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# Study of Mn dissolution from $\text{LiMn}_2\text{O}_4$ spinel electrodes using in situ total reflection X-ray fluorescence analysis and fluorescence XAFS technique

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## Abstract

The dissolution process of Mn from  $\text{LiMn}_2\text{O}_4$  cathode into an electrolyte solution accompanied on electrochemical cycling at various temperature was studied for the first time by in situ methods using a combination of total reflection X-ray fluorescence (TXRF) analysis and a capillary technique. When the in situ cell was cycled at 50°C, the Mn concentrations measured on the 5th, 10th and 15th cycles were determined to be 11, 56 and 393 ppm, respectively. The concentration of Mn in the cell was shown to be the highest at the center of both electrodes. It was also found that dissolution of Mn from the cathode material takes place during the charge rather than the discharge process. Mn K-XANES (X-ray absorption near-edge structure) spectra of the electrolyte solution revealed that Mn exists as  $\text{Mn}^{2+}$ . © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Mn dissolution; In situ analysis; TXRF; XAFS

## 1. Introduction

Lithium manganese oxide spinel is expected to be a promising candidate as a cathode material for lithium secondary batteries. However, spinel has the serious problem of the capacity fading, and it is reported that Mn dissolution from the  $\text{LiMn}_2\text{O}_4$  cathode during cycling is partly responsible [1–4]. Determination of the Mn concentration in the electrolyte solution is essential to understand the dissolution behavior of the cathode material. However, sampling of the electrolyte solution has so far been made by disassembling the cell, since a relatively large amount of sample is necessary for conventional chemical analysis techniques, such as an inductively coupled plasma (ICP) atomic emission spectroscopy [5]. Recently, Jang et al. analyzed the dissolved  $\text{Mn}^{2+}$  ions in the electrolyte using differential pulse polarography [6], though the variation of Mn concentration in the electrolyte solutions during the charge–discharge process could not be determined. Total reflection X-ray fluorescence (TXRF) analysis is the most sensitive X-ray fluorescence technique, which requires a sample volume as small as a few microliters. We have introduced this technique for the first

time to monitor the concentration of Mn in an electrolyte solution during electrochemical cycling. This technique enables us to collect an electrolyte solution without disturbing the electrochemical reaction nor disassembling the cell. In this study, an in situ TXRF cell was developed and optimized to determine the dissolution of Mn during cycling at 25 and 50°C.

Chemical state analysis of Mn in electrolyte is also necessary to reveal the dissolution mechanism of Mn. The X-ray absorption fine structure (XAFS) technique is most suitable for this purpose for transition-metal atoms. However, a conventional transmission XAFS technique could not be applied because the concentration of Mn in the electrolyte solution is extremely low. We solved this problem by using a high sensitivity fluorescence XAFS technique utilizing a multi-element solid-state detector (SSD).

## 2. Experimental

Our newly designed glass-beaker type electrochemical cell for TXRF analysis is shown in Fig. 1. A composite cathode was prepared by mixing  $\text{LiMn}_2\text{O}_4$  with graphite, acetylene black and PVdF, and coated on an Al foil. Li metal

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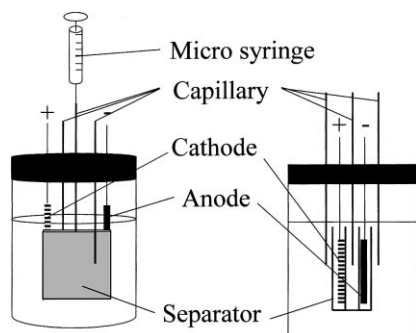


Fig. 1. Schematic representations of the cell developed for the in situ TXRF analysis.

was used as anode. The electrolyte solution was prepared by dissolving 1 M  $\text{LiPF}_6$  into a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The ratio of EC to DMC was set to 2:1 (by volume). The charge–discharge cycles were performed between 3.5–4.3 V at a current rate of  $0.5 \text{ mA/cm}^2$ . Ten micro liters of electrolyte solution were sampled by inserting a fused silica capillary (GL Science) with outer diameter 0.35 mm into the cell. The sampled solution was then dropped on to a filter paper ( $5 \times 5 \text{ mm}^2$ ), which was placed in a quartz tube (5 mm in inner diameter and 10 mm in length) and incinerated at  $1000^\circ\text{C}$  in a crucible using a gas burner. The ash in the tube was dissolved by concentrated HF solution for 12 h in a small Teflon container. After the solution was dried at  $160^\circ\text{C}$ , 50  $\mu\text{l}$  of concentrated nitric acid was added into the Teflon container; 20 ppm Co solution (10  $\mu\text{l}$ ) was then added as an internal standard in the TXRF analysis. The solution was concentrated to ca. 10  $\mu\text{l}$  and transferred onto a sample holder of optically flat pyrex glass plate and vacuum-dried for the TXRF measurement.

