Electrochemical Cell for *in-situ* XAFS Measurements

Ryota Miyahara, Kazuhiro Hayashi, Misaki Katayama,
and Yasuhiro Inada

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

Abstract

We have developed two electrochemical cells for *in-situ* X-ray absorption fine structure (XAFS) measurements of electrode materials in lithium-ion secondary battery (LIB). One has been developed for the 2-dimensional imaging XAFS measurement to monitor the spatial distribution of the electrode reaction in the cathode. The electrochemical cell shows a normal charging/discharging curve and a good cycle performance as a rechargeable battery. In addition, the chemical map of the Mn species has been successfully obtained by the *in-situ* imaging XAFS measurement for the $LiMn_2O_4$ cathode in LIB using the newly developed electrochemical cell. The energy shift of the X-ray absorption edge observed during the charging process indicates the Mn(III) ions in $LiMn_2O_4$ is oxidized to Mn(IV) accompanying the Li(I) ion dissociation, and the spatial distribution of the electrode reaction can be analyzed by the 2-dimentional map of the Mn species. The obtained map indicates inhomogeneous distribution on the cathode sheet. The other cell has been developed for the XAFS measurements in the soft X-ray region below *ca*. 3 keV. It is difficult to apply the transmission mode in such energy region, because the irradiated X-ray is almost absorbed by the sample itself, medium materials, cell windows, and the other parts as the battery. The fluorescence-yield (FY) XAFS is very useful in such low energy region, and thus the electrochemical cell specially designed for the FY XAFS measurements has been developed in this study to expand the target element for the *in-situ* XAFS measurements during the electrochemical processes of LIB. The *in-situ* FY XAFS measurement was successfully performed using the developed electrochemical cell at the K edge of P for the cathode material of $LiFePO_4$. The XANES spectral change during the charging process is perfectly in agreement with the difference between $LiFePO_4$ and $FePO_4$, indicating that the electrochemical reaction proceeds correctly in the developed cell.

1. Introduction

In recent years, the demands for high-performance batteries increase in the world for developing electronic devices, such as cellular phone and notebook computer, and for dealing with environmental problems. Lithium-ion secondary battery (LIB), as a major power source from popular portable electronics to emerging electric vehicles, attracts considerable attention because of the lightweight, high energy density, and long cycle lifetime [1]. It is necessary to understand the electrochemical reactions occurred in the electrodes during the charging and discharging processes to improve the battery performance by developing new electrode materials for LIB. The cathodes of LIB are generally composed of some materials, such as an active material, a conductive additive, and a polymer binder. The electrode is heterogeneous on the scale of the secondary particle size. The chemical reactions are affected by the size and the surface condition of the particles of active material, which affect to the battery performance. It is thus important to understand the reaction distribution in the electrode to establish the next-generation rechargeable battery.

X-Ray absorption fine structure (XAFS) is a powerful technique to analyze the electrochemical reactions, because the analysis of the local structure and the electronic state of an X-ray absorbing atom is selectively available. In addition, the XAFS technique is applicable to both solid and liquid samples without any long-range orders of the atomic arrangement. Such property of the XAFS spectroscopy is very useful to analyze the electrochemically active species in the cathode of LIB. Another advantage of the XAFS technique is the applicability under reaction conditions. The *in-situ* measurements have been widely applied to many heterogeneous catalysts, which are operating under the reaction environments. The battery electrodes are also subjected to the *in-situ* XAFS measurements during the charging and discharging processes, and the special electrochemical cells for such measurements have been reported preciously. However, all such cells are possible to be used with the hard X rays. The XAFS analysis in the soft X-ray region is also very important to study the local structures and electronic states of many elements in functional materials, because the absorption edges are existed for the *K* shell of light elements, such as Mg, Al, S, Cl, P, etc. The development of the electrochemical cell is necessary to carry out the *in-situ* XAFS measurements in the soft X-ray region. In this study, we have thus developed original electrochemical cells for *in-situ* XAFS measurements in the wide X-ray energy region.

The chemical speciation is the most fundamental to clarify the function and reactively of the active materials. Spatially resolved mapping of chemical species is also very important to resolve the reaction mechanisms for many heterogeneous samples like battery electrodes. The understanding of distribution of chemical species is necessary to improve the performance of LIB [2,3]. Although the micro XAFS method is useful to obtain the chemical mapping, the enormous number of XAFS scans using an X-ray micro beam is necessary to cover the objective area of actual LIB electrode with the area of *ca*. 5 x 5 mm^2. The micro XAFS method is thus not suitable for *in-situ* measurements of LIB. Because the XAFS imaging method using 2-dimensional detector can obtain the chemical mapping for a large area (order from mm^2 to cm^2), it is suitable to obtain the distribution of chemical species for the operating LIB electrodes. This technique has been applied to the LIB cathode to visualize the spatial distribution during charging reactions in this study.

