

# Development of Double Element DXAFS Instrument at BL-5

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## Abstract

A new dispersive XAFS system with two polychromator crystals was developed to measure the XAFS spectra simultaneously at two absorption edges. The developed double-element DXAFS (DE-DXAFS) system consists of a double polychromator system involving two polychromator crystals with different curvatures and a position-sensitive detector. *In-situ* XAFS experiments for the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode of the lithium-ion battery demonstrated the ability of the DE-DXAFS technique, which enabled us to get the information about the chemical state change of the Ni and Mn species simultaneously under the battery operation. It is clarified that the redox reactions of the Ni species occur at higher voltage than 4 V for both the charging and discharging processes, and at lower voltage the Mn species works as the active center for the redox reactions.

## 1. Introduction

Many promising active materials for the lithium-ion battery (LIB) cathode such as  $\text{Li}_2\text{MnO}_3$ - $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  include more than one transition metal element [1]. The modification of the transition metal species in the cathode material is effective to improve the structural stability and to control the operating voltage [2]. The redox behaviors of the transition metal elements under the operating condition of LIB are essentially important to discuss the electrochemical reaction of the active material. The X-ray absorption fine structure (XAFS) technique is the most useful tool to determine the oxidation state of the metal element. *In-situ* XAFS analysis for the high-rate charge/discharge processes recently becomes important to develop a high-performance LIB, however, it is impossible to apply the conventional monochromator-scanning XAFS measurement to monitor the redox reactions for more than one element during the fast charging and discharging processes. Therefore, we have designed a new dispersive XAFS (DXAFS) instrument to continuously monitor the chemical state of two transition metal species without any mechanical movements of the measurement equipment.

## 2. Double-Element DXAFS System

The double-element DXAFS (DE-DXAFS) system was developed at BL-5 for experiments using a white X-ray. Figure 1 shows the concept of DE-DXAFS. The XAFS spectra at two energy regions corresponding to the absorption edges of different elements are simultaneously measured using two separated white X-ray beams and two bent crystals as the polychromator. A picture of the developed DE-DXAFS instrument in the experimental hutch of BL-5 is shown in Fig. 2. The polychromator chamber equipped with a manual Z-stage was

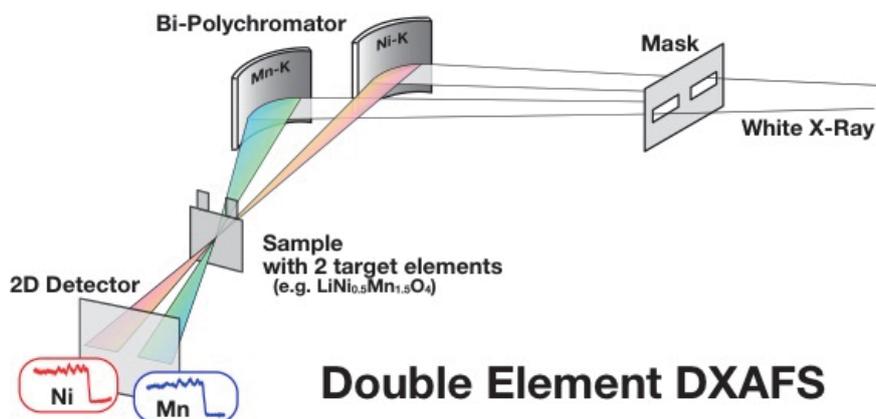
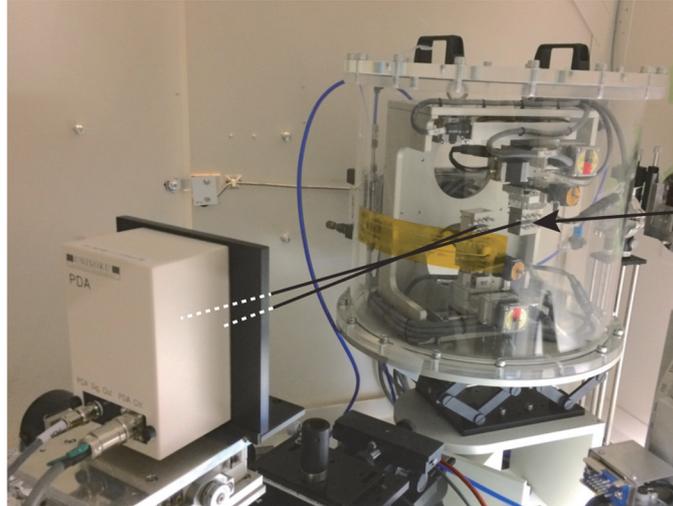
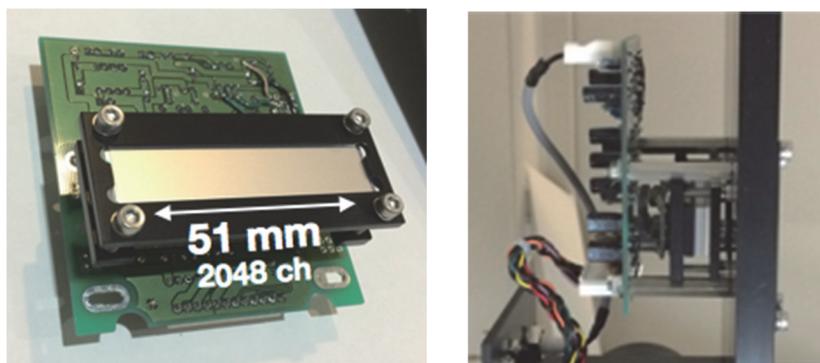


