



ELSEVIER

Journal of Power Sources 97–98 (2001) 377–380

JOURNAL OF
POWER
SOURCES

www.elsevier.com/locate/jpowsour

Mechanisms of manganese spinels dissolution and capacity fade at high temperature

Takayuki Aoshima*, Kenji Okahara, Chikara Kiyohara, Kenji Shizuka

Mitsubishi Chemical Corporation, 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan

Received 6 June 2000; received in revised form 11 November 2000; accepted 11 December 2000

Abstract

Tests on the stability of spinels stored at different states of charge were performed. It was found that Mn dissolution took place irreversibly from the charged state with formation of MnF_2 , ramsdellite- $\text{Li}_{0.5}\text{MnO}_2$. In the discharged state, the Mn at the surface of the LiMn_2O_4 was in equilibrium with a soluble species, which leads to an increase in the cathode resistance. It was found that the amount of the dissolved Mn increased with increasing LiPF_6 concentration and that 2 equiv. of PO_2F_2^- were generated. Concurrent formation of carbonate decomposition products, such as CO_2 , C_2H_4 , EtOH, Et_2O , and AcOEt, suggests that the mechanism of Mn dissolution from the charged state was composed of the following steps: the initial decarboxylation of electrolyte catalyzed by λMnO_2 to give EtOH, followed by reduction of λMnO_2 by EtOH to give acetate and MnO, and then Mn dissolution via Mn–O bond activation assisted by LiPF_6 . © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mn dissolution; Lithium manganese oxides; Capacity fade; Storage

1. Introduction

The spinel LiMn_2O_4 is one of the most promising cathode materials for lithium secondary batteries. Although the LiMn_2O_4 system exhibits good electrochemical performances at room temperature, the disadvantage of the LiMn_2O_4 system is a capacity fade during charge–discharge cycling or storage at high temperature. It is well known that this deterioration is mainly caused by Mn dissolution from spinel [1]. Many mechanisms for Mn dissolution from spinel have been proposed [1,2], however, the detailed mechanism is still ambiguous. In this study, the mechanism of Mn dissolution from spinels was investigated to elucidate the factors that influence capacity fade in lithium secondary batteries.

2. Experimental

2.1. LiMn_2O_4

The compound $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4$ was obtained from a mixture of Mn_2O_3 and $\text{LiOH}\cdot\text{H}_2\text{O}$, according to the following

procedure. The mixture of Mn_2O_3 and $\text{LiOH}\cdot\text{H}_2\text{O}$ at a molar ratio of $\text{Mn}_2\text{O}_3/\text{LiOH}\cdot\text{H}_2\text{O} = 1/1.04$ was preheated in air at 500°C for 24 h and then calcined at 780°C for 24 h. The resulting mixture was slowly cooled at rate of $0.2^\circ\text{C}/\text{min}$, held at 450°C for 24 h and subsequently quenched to room temperature.

2.2. λMnO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$ (two-phase)

2.2.1. Electrochemical method

Composite cathodes (about 24 mg) which consisted of 75 wt.% spinel powder, 20 wt.% acetylene black and 5 wt.% PTFE were pressed onto an Al current collector and assembled in a CR2030 coin-type Li/LiMn₂O₄ cell. The electrolyte used was 1 M LiPF_6 EC/DMC/DEC (2:2:1 by volume (Mitsubishi Chemical)). Cells were cycled between the voltage limits of 3.2 and 4.35 V with a current density of $0.2 \text{ mA}/\text{cm}^2$. Three types of cathode were obtained by recovering the cathodes of the Li/LiMn₂O₄ cells at fully charged, 100 mAh/g charged and fully discharged states.

2.2.2. Chemical method

The suspension of $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4$ powders (6.6 g) in a solution (180 ml) of H_2SO_4 at pH 1.0 and 2.16 were stirred for 6 h at room temperature to give $\text{Li}_{0.14}\text{Mn}_{1.98}\text{O}_4$

* Corresponding author. Tel.: +81-45-963-4399; fax: +81-45-963-3974.
E-mail address: taoshima@rc.m-kagaku.co.jp (T. Aoshima).

Table 1

Capacity loss of the cathodes at various states of charge after Mn dissolution in 1 M LiPF₆ EC/DMC/DEC (2:2:1 by volume) at 70°C for 2 weeks

Charged state of the cathode	Capacity (mAh/g)		Concentration of dissolved Mn (mM)
	Fresh	After storage for 14 days	
Full discharged	126	30	0.47
100 mAh/g charged	126	93	0.89
Full charged	126	122	0.64

(λMnO_2) and $\text{Li}_{0.28}\text{Mn}_{1.98}\text{O}_4$ ($\text{Li}_x\text{Mn}_2\text{O}_4$ (two-phase)) powders, respectively [3].

