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Journal of Power Sources 97–98 (2001) 454–457

JOURNAL OF
POWER
SOURCES

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Lattice parameter as a measure of electrochemical properties of LiMn_2O_4

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Received 20 June 2000; accepted 7 January 2001

Abstract

Many factors affect the electrochemical properties of LiMn_2O_4 . Among these factors the amount of Mn^{3+} is an important factor which largely influences the capacity and capacity fading. However, it is difficult to detect the amount of Mn^{3+} by chemical titration method. In this research we try to relate the amount of Mn^{3+} with the lattice parameter. Lattice parameter is easy to measure. Therefore, if the amount of Mn^{3+} can be deduced by the lattice parameter, it will be very helpful to control and design the electrochemical properties of LiMn_2O_4 . The results show a good relationship among the lattice parameter, the amount of Mn^{3+} and the capacity. Thus, lattice parameter could be used to deduce the electrochemical properties of LiMn_2O_4 , although many works are still needed to construct a firm relationship. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: LiMn_2O_4 ; Lattice parameter; The amount of Mn^{3+} ; Capacity; Parameter

1. Introduction

Recently, the size of portable electronic products such as cellular phone, notebook computer and video camera, become to be very small due to the development of LSI, VLSI. And the demands for the lighter, smaller and powerful secondary battery increases with the population of these electronic devices. Nowadays lithium secondary battery is the most promising battery for the portable electronic devices. Thus, many works have been focused on the improvement of battery performances. The important electrochemical properties of lithium secondary battery, such as capacity and capacity fading, largely depend on the characteristics of cathode material. Therefore, it is an urgent research target to understand the relationship between powder characteristics and electrochemical properties of materials. With this knowledge, we could tailor the structure, composition, stoichiometry and powder size of materials to obtain the designed electrochemical properties.

LiMn_2O_4 spinel oxide is a good candidate material for a cathode of lithium secondary battery due to its economical and non-toxic advantages. Nevertheless the capacity fading is a shortcoming of this material [1–4]. The capacity fading has been ascribed to several possible factors: (i) instability of

organic-based electrolyte at the high voltage region, (ii) dissolution of the LiMn_2O_4 electrode into the electrolyte (as Mn^{2+}), (iii) inhomogeneous local structure of LiMn_2O_4 , and (iv) the onset of Jahn–Teller effect in deeply discharged electrodes. However, these factors might be incorporated to induce the capacity fading. For example, the onset of Jahn–Teller distortion and inhomogeneous local structure could accelerate the dissolution of the LiMn_2O_4 into the electrolyte.

Another aspect which affects the electrochemical properties is the powder characteristics. Powder characteristics, such as size, shape, homogeneity and stoichiometry, are also reported to have a profound effect on the electrochemical properties [5–7]. Especially stoichiometry is known to have a relation with the capacity and capacity fading. In LiMn_2O_4 , Mn^{3+} and Mn^{4+} coexists. In fact, stoichiometry is related to the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio. And this $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio influences the electrochemical properties. Therefore, one of the important factors we must consider is a $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio. However, it is difficult to measure it by titration method.

In this research, we try to relate the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio with the lattice parameter. Measuring the lattice parameter is very simple. Usually it takes as long as 30 min, and sample preparation is very easy. If the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio could be deduced by measuring the lattice parameter, it will be very helpful in controlling the powder characteristics.

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2. Experimental

LiMn_2O_4 powders were prepared by the emulsion drying method [8]. The LiMn_2O_4 was also prepared by a solid-state reaction using Li_2CO_3 (Aldrich, 99.9997%) and MnO_2 (Aldrich, 99%) as starting materials. These reagents were mixed in an agate mortar. A stoichiometric mixture of powders was calcined at 850°C for 24 h. The powders were analyzed by the automated X-ray diffractometer using $\text{K}\alpha$ radiation to identify the crystalline phases. The chemical composition of the powders were determined by the atomic absorption spectroscopy (AAS) and chemical titration methods. The electrochemical properties of the LiMn_2O_4 powders were investigated in an electrochemical cell which comprised a cathode, an anode and an electrolyte of 1 M LiPF_6 in EC (ethylene carbonate)–DEC (diethylene carbonate) solution. The charge and discharge characteristics of the cathode were evaluated at a current of 0.1 mA cm^{-2} in the range 2.9 to 4.4 V Li/Li^+ . All electrochemical experiments were conducted at room temperature in a glove-box filled with high purity argon gas (99.999%).