Fig. 1 Conceptual image of double-element DXAFS instrument.



**Fig. 2** Newly developed DE-DXAFS instrument in the experimental hutch of BL-5.

made of acrylic resin and was designed to be portable for the experiments at the other synchrotron facilities. The chamber has a Be window for the incident white X-ray beam and a wide polyimide film window covered the  $2\theta$  angle from  $-5^\circ$  to  $60^\circ$  for the diffracted X-ray beam from the polychromator. Two sets of the goniometer to control the polychromator position and its incidence angle are placed in the chamber, in which the He gas is flowed to replace the atmosphere. The Si(111) crystal (0.5 mm thickness) used as the polychromator is cylindrically bent in the crystal holder with a fixed curvature, in which the cooling water is circulated. The white X-ray beam passes through a mask with two rectangle holes, and the generated white X-ray beam irradiates to each polychromator. The diffracted and polychromatic X-rays are focused at a point outside the polychromator chamber. For the DE-DXAFS instrument, it is necessary that two polychromatic X-rays with the different X-ray energies are focused at the same position, where the sample is placed. The diverged X-rays transmitted through a sample reach to a position-sensitive detector. In this study, a photodiode array detector with 2048 sensing elements is used as the detector. A Tl-doped CsI scintillator with a fiber plate is optically coupled with the photodiode array to convert the X-ray to the visible light (see Fig. 3). The

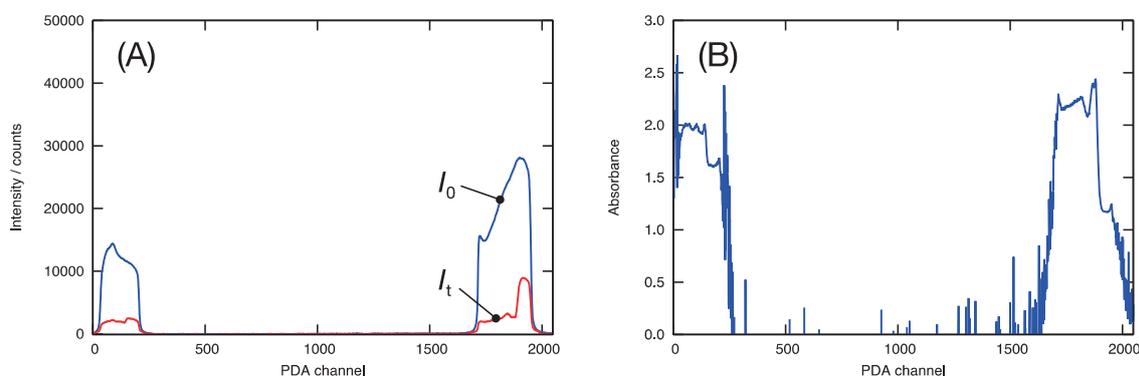


**Fig. 3** The position-sensitive photodiode array detector coupled with a Tl-doped CsI scintillator.

curvature of the polychromator crystal relates to the position of the focal point, and thus it restrains the target absorption edge because the two X-ray beams reflected by the required angle to get the desired X-ray energy must reach to the same focal point. We have designed two crystal holders with the curvature radius of 3000 mm and 1810 mm in order to obtain the X-ray energy for the XAFS measurements at the Ni and Mn K edge. The actual focal points and the light paths of the polychromatic X-rays were monitored using a 2-dimensional detector to align precisely the two polychromator. When the positions of two focal beams were perfectly matched, the half width of the piled focal beam was 0.38 mm when the horizontal widths of white X-rays were 5 mm. The available X-ray energy was calibrated by referring the absorption edge of the reference sample.