2.3. Lithiated anode

Composite anodes (about 24 mg) which consisted of 92.5 wt.% graphite, 7.5 wt.% PVDF were assembled in a CR2030 coin-type Li/graphite cell. The electrolyte used was 1 M LiPF₆ EC/DEC (3:7 by volume). The cut-off potentials for the discharge and charge limit were fixed at 1.5 V and 3 mV, respectively, with a current density of 0.2 mA/cm². Fully charged and discharged anodes were obtained by recovering the anodes of the cells at fully charged and discharged states.

2.4. Storage of lithium manganese oxide powders, cathode and anode

Typical experiments were performed as follows. The total amount of 160 mg of lithium manganese oxide powders were soaked in 1 M LiPF₆ EC/DEC (3:7 by volume (Mitsubishi Chemical)) (8 ml) under argon in Teflon container and the container was left in an oven at 70°C for a few weeks. The concentrations of Li and Mn in the solids were determined by atomic absorption spectroscopy and chelate back-titration method, respectively, and the average Mn valences were measured by iodometry. Inductively coupled plasma atomic emission spectroscopy (JOBIN YVON JY 38S) and anion-exchange chromatography (Dionex DX-120) were used for the quantitative analyses of Mn and anion in solution, respectively. The same procedure was used for the storage of a cathode and an anode except 5 and 2 ml of electrolyte were used, respectively. The performances of the cathode after storage at 70°C for 2 weeks were evaluated by reassembling in a CR2030 coin-type Li/LiMn₂O₄ cell between the voltage limits of 3.2 and 4.35 V with a current density of 0.2 mA/cm².

3. Results and discussion

3.1. Storage of cathodes at different charged states at 70°C in 1 M LiPF₆ EC/DMC/DEC

The storage of cathodes at various charge depths was first investigated to evaluate their electrochemical performances.

The results are summarised in Table 1. The largest capacity loss was observed in the case of the discharged cathode. In this case, the capacity loss was induced by the increase in the polarisation of cathode, as reported previously [4,5]. However, the capacity loss is not linked to the extent of spinel dissolution. In order to clarify the connection between Mn dissolution and cathode deterioration, we have investigated Mn dissolution in detail by using various spinel compounds, LiMn₂O₄, Li_xMn₂O₄ (two-phase) and λMnO_2 , corresponding to the composition of the cathodes at various states of charge.

3.2. Mn dissolution from various spinel compounds

The storage of the spinels was performed in 1 M LiPF₆ EC/DEC at 70°C for a few weeks. The results are summarised in Table 2, which includes the properties of fresh spinels for comparison. The amount of dissolved Mn from Li_xMn₂O₄ (two-phase) and λMnO_2 increased continuously with storage times, while that from LiMn₂O₄ was almost constant after the small amount of dissolved Mn appeared initially.¹ In the case of LiMn₂O₄, even if an electrolyte containing dissolved Mn and HF was used, the amount of the dissolved Mn reduced to that when an electrolyte with no additive was used.² These results indicate that the Mn at the surface of the LiMn₂O₄ is in equilibrium with a soluble species.

No remarkable spectral change was observed in XRD spectra of the stored LiMn₂O₄. In contrast, for the Li_xMn₂O₄ (two-phase) and the λMnO_2 , a broadening of XRD spectra was observed with the growth of extra peaks, which were identified as MnF₂, ramsdellite–LiMn₂O₄ [6]. Additionally average Mn valence of spinel decreased with storage time. These results clearly show that Mn dissolution from Li_xMn₂O₄ (two-phase) and λMnO_2 took place according to oxidation mechanism. Interestingly, XRD and Raman analyses of Li_xMn₂O₄ (two-phase) revealed that this material transforms from a two-phase structure into one-phase

¹ The ESR spectra of the stored solutions showed that the dissolved Mn species from LiMn₂O₄ are monomeric Mn(II), while that from λMnO_2 the mixture of monomeric, dimeric and polymeric Mn(II). The ESR data at 133 K: $g = 2.009$ (six lines, $A = 96$ G) for monomer; $g = 2.029$ (11 lines, $A = 41$ G) for dimer; $g \sim 2$ (broad singlet) for polymer.

² The electrolyte containing dissolved Mn and HF was obtained by storage of λMnO_2 . The concentration of dissolved Mn decreased from 5.1 to 0.5 mM after storage of LiMn₂O₄ at 70°C for a week.