3. Results and discussion

Fig. 1 shows the variation of lattice parameters of LiMn_2O_4 as a function of calcination time and temperature. As shown the lattice parameters increases with time and temperature. What is the reason of this lattice parameter change? The result of XRD phase analysis shows that peak shape and intensity ratio of each plane for each sample does not change (Fig. 2). Therefore, it could be concluded that the phase change and ion movement is not the reason of this lattice parameter variation. Then why does the lattice parameter change with temperature and time? Let us discuss about this reason.

The crystal structure of LiMn_2O_4 is a normal spinel. This spinel structure has 32 octahedral sites. Manganese ions occupy half of these octahedral sites. The charge valencies of manganese ions are Mn^{3+} and Mn^{4+} . Thus, each ion occupies the eight octahedral sites, respectively. In octahedral sites, coordination number 6, the ionic radius of Mn^{4+} is 0.54 \AA [9]. However, the ionic radius of Mn^{3+} depends on the spin state. In the low spin state (LS) the ionic radius is 0.58 \AA , but in the high spin state (HS) the ionic radius is 0.65 \AA . In this case, the ionic radius difference between Mn^{3+} (LS) and Mn^{4+} is as small as 0.04 \AA , but the difference between Mn^{3+} (HS) and Mn^{4+} is 0.11 \AA . Therefore, if the amount of Mn^{3+} (HS) increases, the lattice parameter also increases. Thus, the increase of lattice parameter observed in Fig. 1 is found to be due to the increase of the amount of Mn^{3+} (HS). That is, thermal treatment changes the valance state of transition element manganese ion. This may be the reason for the lattice parameter variation observed in Fig. 1.

In this case, there are two possibilities. One is the transition from Mn^{4+} to Mn^{3+} (HS), the other is the transition

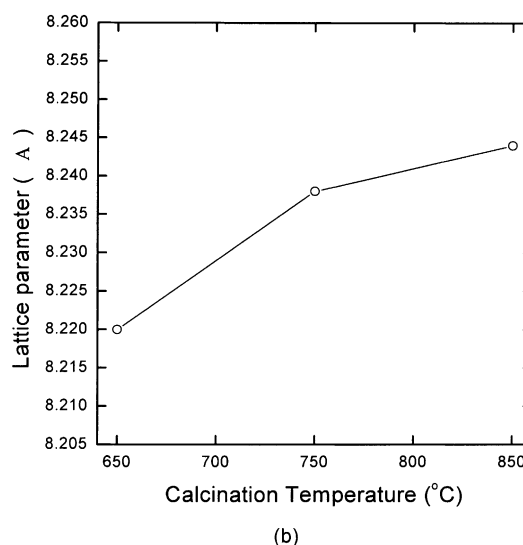
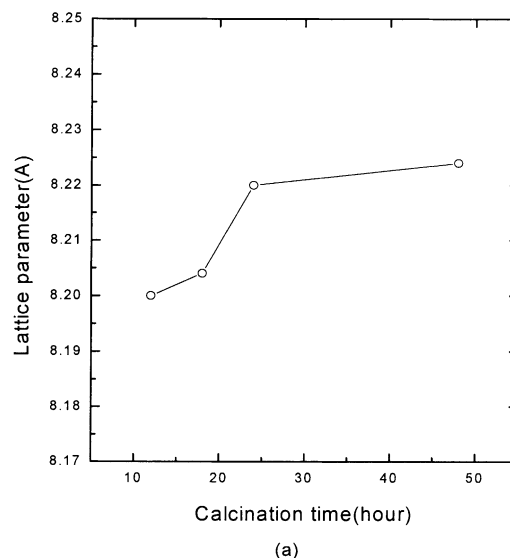
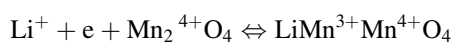


Fig. 1. Lattice parameter variation with (a) calcination time and (b) calcination temperature.