### 3. XANES Spectra Measured by the DE-DXAFS Instrument

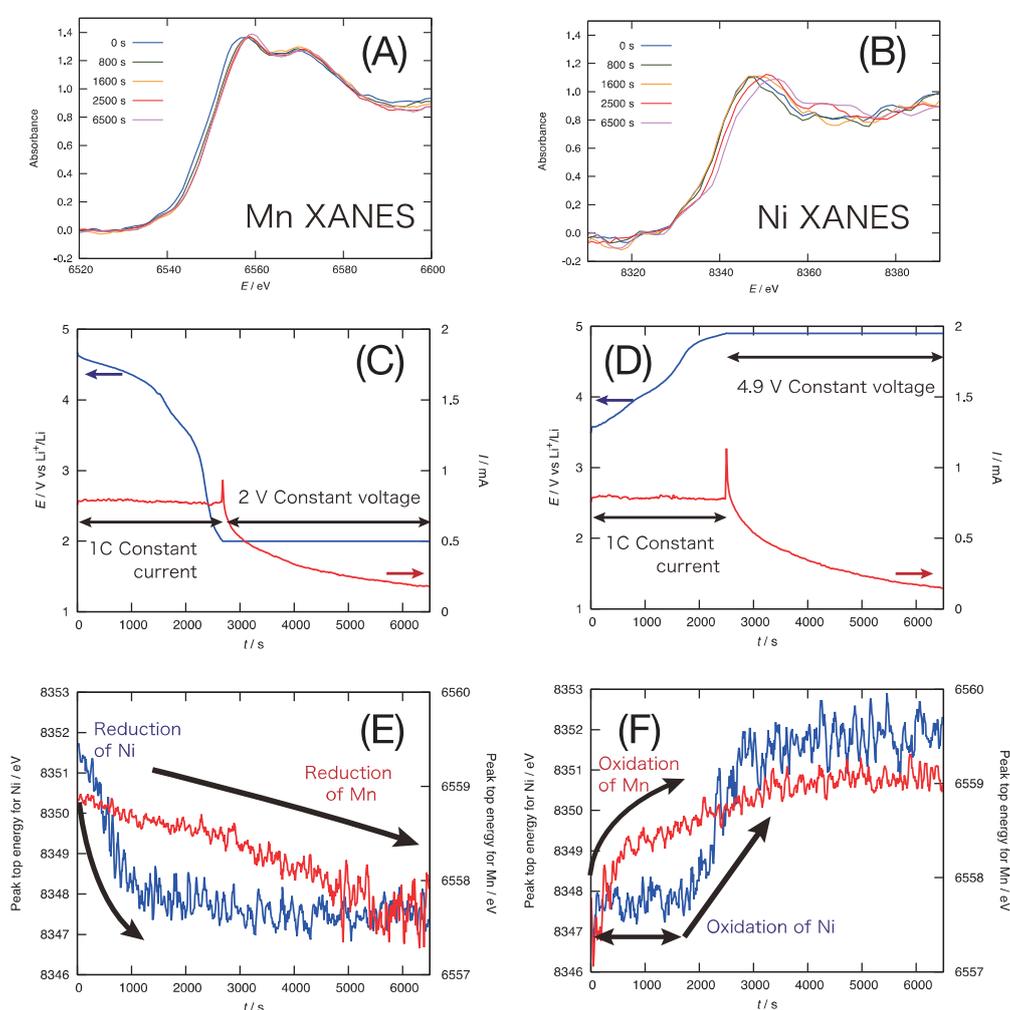
Figure 4(A) shows the raw data of the transmitted X-ray intensities measured by the DE-DXAFS instrument for the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode sheet. The intensities of two polychromatic X-rays with the energies around the Mn and Ni K edge were measured using the same detector without the sample in the light path to obtain the  $I_0$  data, which is shown by the blue curve in Fig. 4(A). After the sample was placed at the focal point, the transmitted intensities were measured to obtain the values of  $I_t$ . The X-ray absorbance at the Mn and Ni K-edge is calculated by taking  $\ln(I_0 / I_t)$  and is given in Fig. 4(B). As clearly seen in Fig. 4(B), two absorption edges of the Mn and Ni elements are observed simultaneously at the different area of the detector. In this case, the Mn and Ni K edge was appeared at *ca.* 1890 ch and *ca.* 147 ch, respectively. Although the available energy range was limited, the XANES spectra were successfully obtained with the proper energy resolution in spite of the large horizontal emittance of the light source at the SR Center as seen in Fig. 4(B) when the detector was placed at a sufficiently distant position from the focal point.