Table 2
Results of the storage of the various spinels in 1 M LiPF₆ EC/DEC (3:7 by volume) at 70°C

Spinels		Storage time (days)			
		Initial	7	14	21
LiMn ₂ O ₄	Mn ²⁺ concentration (mM)	0	0.6	1	1
	Lattice parameters (Å)	8.230(1)	8.233(2)	8.228(1)	8.227(1)
	Average Mn valence	3.565	3.536	3.532	3.528
Li _x Mn ₂ O ₄ (two-phase)	Mn ²⁺ concentration (mM)	0	4	12	29
	Lattice parameters (Å)	8.105(3) 8.063(2)	8.053(3)	8.047(2)	8.043(2)
	Average Mn valence	3.895	3.871	3.832	3.686
λMnO ₂	Mn ²⁺ concentration (mM)	0	5	17	36
	Lattice parameters (Å)	8.048(1)	8.044(1)	8.044(1)	8.045(1)
	Average Mn valence	3.974	3.916	3.832	3.666

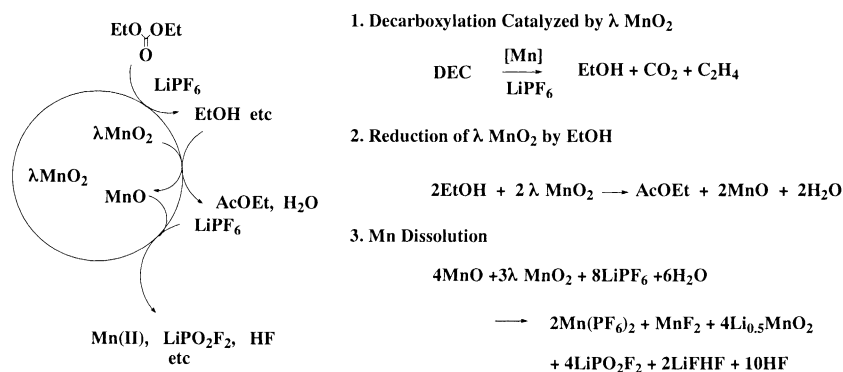


Fig. 1. Proposed mechanism of Mn dissolution from λMnO₂.

structure of λMnO₂ initially during Mn dissolution. These features appear to be attribute to the instability of two-phase structure of LiMn₂O₄ system, as proposed by Xia et al. [7].

3.3. Mechanism of Mn dissolution from λMnO₂

In Mn dissolution, LiPF₆ plays a very important role. The amount of the dissolved Mn increased with LiPF₆ concentration by a factor 2 and the formation of 2 equiv. of PO₂F₂⁻ with the dissolved Mn in solution and the deposition of F⁻, PO₂F₂⁻ and PO₃F²⁻ salts in powder were observed. No Mn dissolution was observed in the absence of LiPF₆.

Furthermore, during the course of Mn dissolution, the carbonate decomposition products, such as CO₂, C₂H₄, EtOH, Et₂O, and AcOEt were detected. From these results, we proposed a mechanism of Mn dissolution composed of three steps: (i) the decarboxylation of electrolyte catalysed by λMnO₂ to give EtOH; (ii) reduction of λMnO₂ by EtOH [8] to give MnO and acetate; (iii) Mn dissolution via Mn–O bond activation assisted by LiPF₆, as shown in Fig. 1.

3.4. Mechanism for the capacity fade

It was found in this study that the dissolved Mn was deposited mainly on a graphite anode when in the charged

state.³ It can be interpreted from these results that capacity fade is caused by a combination of anode and cathode deteriorations. Namely, the capacity fade is mainly induced by the increase in the anode resistance and the decrease in the amount of cyclable Li in the charged state. And also the deposition of MnF₂, ramsdellite–Li_{0.5}MnO₂ and Li salt such as Li₂PO₃F, may lead to the increase in polarisation of the cathode. In contrast, when the battery is in the discharged state, dissolved Mn forms a passivating layer on the cathode, leading to an increase in the cathode resistance. The dissolved Mn in this case appears to be forming in a manner, such as previously observed in our model system. Other aspects of this mechanism are currently under investigation.

References

- [1] P. Arara, R.E. White, M. Doyle, J. Electrochem. Soc. 145 (1998) 3647 and references therein.
- [2] A. Du Pasquier, A. Blyr, P. Courjal, D. Larcher, G. Amatucci, B. Gerand, J.-M. Tarascon, J. Electrochem. Soc. 146 (1999) 428 and references therein.

³ The concentration of dissolved Mn decreased from 10.8 to 5.74 mM and 9.84 mM after storage of the charged and discharged anodes at 70°C for a week, respectively.

- [3] J.C. Hunter, *J. Solid State Chem.* 39 (1981) 142.
- [4] A. Blyr, C. Sigala, G. Amatucci, D. Guyomard, Y. Chabre, J.-M. Tarascon, *J. Electrochem. Soc.* 145 (1998) 194.
- [5] H. Huang, C.A. Vincent, P.G. Bruce, *J. Electrochem. Soc.* 146 (1999) 481 and references therein.
- [6] M.M. Thackeray, M.H. Rossouw, R.J. Gummow, D.C. Liles, K. Pearce, A. De Kock, W.I.F. David, S. Hull, *Electrochim. Acta* 38 (1993) 1259.
- [7] Y. Xia, Y. Zhou, M. Yoshio, *J. Electrochem. Soc.* 144 (1997) 2593.
- [8] Y. Wang, J. Reimers, IMLB, Edinburgh, 1998.