Cu  $K\alpha$  X-ray radiation from an X-ray tube was used as an excitation source in the TXRF measurement. The incident X-rays were monochromated by a  $\text{LiF}(200)$  monochromator and the X-ray beam with  $0.05 \text{ (H)} \times 20 \text{ (V)} \text{ mm}$  size was obtained by slits. A standard solution for preparation of a calibration curve was made by diluting the Mn standard solution (1000 ppm) with the electrolyte solution.

Mn K-X-ray absorption near-edge structure (XANES) spectra of the electrolyte solution sampled after cycling at 25, 50 and  $80^\circ\text{C}$  were measured in the fluorescence detection mode. Standard samples as references for various oxidation states of Mn were prepared by mixing powder reagents with BN powder. The measurements were carried out at BL-12C, Photon Factory (PF), High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. A  $\text{Si}(111)$  double-crystal monochromator was used. The intensity of the incident beam was measured by the ionization chamber detector and that of the fluorescent X-rays by a 19-element pure-Ge SSD (CANBERRA: GL0110P) at room temperature. The ordinate scale of the XANES spectra was normalized to the peak maximum point of the white line peak.

### 3. Results and discussion

Though electrolyte solutions were repeatedly sampled from the cell for TXRF analysis during the charge–discharge cycles, our in situ cell showed good cycling performance. This result demonstrates that the sampling of 10  $\mu\text{l}$  electrolyte solution does not affect the cycling performance of the cell. Since the concentration versus XRF intensity calibration curve showed good linearity from 3 to 500 ppm as Mn concentration, it can be concluded that the Mn concentration in the electrolytes can be analyzed successfully by our in situ TXRF technique. Fig. 2 (a) shows Mn dissolution after cell cycling at 25 and  $50^\circ\text{C}$ . The Mn concentration in the solution after 10 charge–discharge cycles was below the detection limit of this method at  $25^\circ\text{C}$ , while the concentration was found to be 8 ppm after 15th cycles. On the other hand, the Mn concentrations in the electrolyte solution at  $50^\circ\text{C}$  were determined to be 11, 56 and 393 ppm after the 5th, 10th and 15th charge–discharge cycles, respectively. Our results showed that the dissolution of Mn was accelerated at elevated temperatures and for higher cycle-number. A similar tendency was reported by Xia et al. [7]. The distribution of Mn concentration in the cell after the charge–discharge cycles was also measured at  $25^\circ\text{C}$ ; the result is shown in Fig. 2 (b). The Mn concentration was the highest at the center of the two electrodes. Their concentration difference

