# Speciation of Mn Catalyst of Lithium-Air Secondary Battery

**Tomohiro Hosokawa, Misaki Katayama, and Yasuhiro Inada**

*Department of Applied Chemistry, Graduate School of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan*

## 1. Introduction

Metal-air battery is a promising system as the high capacity secondary battery. The cathode reaction of the metal-air battery involves the oxidation/reduction reactions of molecular oxygen. A cathode catalyst such as $MnO_2$ is effective to improve the energy efficiency and the cyclic performance. However, the catalytically active species under the operating conditions is still unknown. In this study, we have clarified the chemical state of the Mn catalyst in the cathode material of the lithium-air battery during the discharging and charging processes by means of the X-ray absorption fine structure (XAFS) technique.

## 2. Experimental

Mn catalyst was supported on an electric conductor, Ketchen Black (KB). An aqueous solution of potassium permanganate was suspended by the KB powder and was added an aqueous solution of manganese sulfate and nitric acid. The mixture was refluxed for 24 h. The obtained slurry sample was washed by water and dried at 383 K for 12 h, and then calcined in air at 523 K for 2 h. The cathode sheet was prepared by coating the slurry mixture of Mn catalyst supported on KB and polyvinylidene difluoride with 1-methyl-2-pyrrolidone on Al mesh. A lithium-air battery cell was assembled by the cathode sheet, a separator sheet, a Li metal sheet, and 1 mol $dm^{-3}$ $LiPF_6$ solution in a 3:7 (v/v) mixture of ethylene carbonate and ethyl methyl carbonate. The cell made of stainless steel has two valves to flow the $O_2$ gas, which is saturated by the electrolyte solvent. All electrochemical experiments were curried out after flowing the $O_2$ gas for 30 min. The cut-off voltage was set to 4.3 V for charging and to 2.0 V for discharging. The battery capacity was calculated using the measured current per 1.0 g of the cathode material. The XAFS measurements were carried out at BL-3 for the cathode sheet taken from the disassembled cell at some specific charging and discharging states. The Mn K-edge XANES spectra were collected by the transmission mode.

## 3. Results and discussion

The charging and discharging curves of the present lithium-air battery are shown in Fig. 1. The curve for the first discharging step showed a plateau at 2.7-2.5 V, and the cell capacity was

274 mA h $g^{-1}$. At the next charging process, two steps at 3.2-3.4 V and 4.1-4.2 V were observed, and the charging capacity was comparable to that for the first discharging step. Although the cell voltage for the second discharging process was similar to that for the first process, the discharge capacity increased by about 60 mA h $g^{-1}$. Figure 2 shows the XANES spectra during the charging and discharging processes. The Mn species was first mixed state of $MnO_2$ and $Mn_3O_4$ before the first discharging step (a), and was quantitatively reduced to $Mn_3O_4$ at the initial stage of the discharging process (b). After that, the $Mn_3O_4$ state was kept until the final stage of the charging process (i). Although $Mn_3O_4$ was partially oxidized at around 4.3 V at (j), it was regenerated at the biginning of the next discharging process (k and l). The $Mn_3O_4$ state again existed during the discharging process, and a part of $Mn_3O_4$ was further reduced to the Mn(II) state at the end of the discharging process (o).

The present study clearly demonstrated that the active Mn species is practically $Mn_3O_4$ for the present lithium-air battery and that the initially prepared $MnO_2$ species on KB is unstable at the working electrode potential during the discharging process.

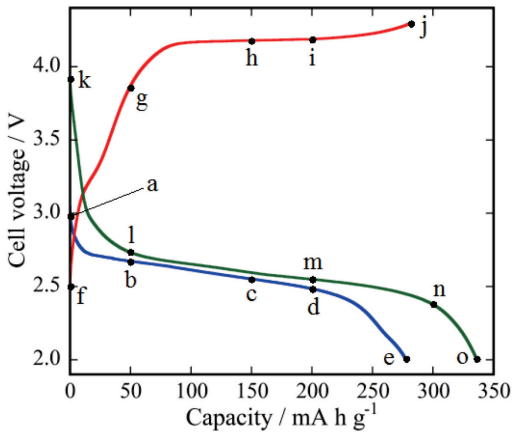


**Fig. 1** Charging and discharging curves of lithium-air battery. First discharging (blue), charging (red), and second discharging process (green). The points of the XAFS measurements are marked with filled circles (a–o).

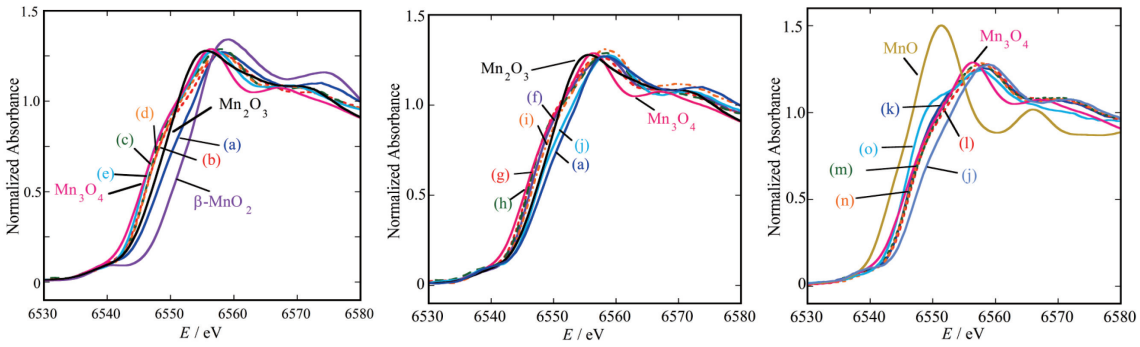


**Fig. 2** Mn K-edge XANES spectra for the cathode of lithium-air battery at a variety of state of charge and discharge. The labels of a–o correspond to those in Fig. 1.