from Mn^{3+} (LS) to Mn^{3+} (HS). Fig. 3 shows the dependence of valance state on the calcination temperature. Valance state was calculated by titration method. As shown the valance state decreases with temperature. This indicates that the transition of manganese ion is from Mn^{4+} to Mn^{3+} (HS). Thus, the amount of Mn^{3+} (HS) increases with calcination temperature. Therefore, it is found that the reason of the lattice parameter increase is due to the transition of manganese ion from Mn^{4+} to Mn^{3+} (HS). Interesting thing is that the lattice parameter is closely related to the amount of Mn^{3+} .

In LiMn_2O_4 , the amount of Mn^{3+} has a close relation with the electrochemical properties. During charge and discharge, the change of manganese valance state occurs as follows:



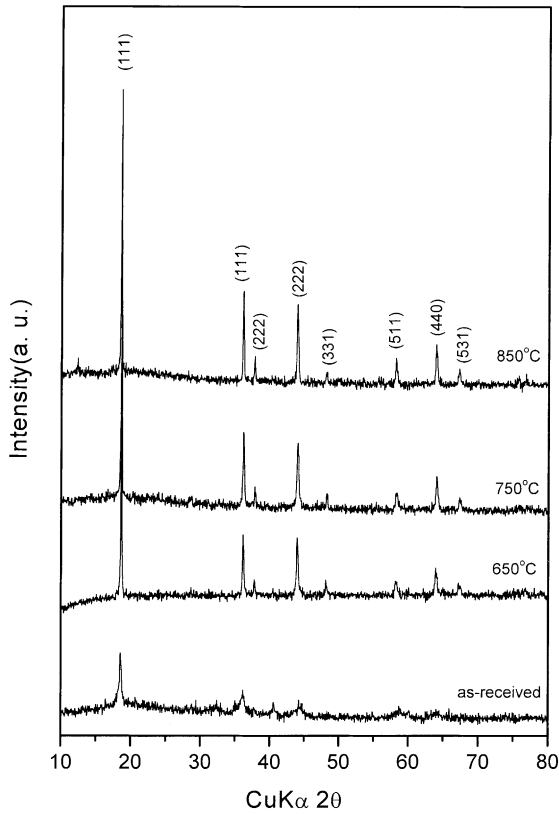


Fig. 2. X-ray diffraction patterns of powders: calcined at each temperatures for 24 h prepared by emulsion drying method using LiNO_3 .

As shown the capacity of LiMn_2O_4 is determined by the amount of Mn^{3+} . Capacity increases with the increase of the amount of Mn^{3+} , and decreases with the decrease of Mn^{3+} . However, Mn^{3+} induces the capacity fading. The Mn^{3+} in the LiMn_2O_4 is in high spin state as it was found in lattice

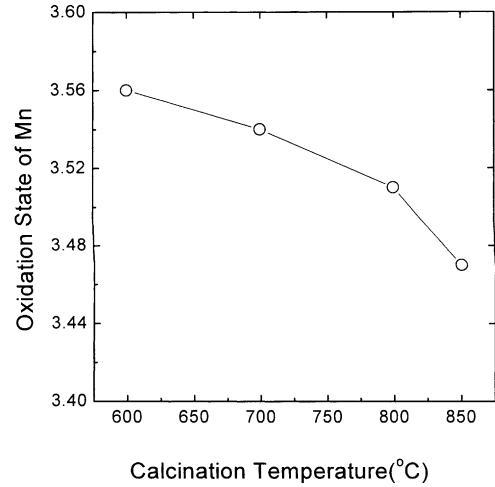


Fig. 3. Dependence of oxidation state of Mn on the calcinations temperature.