2. Experimental

2.1 Electrochemical cell for *in-situ* imaging XAFS measurements

The picture of electrochemical cell for the *in-situ* imaging XAFS measurements 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 X-ray beam by using a holder made of Teflon® to maintain the electric isolation. Fig. 2 schematically shows the cross section of the newly developed 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 Cu-Ni sheet (20 μm thickness) by a Ni wire (1 mm diameter), 1 M solution of $LiPF_6$ dissolved in a mixture of ethyl carbonate (EC) and ethyl methyl carbonate (EMC) (EC : EMC = 3 : 7 v/v)) as the electrolyte solution, 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 onto the Al sheet. 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 by *N*-methyl-2-pyrrolidone in the slurry. The LMO powder was prepared by the solid-state reaction [4].

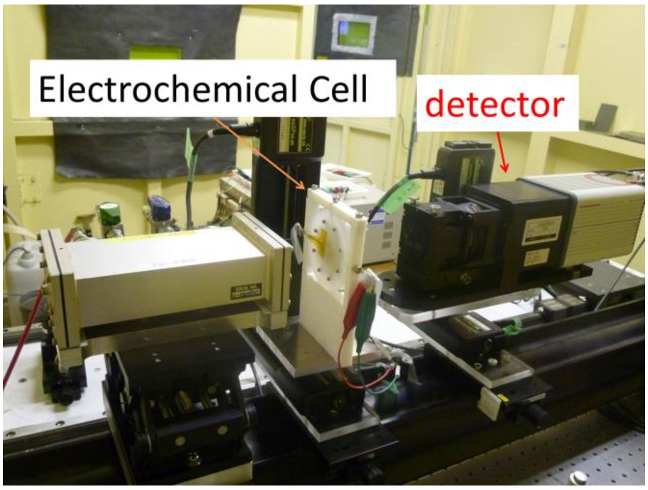

Figure 1. The picture of electrochemical cell for imaging XAFS measurements.

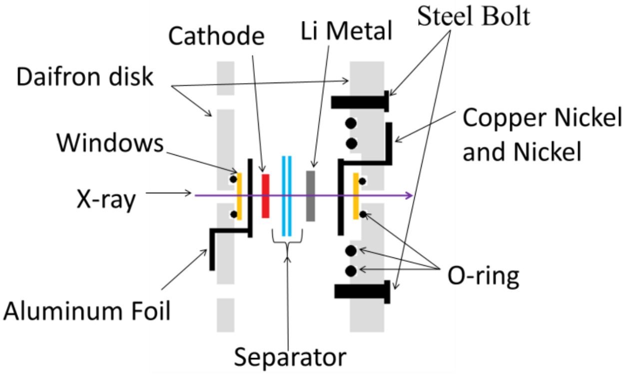

Figure 2. The schematic diagram of the electrochemical cell for imaging XAFS measurements.

The charging/discharging operations were performed in the voltage range of 3.0-4.3 V at a current rate of 0.2 C by the electrochemical instrument HJ1001SD8 (Hokuto Denko). The 2D-imaging XAFS measurements were carried out at BL-4 of the SR Center of Ritsumekan

University and at NW2A of PF-AR in High Energy Accelerator Research Organization at the vicinity of the Mn K edge in the transmission mode. The Ge(220) and Si(111) double crystal monochromator was used, respectively. The incident X-ray intensity was measured by the ionization chamber, and the transmitted X-ray intensity was detected by 2-dimensional X-ray detector (Flash2.8, Hamamatsu Photonics).

2.2 Electrochemical cell for *in-situ* XAFS measurements in soft X-ray region

The picture of electrochemical cell is shown in Fig. 3 for *in-situ* XAFS measurements in the soft X-ray region. The cell is composed of three parts. The parts made of stainless steel (Part A and B in Fig. 3) are used for the collector of cathode and anode, respectively. The other made of Teflon® (Part C in Fig. 3) is used as the main body of this cell. The cell is set in BL-10 of the SR Center of Ritsumeikan University by using an acrylic holder to maintain the electronic isolation. A cross section of the cell is schematically shown in Fig. 4. The cell is composed of a metallic Li anode (200 μm thickness), 1 M solution of $LiBF_4$ dissolved in a mixture of EC and EMC (EC : EMC = 3 : 7 v/v)), two sheets of Celgard® monolayer polypropylene separator impregnated with the electrolyte solution, and a cathode material applied onto a Kapton® film as the X-ray window. The dried slurry of $LiFePO_4$ (LFP) (TODA), the acetylene black powder, and the binder material suspended in *N*-methyl-2-pyrrolidone was applied, dried, and pressed on the Kapton® film.