**Fig. 4** The raw data of the transmitted X-ray intensities measured by the DE-DXAFS instrument for the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode sheet (A) and the X-ray absorbance at the Mn and Ni K-edges calculated by taking  $\ln(I_0 / I_t)$  (B).

#### 4. *In situ* Measurement for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode of LIB

The DE-DXAFS measurement has been carried out during the charging/discharging processes for the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode of LIB. The XANES spectra at the Mn and Ni K edges were measured simultaneously for the operating LIB. The observed XANES spectral change at the Mn and Ni K edge is shown in Fig. 5(A) and 5(B), respectively, during the charging process of the over-lithiated state ( $\text{Li}_{1.2}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ) which has been generated by the constant voltage discharging at 2.0 V. The energy shift of the absorption edge was clearly observed for both elements. The cell voltage and current are depicted in Fig. 5(C) and 5(D) as a function of time for the discharging and charging process, respectively. The constant current discharging and charging process was carried out with the rate of 1 C and was followed by the constant voltage discharging and charging process at 2.0 V and 4.9 V, respectively. The constant voltage discharging process was performed to generate the over-lithiated state, and the total discharge



**Fig. 5** XANES spectra of charging process for Mn (A) and Ni K-edge (B); Electric current and cell voltage for the discharging process (C) and the following charging process (D); Time-course of the energy of the white line peak for the discharging process (E) and the charging process (F).

capacity was 180 mA h g<sup>-1</sup>, which corresponded to 123 % of the theoretical capacity of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>. Almost all Li<sup>+</sup> was then released at the followed charging process with the capacity of 179 mA h g<sup>-1</sup>.

The X-ray energy of the white line peak of the XANES spectrum is plotted as a function of time for the discharging and charging process in Fig. 5(E) and 5(F), respectively. The fully delithiated Ni<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> state has been generated at the beginning of the discharging process, and it is then obviously demonstrated that the reduction of the Ni center precedes the valence change of the Mn center. It is also demonstrated that the high cell voltage at over 4 V is originated from the reduction of the Ni species and that the Mn species keeps its chemical state during the first constant current discharging step. When the valence change of the Ni species is finished, the cell voltage is dropped to less than 3.5 V. After that, the valence state of the Mn species is gradually changed during the constant voltage discharging process at 2.0 V, where the Ni species is kept unchanged. On the contrary, the charging process is initiated by the oxidation of the Mn species at the cell voltage of *ca.* 3.5-4.2 V. The oxidation of the Ni species follows the oxidation of Mn after the charging voltage reaches to 4.5 V. The simultaneous measurements of the chemical state change for the Mn and Ni species have been first achieved by the DE-DXAFS technique, and the results clearly indicate the different phase of the chemical state change for the transition metal elements.

## 5. Conclusion

The newly designed DE-DXAFS instrument was developed at BL-5 of the SR Center. The DE-DXAFS instrument was applied to the *in-situ* experiments for the LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode of LIB. The chemical states of both the Mn and Ni species were simultaneously observed during the discharging and charging processes. The redox reactions of the Ni species occur at higher voltage than 4 V for both processes, and at lower voltage the Mn species works as the active center for the redox reactions. The present study shows the dynamic changeover for the chemical state of two metal elements, and such data is very important to clarify the electrochemical reaction for the next-generation electrode materials, which contain more than one transition metal element. The DE-DXAFS instrument is expected to become a powerful tool for the mechanistic analysis and will provide the useful information for the material design.

## References

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