Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Power Sources 154 (2006) 273–275
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

Correlation of oxygen deficiency with discharge capacity at 3.2 V for $(LiMn)_3O_{4-z}$

Masaki Yoshio, Hideyuki Noguchi*, Hongyu Wang, Xiaoqing Wang

Department of Applied Chemistry, Saga University, 1 Honjo, Saga 840-8502, Japan

Received 18 February 2005; received in revised form 14 March 2005; accepted 14 March 2005
Available online 13 June 2005

Abstract

Oxygen-deficient spinel $(LiMn)_3O_{4-z}$ was successfully synthesized by melt-impregnation method. The chemical composition of each spinel sample was carefully analyzed and the value of z was correlated with its discharge capacity at about 3.2 V ($C_{3.2V}$). The linear relationship between $C_{3.2V}$ and z was theoretically deduced from the structural consideration of $(LiMn)_3O_{4-z}$.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Oxygen deficiency; Spinel; 3.2 V plateau; Structure around deficiency

1. Introduction

Spinel $LiMn_2O_4$ is a promising cathode material for lithium-ion batteries by virtue of its low cost and non-toxicity. However, the severe capacity fading of the spinel upon cycling at elevated temperature may obstacle its further utilization. There have been many mechanisms proposed regarding to this problem, such as Mn dissolution into the electrolytes due to a disproportion of Mn^{3+} [1,2] electrolyte decomposition on the cathode surface causing impedance rise [3], Jahn-Teller distortion [3,4], and so on. Recently, we have found that the capacity fading is actually closely related to oxygen deficiency [5,6] which is denoted as the z value in $(LiMn)_3O_{4-z}$. From another viewpoint, Tachibana et al. have measured carefully the heat capacity (C_p) values for a series of spinel samples ($0 < z < 0.09$) within the temperature range from 2 to 420 K. They associated the anomalities in C_p with the oxygen nonstoichiometry [7].

From the previous studies, it is well known that oxygen deficiency is always present in extra-heated spinel samples [8,9]. In the charge–discharge profiles for this kind of samples (as shown in Fig. 1), a 3.2 V discharge plateau usually appears, together with 4.5 V charge–discharge plateaus delivering the equivalent capacity. Gao and Dahn have ascribed the 3.2 V discharge plateau to oxygen deficiency and suggested to use it as a “qualitative indicator for detecting oxygen deficiency” [9]. Instead, we have explored the quantitative relationship between the 3.2 V plateau length and oxygen vacancy degree [10]. A roughly linear dependency was discovered between the logarithms of $0.5C_{4V}/C_{3.2V} + 1$ and $1/z(0.5C_{4V}/C_{3.2V} + 1)$ equals to $(C_{4V} + C_{3.2V} + C_{4.5V})/(C_{3.2V} + C_{4.5V})$, and $C_{3.2V}$ equals to $C_{4.5V}$. By extrapolation of the above linear dependency, the linear coefficient of about 466 between $C_{3.2V}$ and z was obtained. Nevertheless, the scarcity of points (only three samples) in our previous study would inevitably give rise to some small errors in the derived linear dependency and affect the accuracy of the coefficient.

In this communication, we enriched the oxygen-deficient spinel sample sources and elaborated the linear relationship between the logarithms of $0.5C_{4V}/C_{3.2V} + 1$ and $1/z$, which enables the exact calibration of the linear coefficient between $C_{3.2V}$ and z. Furthermore, we also deduced the linear relationship between $C_{3.2V}$ and z directly from structure consideration. The comparison between the experimentally and theoretically deduced linear coefficients will be present.

* Corresponding author. Tel.: +81 952 28 8674; fax: +81 952 28 8591.
E-mail address: noguchih@cc.saga-u.ac.jp (H. Noguchi).

0378-7753/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2005.03.232

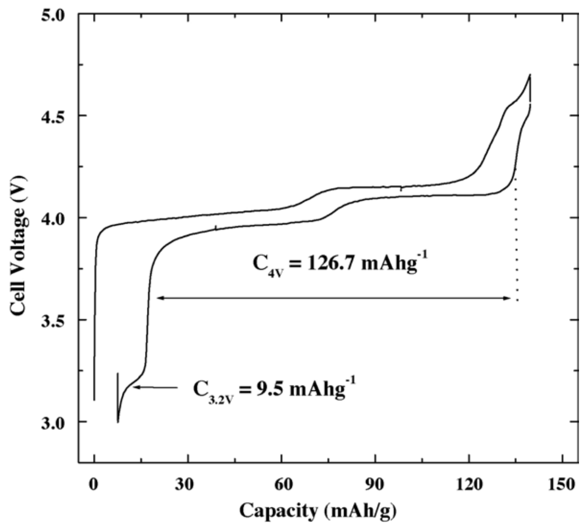

Fig. 1. Charge/discharge curve of $Li_{1.002}Mn_{1.998}O_{3.981}$.

