Development of Electrochemical Cell for *in-situ* XAFS Measurement

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1. Introduction

In recent years, the demand for high-performance batteriesincreases in the worldfor developing electronic devices, such as cellular phone and notebook computer, and for dealing with environmental problems. Lithium-ion secondary battery(LIB) with high capacitiesisthus expected for the wide utilization as the electronic power sources. To develop new functional materials for LIB, it is necessary to understand the electrochemical reactionsoccurred in the electrodes during the charging and discharging processes to improve the performance. X-ray Absorption Fine Structure (XAFS) is a powerful technique for the analysis of the electrochemical reactions, because it affords the information about the local structure and the electronic statefor an X-ray absorbing atom.In addition, the XAFS technique is applicable to both solid and liquid samples without any long-range order of the atomic arrangement. Such property of the XAFS spectroscopy is very useful to analyze the electrochemically active species of the cathode in LIB. In this study, wehavethus developedan original electrochemical cell for the *in-situ* XAFS measurement to investigatethe electrochemical reactions of LIB by means of the XAFS technique.

2. Experiment

The picture of electrochemical cell for the*in-situ* XAFS measurement is shown in Fig. 1. The main housing of the cell is composed of a pair of disks made of Daiflon®, and the cell is set in the experimental hutch of BL-3 by using a holder made of Teflon® to maintain the electronic isolation. Fig. 2 schematically shows the cross section of the cell. The cell is composed of the Daiflon® disk with a Kapton® film as the X-ray window,a metallic Li anode (200 μm thickness)contacted with a copper-nickel sheet (20 μm thickness) with a nickel wire (1 mm diameter), an 1M solution of

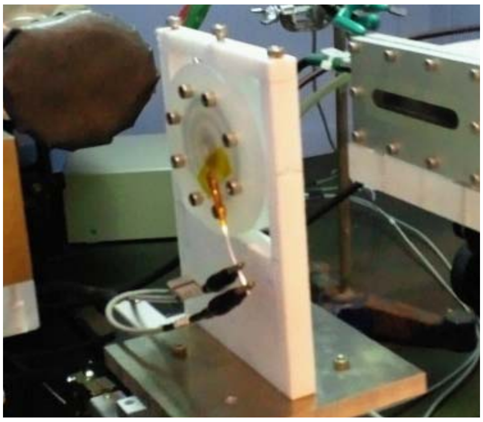

Fig. 1: The picture of electrochemical cell newly developed in this study.

$LiPF_6$ dissolved in a mixture of ethyl carbonate (EC) and ethyl methyl carbonate (EMC) (EC:EMC = 3:7 vol.%)), two sheets of Celgard® monolayer polypropylene separator impregnated with the electrolyte solution, and a cathode disk contacted with an Al sheet (20 μm thickness) as the collector. The cathode disk was prepared by pressing the dried slurry, in which the active material of $LiMn_2O_4$ (LMO), the acetylene black powder (Denka Black CA-250, Denka), and the binder material (KF polymer, Kureha) were suspended in *N*-methyl-2-pyrrolidone. The LMO powder was prepared by the solid-state reaction.

The charging/discharging operationwas performed in the voltage range of 3.0-4.3 V at a current rate of 0.2 C by use of HZ-5000 (Hokuto Denko).The XAFS measurements were carried out at BL-3 of the SR Center, Ritsumeikan University at the vicinity of the Mn K edge in the transmission mode. The Si(220) double crystal monochromator was used, and the incident and transmitted X-ray intensities were measured by the ionization chambers flowed by the mixture gas of N_2 and Ar.

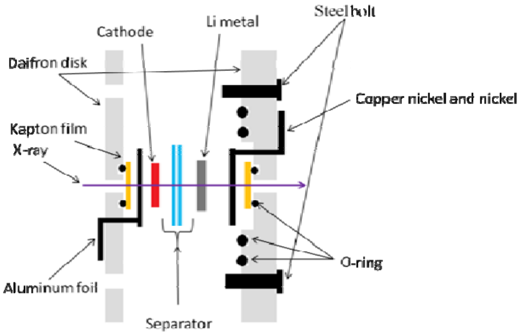

Fig. 2: The schematic diagram of the electrochemical cell.

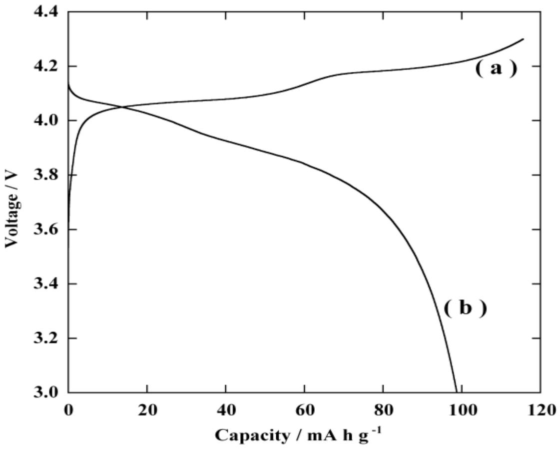

Fig. 3: The charging (a) and discharging (b) curve operated in the developed cell.

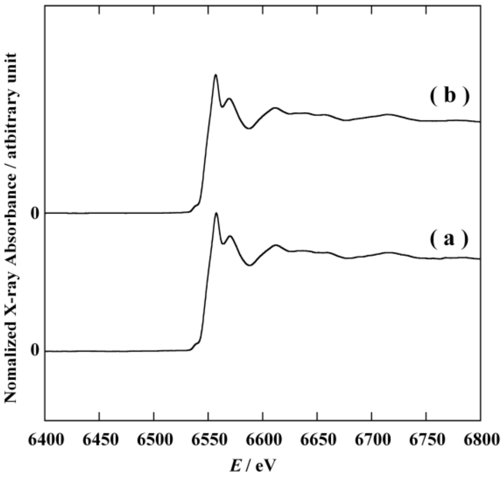

Fig. 4: XANES spectra of LMO in the developed cell (a) and without the cell (b).

3. Results and Discussion

The charging/discharging curve is shown in Fig. 3. It is known that LMO shows two distinct plateau regionsin voltage range of 3.8-4.0 V and 4.0-4.2 V and that the regions are related to the phase transition of cubic structure of LMO. The two distinct regionsare clearly observedin Fig. 3, indicating the correct working of the developed cell.

The XANES spectra of LMO are compared in Fig. 4 with and without the newly developed electrochemical cell.The spectra are perfectly in agreement, and it is thus found that the electrochemical cell does not influence the XAFS measurements.Figs. 3 and 4 clearly demonstrated that it becomes possible to perform the *in-situ* XAFS measurements by use of the newly developed electrochemical cell during the charging and discharging processes of LIB.