.
- [4] M.M. Thackeray, P.J. Johnson, L.A. De Picciotto, P.G. Bruce, J.B. Goodenough, Mater. Res. Bull. 19 (1984) 179.
- [5] J.M. Tarascon, E. Wang, F.K. Shokoohi, W.R. McKinnon, S. Colson, J. Electrochem. Soc. 138 (1991) 2859.
- [6] M.M. Thackeray, W.I.F. David, P.G. Bruce, J.B. Goodenough, Mater. Res. Bull. 18 (1983) 461.
- [7] Y. Xia, H. Noguchi, M. Yoshio, J. Solid State Chem. 119 (1995) 216.
- [8] Y. Xia, Y. Zhou, M. Yoshio, J. Electrochem. Soc. 144 (1997) 2593.
- [9] A. Blyr, C. Sigala, G. Amatucci, D. Guyomard, Y. Chabre, J.M. Tarascon, J. Electrochem. Soc. 145 (1998) 194.
- [10] S.J. Wen, T.J. Richardson, L. Ma, K.A. Striabel, P.N. Ross Jr., E.J. Cairns, J. Electrochem. Soc. 143 (1996) L136.
- [11] A.D. Robertson, S.H. Lu, W.F. Howard Jr., J. Electrochem. Soc. 144 (1997) 3505.
- [12] A. Du Pasquier, A. Blyr, P. Courjal, D. Larcher, G. Amatucci, B. Gerand, J.M. Tarascon, J. Electrochem. Soc. 146 (1999) 428.

- [13] H. Huang, C.A. Vincent, P.G. Bruce, *J. Electrochem. Soc.* 146 (1999) 3649.
- [14] J. Cho, M.M. Thackeray, *J. Electrochem. Soc.* 146 (1999) 3577.
- [15] Y. Gao, J.R. Dahn, *J. Electrochem. Soc.* 143 (1996) 100.
- [16] Y. Gao, J.R. Dahn, *Solid State Ionics* 84 (1996) 33.
- [17] Y. Yagi, Y. Hideshima, M. Sugita, H. Noguchi, M. Yoshio, *Electrochemistry* 68 (2000) 252.
- [18] M.R. Palacin, Y. Chabre, L. Dupont, M. Hervieu, P. Strobel, G. Rousse, C. Masquelier, M. Anne, G.G. Amatucci, J.M. Tarascon, *J. Electrochem. Soc.* 147 (2000) 845.
- [19] D. Aurbach, Y. Gofer, *J. Electrochem. Soc.* 138 (1991) 3529.
- [20] D. Aurbach, A. Zaban, A. Schlecter, Y. Ein-Eli, E. Zenigard, B. Markowsky, *J. Electrochem. Soc.* 142 (1995) 2873.