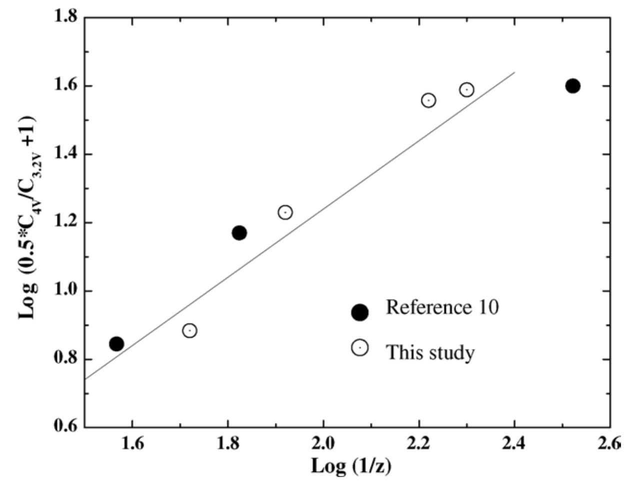

Fig. 2. Plot of log(0.5 × $C_{4V}/C_{3.2V}$ + 1) against log(1/z).

2. Experimental

The spinel samples were prepared by melt-impregnation method as follows. The mixture of Mn_3O_4 (Tosoh, Japan) and LiOH was pre-calcined 500 °C for 5 h in air, and then post-calcined at the temperature range of 700–900 °C in air. Some details of the spinel samples are listed in Table 1. The chemical composition of each sample was determined as described in our previous study. The powder X-ray diffraction (XRD) using Cu Kα radiation was employed to identify the crystalline phase of the synthesized samples. The electrochemical characterizations were performed using a screw cell, which consists of a cathode and a lithium metal anode separated by a porous polypropylene film. The cathode was fabricated with 20 mg of accurately weighed active material and 10 mg of conductive binder (Teflonized acetylene black (TAB)). The electrolyte was a mixture of 1 M $LiPF_6$–ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:2 by volume) (Ube Kozan). The charge and discharge current density was 0.4 mA cm^{-2} with the cut-off voltage of 3.0–4.75 V.

3. Results and discussion

Fig. 2 plots the logarithm of $0.5C_{4V}/C_{3.2V} + 1$ against the logarithm of 1/z. Besides the three solid points applied in our previous study, four dashed points were added in the present research. A straight line with the slope near 1 could be drawn, along which all the points distributed at both sides equally. The extrapolation of this line until log(1/z) approaches 0 could get the crossover point, which bears a direct relationship with the portion of oxygen defect-coordinated Mn atoms to the whole Mn atoms in spinel. Thus, $C_{3.2V}$ could be calculated from the crossover point if the capacity for $LiMn_2O_4$ is 148 mAh g^{-1}. Our previous research on 3.2 V capacity has suggested that one oxygen vacancy affects on ca. six Mn^{3+} ions based on the value of crossover point [10]. Since the molar ratio of $Mn^{3+}/(Mn^{3+} + Mn^{4+})$ is assumed to be ca. 0.5 in the spinels, totally 12 Mn ions would participate in the 3.2 V plateau.

Once we consider the oxygen-deficient spinel structure as schematically shown in Fig. 3, we could derive almost the same quantitative relationship. In spinel, one oxygen vacancy give rise to three Mn ions with the coordination number of 5 (MnO_5), which links with three MnO_6 octahedrons across O atom. Therefore, 1 mol defect oxygen forms 12 Mn atoms (three sets of MnO_5–$(MnO_6)_3$) which contribute to the two equivalent plateaus at 3.2 and 4.5 V. Assume that the molar ratio of $Mn^{3+}/(Mn^{3+} + Mn^{4+})$ is 0.5 and 1 mol Mn^{3+} in $LiMn_2O_4$ delivers 148 mAh g^{-1} capacity, we could obtain the following equation for the capacity of 12z mole Mn in $LiMn_2O_{4-z}$:

$$C_{3.2V} + C_{4.5V} = 148 \times 12z \times 0.5$$

Table 1
Chemical composition of oxygen-deficient spinel samples

Heating temperature (°C)	Chemical composition	z in $(LiMn)_3O_{4-z}$	Remark
700	$Li_{1.010}Mn_{1.990}O_{3.995}$	0.005	This study
750	$Li_{1.005}Mn_{1.994}O_{3.994}$	0.006	This study
800	$Li_{1.010}Mn_{1.990}O_{3.988}$	0.012	This study
800	$Li_{1.015}Mn_{1.985}O_{3.997}$	0.003	Ref. [10]
850	$Li_{1.002}Mn_{1.998}O_{3.981}$	0.019	This study
850	$Li_{1.016}Mn_{1.984}O_{3.985}$	0.015	Ref. [10]
900	$Li_{1.013}Mn_{1.987}O_{3.973}$	0.023	Ref. [10]