Table 1
Chemical composition and lattice parameters variation with sample preparation condition

Sample	Chemical formula	Lattice parameter (\AA)
Solid state reaction (Sa)	LiMn_2O_4	8.252
Emulsion ($\text{LiOH}\cdot\text{H}_2\text{O}$) (Ea)	$\text{Li}_{1.124}\text{Mn}_2\text{O}_4$	8.027
Emulsion (LiNO_3) (Eb)	$\text{Li}_{1.028}\text{Mn}_2\text{O}_4$	8.244

parameter analysis. This high spin state Mn^{3+} causes the Jahn–Teller distortion in the lattice. Therefore, lattice distortion increases with the amount of Mn^{3+} , which is the one of factors causing capacity fading. If the amount of Mn^{3+} is decreased by the lithium excess or cation substitution, the

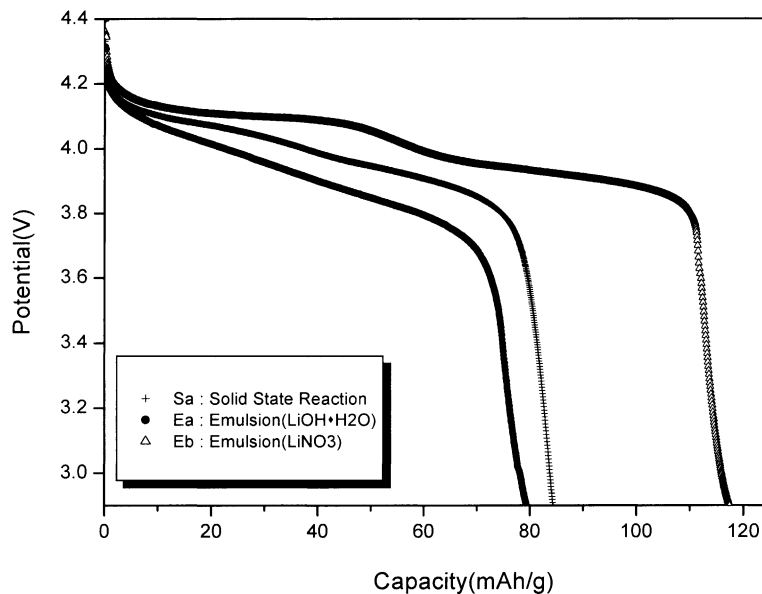


Fig. 4. Discharge curves of cells of $\text{Li}/1 \text{ M LiPF}_6 \text{ EC-DEC solution}/\text{LiMn}_2\text{O}_4$ electrode with samples of different compositions and lattice parameters.

capacity fading is also found to decrease. Therefore, the amount of Mn^{3+} in the LiMn_2O_4 plays a key role in determining the electrochemical properties of LiMn_2O_4 .

Chemical titration is the most appropriate method to measure the amount of Mn^{3+} . However, this method is difficult and takes a lot of time and effort. We found that there exists a relation between lattice parameter and $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio. Therefore, although it is relative and indirect, we can deduce the amount of Mn^{3+} from the lattice parameter. That is, lattice parameter depends sensitively on the ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$. Therefore, lattice which indirectly shows the amount of Mn^{3+} could be used to deduce the electrochemical properties of LiMn_2O_4 .

Table 1 shows the chemical composition and lattice parameter for different samples. The chemical compositions were determined by the AAS (Atomic Absorption Spectroscopy). Sample Ea which has a excess lithium shows a smaller lattice parameter because excess lithium decreases the amount of Mn^{3+} . Thus, it is certain that a relation exists between lattice parameter and chemical composition. Fig. 4 shows discharge curves for different samples. Capacity of sample Ea is smaller than that of the other samples as it is expected. However, sample Sa shows a smaller capacity although it has the largest lattice parameter. In this case, the inhomogeneous distribution of composition may cause the incomplete electrochemical reaction, smaller capacity. Chemical and XRD analysis analyzes the sample in macroscopic scale. Thus, microscopic inhomogeneity is not detected. Therefore, the electrochemical properties of LiMn_2O_4 could be deduced by measuring the lattice parameter on the condition of homogeneous distribution of composition.

4. Conclusion

We found that the lattice parameter is proportional to the amount of Mn^{3+} in LiMn_2O_4 . Mn^{3+} plays a key role in determining the electrochemical properties. Therefore, lattice parameter could be used to deduce the electrochemical properties of LiMn_2O_4 .

Acknowledgements

This work was supported by grant no. 97-03-00-05-01-3 from the Basic Research Program of the KOSEF (Korea Scientific and Engineering Foundation).

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