The charging operation was performed in the voltage range of 0.5-5.0 V at a current rate of 0.1 C by HJ1001SD8. The *in-situ* XAFS measurements in soft X-ray region were carried out at BL-10 of the SR Center of Ritsumeikan University at the vicinity of the P K edge in the fluorescence-yield (FY) mode. The Ge(111) double crystal monochromator was used. The incident X-ray intensity was measured using a Cu mesh. The

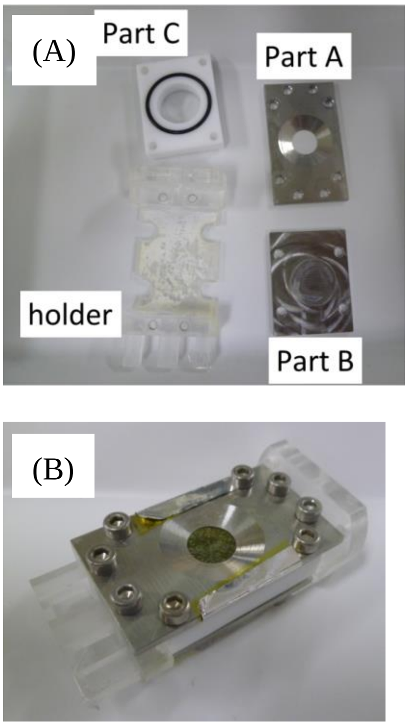

Figure 3. The picture of newly developed electrochemical cell for *in-situ* XAFS measurements in soft X-ray region.

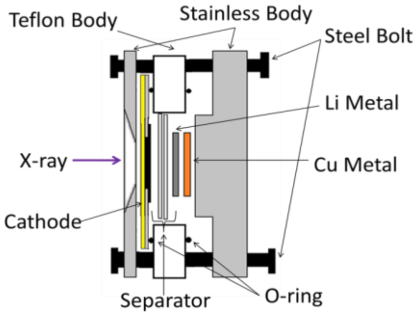

Figure 4. The schematic diagram of the electrochemical cell for *in-situ* XAFS measurement in soft X-ray region.

silicon drift detector (TXD2300H50, Techno X) was used to measure the fluorescence intensity. The cell was put under the He atmosphere.

3. Results and Discussion

3.1 *In-situ* imaging XAFS measurement for $LiMn_2O_4$ cathode

A result of the capacity measurement is shown in Fig. 5A for the LMO cathode operated in the developed electrochemical cell by comparing with that in a standard test cell of LIB. It is known that LMO shows two distinct plateau regions in voltage range of 3.8-4.0 V and 4.0-4.2 V and that the regions correspond to the phase transitions of the cubic structure [5]. The two plateaus are clearly observed in Fig. 5A. The cycle performance is represented in Fig. 5B, and it is found that the battery capacity keeps almost constant for 15 cycles. These results indicate the correct working of the developed electrochemical cell.

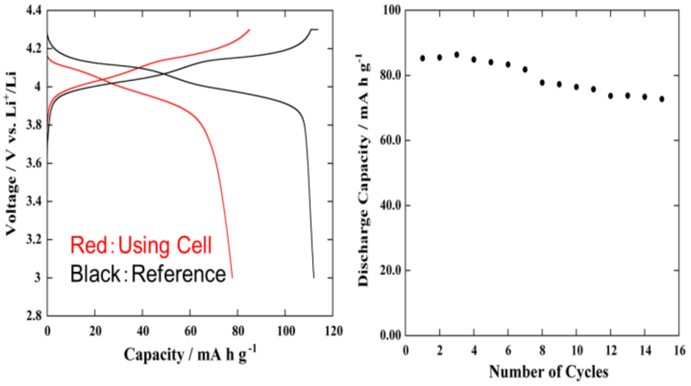

Figure 5. The battery capacity (A) and the cycle property (B) measured using the newly developed *in-situ* cell for the imaging XAFS measurements.