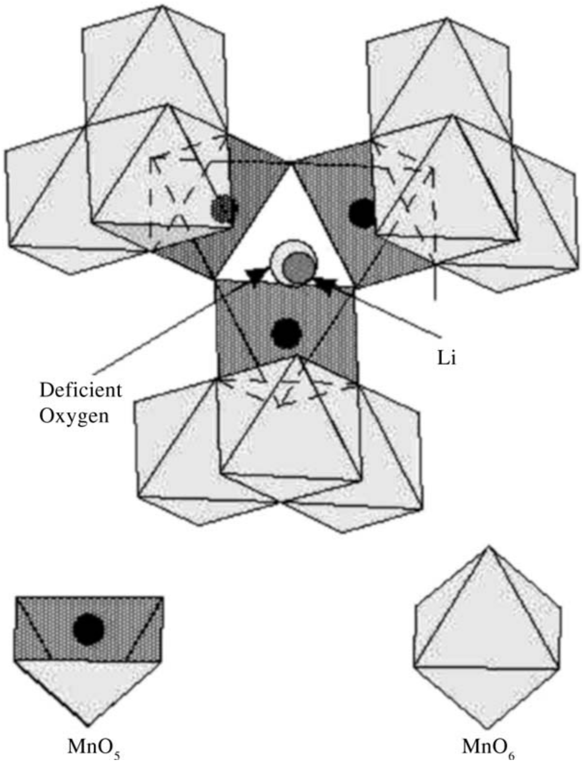

Fig. 3. Structure of oxygen-deficient spinel.

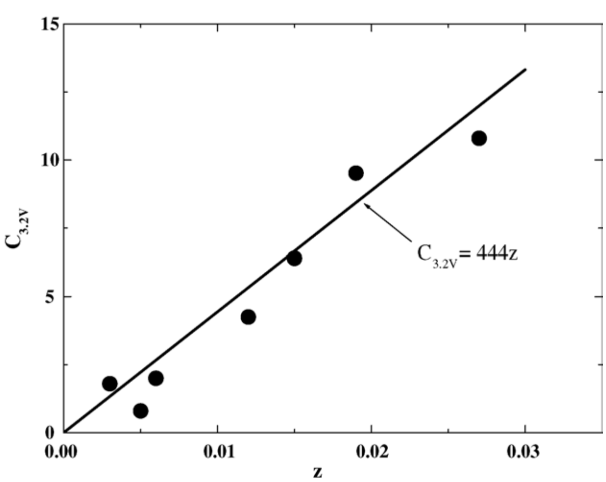

Fig. 4. Relationship between $C_{3.2\mathrm{V}}$ and z.

Since $C_{3.2\mathrm{V}}$ equals to $C_{4.5\mathrm{V}}$, the capacity at 3.2 V could be deduced as follows:

$$C_{3.2\mathrm{V}} = 148 \times 12z \times 0.5 \times 0.5 = 444z$$

The theoretical coefficient value of 444 agrees very well with the coefficient value obtained from the crossover point in Fig. 2. The consistence between the theoretically calculated and experimentally extrapolated linear coefficients verifies the validity of the above equation. Moreover, the above equation provides a very convenient and precise ruler to measure oxygen defect in spinel, even without accurate chemical analysis. To further confirm the accuracy of the above equation, we plot $C_{3.2\mathrm{V}}$ against $444z$ as shown in Fig. 4. The linear dependency in this figure fits the equation very well.

4. Conclusion

In conclusion, investigations on the oxygen-deficient spinel $(LiMn)_3O_{4-z}$ samples reveal that the discharge capacity at 3.2 V equates to $444z$. This linear relationship is carefully correlated by means of both the theoretical and experimental evaluations and proves accurate.

References

[1] Y. Xia, Y. Zhou, M. Yoshio, J. Electrochem. Soc. 144 (1997) 2593.
[2] D.H. Jang, Y.J. Shin, S.M. Oh, J. Electrochem. Soc. 143 (1996) 2204.
[3] R.J. Gummov, A. de Kock, M.M. Thakeray, Solid State Ionics 69 (1994) 59.
[4] M.M. Thakeray, Y. Shao-Horn, A.J. Kahaian, Electrochem. Soc. Interface 1 (1998) 7.
[5] Y. Xia, T. Sakai, T. Fujieda, X. Yang, X. Sun, Z. Ma, J. McBreen, M. Yoshio, J. Electrochem. Soc. 148 (2001) 723.
[6] X. Wang, H. Nakamura, Masaki Yoshio, J. Power Sources 110 (2002) 19.
[7] M. Tachibana, T. Tojo, H. Kawaji, T. Atake, M. Yonemura, R. Kanno, Phys. Rev. B 68 (2003) 094421.
[8] J.M. Tarascon, W.R. McKinnon, F. Coowar, T.N. Bowmer, G. Amatucci, D. Guyomard, J. Electrochem. Soc. 141 (1994) 1421.
[9] Y. Gao, J.R. Dahn, J. Electrochem. Soc. 143 (1996) 100.
[10] Y. Yagi, Y. Hideshima, M. Sugita, H. Noguchi, M. Yoshio, Electrochemistry 68 (2000) 252.