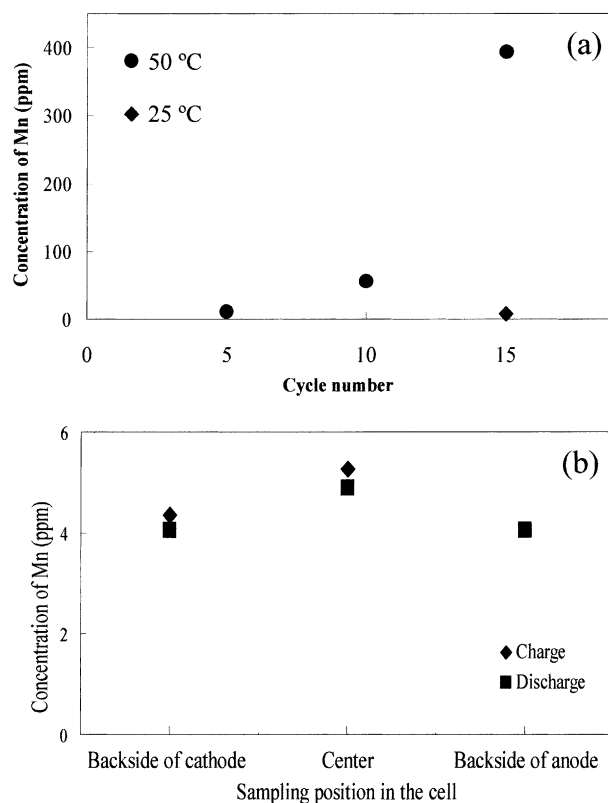


Fig. 2. (a) The concentration of Mn in the electrolyte solution as a function of cycle number, and (b) variation of the Mn concentration in the cell sampled at the charge and discharge state.

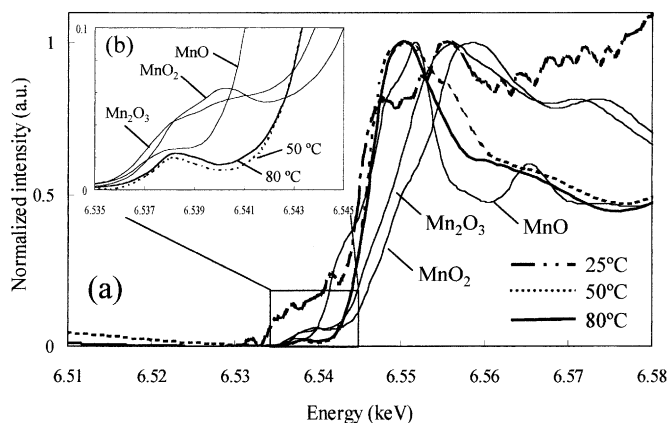


Fig. 3. (a) Mn K-XANES spectra, and (b) close-up view of the pre-edge region of the XANES spectra of standard materials and the electrolyte solution after cycling at 25, 50 and 80°C.

was not significant on the reverse sides of the electrodes. The Mn concentration tends to increase after charging. These observations suggest that the dissolution of Mn from  $\text{LiMn}_2\text{O}_4$  spinel occurs during the charge process, followed by diffusion in the cell during the discharge process.

Mn K-XANES spectra of the electrolyte solutions sampled at 25, 50 and 80°C and for the reference materials are shown in Fig. 3 (a). The edge positions of the electrolytes sampled at 50 and 80°C show that the oxidation state of the dissolved Mn ion is  $\text{Mn}^{2+}$ . The quality of the XANES spectrum for the sample at 25°C was poor because of the low concentration of the dissolved Mn. The pre-edge absorption at around 6.54 keV is due to the  $1s \rightarrow 3d$  absorption, which is a forbidden transition for octahedral ( $\text{O}_h$ ) symmetry by the dipole selection rule. It is known that this pre-edge peak well reflects the oxidation state of Mn [8]. As can be seen in Fig. 3 (b), the peaks at 6.538 keV of the electrolyte solutions can be ascribed to the  $\text{Mn}^{2+}$  ion by comparison with the reference materials. This observation supports the above interpretation of the XANES spectra based on the edge positions. The present analysis has revealed that dissolution of  $\text{LiMn}_2\text{O}_4$  is accompanied by reduction of Mn to  $\text{Mn}^{2+}$ . If Mn dissolves into the solution as  $\text{Mn}^{3+}$ , it undergoes the disproportionation reaction  $2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$  [7]. However, as can be seen from Fig. 3 (b), the existence of  $\text{Mn}^{4+}$  could not be detected in the electrolyte solution. The present results support the

hypothesis proposed by Aoshima et al. [9] that the dissolution of Mn takes place in the charged state (i.e. when the state of the cathode is  $\lambda\text{-MnO}_2$ ), which is then reduced to MnO by the action of EtOH at the cathode and dissolved into the solution.

#### 4. Summary

In situ determination of Mn concentration in the electrolyte has been carried out successfully using a combination of TXRF and a capillary technique. Mn concentration in the electrolyte solution increased with increasing the cycle number at higher temperatures. The Mn K-edge XANES spectra has shown that the Mn ion in the electrolyte solution is present as  $\text{Mn}^{2+}$ . A dynamical change in concentration and chemical state of Mn in the electrolyte can thus be shown experimentally for the first time.

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