Figure 6 shows the XANES spectra of LMO measured using the developed *in-situ* cell. It is clearly observed that the absorption edge is shifted to the higher energy together with the charging progress, because the oxidation of the Mn(III) species to Mn(IV) is accompanied by the Li^+ ion extraction. The peak top energy at the white line of XANES spectrum is used to the measure of the oxidation state of the Mn species. The chemical state of the Mn species on the cathode sheet can be estimated on the basis of the peak-top energy, which is related to the charging progress. It should be noted that the XAFS measurements have been carried out in the transmission

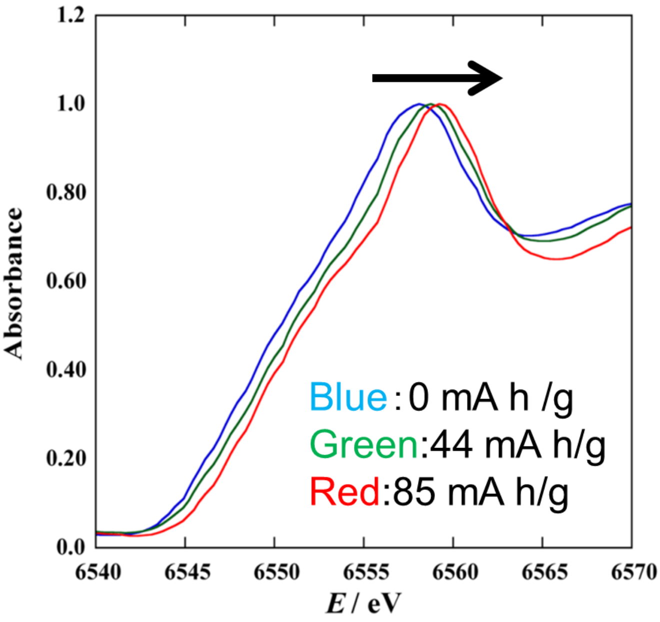

Figure 6. XANES spectral change during the charging reaction of the LMO cathode measured at the Mn K edge using the developed *in-situ* cell.

mode. The observed energy shift is the result of the average for all Mn species existed in the X-ray light path. A 2-dimentional measurement of XANES spectra for a cathode sheet can reveal the spatial distribution of the Mn species with different chemical state. The progress of the electrode reaction is thus resolved spatially on the cathode sheet according to the obtained chemical state map.

Three maps are given in Fig. 7 at three different charging depths. In Fig. 7, the blue and red pixels respectively indicate the regions containing the Mn species with the lower and higher oxidation state. The pixel color has been judged according to the peak-top energy of the XANES spectrum as explained in Fig. 7. The inhomogeneous distribution of the chemical state is clearly observed at the intermediate charging depth. The inhomogeneous electrode reaction has also observed for the cathode of $LiFePO_4$ (LFP) [3], for which the electrode reaction starts at a certain position. The reaction progresses radially from the position, and the oxidized $FePO_4$ species forms a domain with the size of 100 μm order at the intermediate charging state. The formation of such domains is ascribed by the favorable electric conductance in the cathode material. In the case of LMO, the spot is also observed but the size is very small in comparison with the case of LFP. Many small spots are spread around the cathode sheet. The random distribution of the spots is considered to relate to the small and homogeneous particles of LMO.

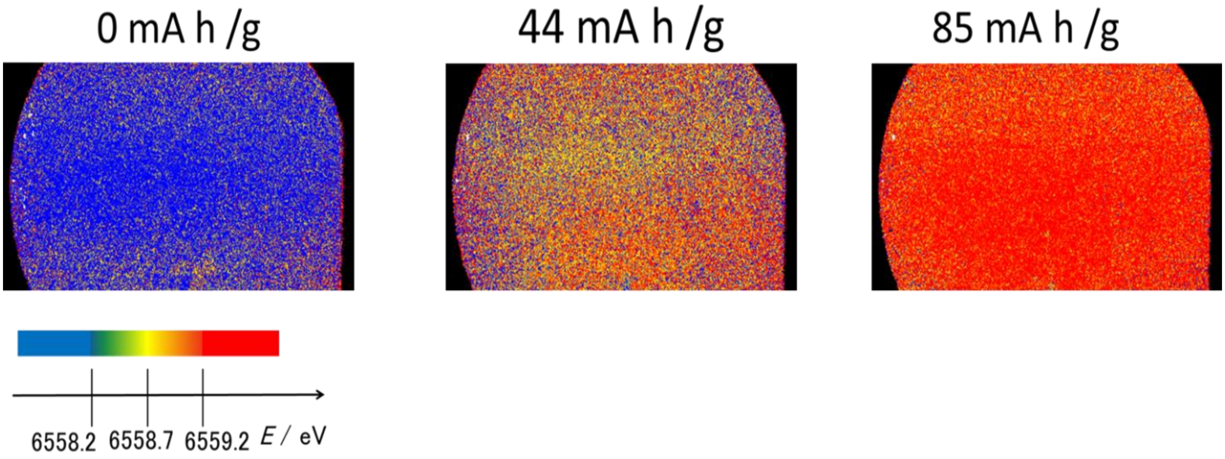

Figure 7. The chemical state map of the Mn species for the LMO cathode obtained by *in-situ* imaging XAFS measurement.

3.2 *In-situ* XAFS measurement at P K edge for $LiFePO_4$ cathode

The XAFS spectral change at the P K edge is given in Fig. 8 during the charging process of the LFP cathode obtained by the XAFS measurements using the developed *in-situ* cell. The energy shifts of the absorption edge and the white-line peak top are clearly observed, and the spectral change is perfectly in agreement with the difference between LFP and $FePO_4$. The appearance of a weak pre-edge peak at around 2148 eV also supports the formation of $FePO_4$. The perfect agreement of the final XANES spectrum with that of $FePO_4$ strongly demonstrates that the newly developed *in-situ* XAFS cell works correctly as an electrochemical cell under the He atmosphere in the beamline chamber of BL-10.

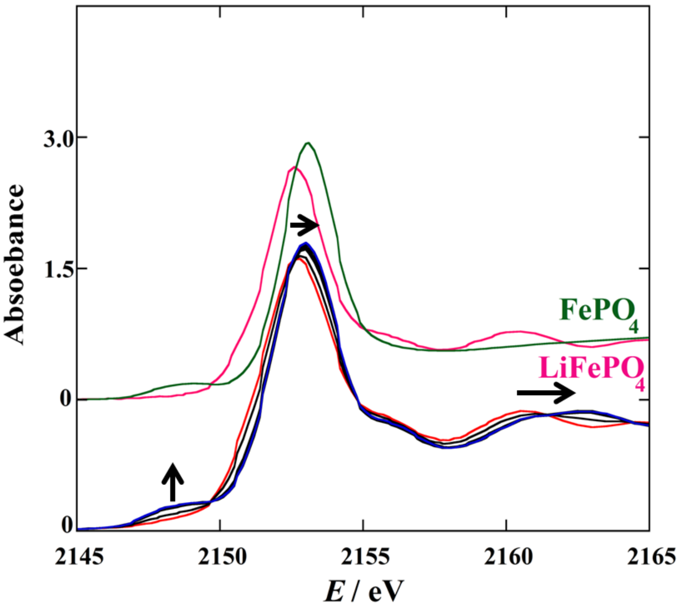

Figure 8. XANES spectral changed at the P K edge during the charging process of the $LiFePO_4$ cathode measured using the developed *in-situ* electrochemical cell for the soft X-ray region.

Because there is an opening area in the electron correcting Al foil of the cathode at the X-ray irradiating position of the *in-situ* cell, the inner electric resistance as the battery is considerably higher than the standard test cell and the developed in-situ XAFS cell for the imaging XAFS measurements. The X-ray focusing at the sample position is quite effective to restrain the opening area, leading to reduce the inner resistance of the *in-situ* XAFS cell. The application of a metal-deposited Capton® film to the cell window can improve the electrochemical performance, because such film has the electron-correcting function for the cathode. The cathode active material is directly applied onto the metal-deposited film, and then the incident and the fluorescent X rays can transmit the film to achieve the fluorescence XAFS measurements.

4. Conclusion

Two original electrochemical cells for *in-situ* XAFS measurements have been developed for imaging and fluorescence XAFS method. The latter is applicable to the soft X-ray region. The spatially resolved XAFS imaging has been successfully performed under the operating conditions for the charging process using the developed *in-situ* cell for the LMO cathode of LIB. The randomly distributed small spots, at which the electrode reaction is completed, have been observed at the intermediate stage. The spatial distribution and the size of the spot are intimately related to the electrochemical performance as the secondary battery. In addition, it has succeeded to observe the electrode reaction from LFP to $FePO_4$ at the P K edge by the *in-situ* XAFS cell for the soft X-ray region. The expansion of target elements for *in-situ* XAFS measurements is quite effective to analyze the electrochemical reactions occurred in the electrode. Such applications will become important to interpret the reaction mechanisms for the next-generation secondary batteries.

Acknowledgement

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Reference

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