

Development of 2-Dimensional Imaging XAFS System at BL-4

Koichi Sumiwaka¹, Misaki Katayama², Yasuhiro Inada²

- 1) *Department of Applied Chemistry, College of Science and Engineering, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan*
- 2) *Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan*

Abstract

The 2D-imaging XAFS system has been developed at BL-4 of the SR Center. The system is mainly composed of the ionization chamber for the I_0 measurement, the sample stage, and the two-dimensional CMOS image sensor to measure the transmitted X-ray intensity. The X-ray energy shift in the vertical direction, which is come from the vertical divergence of the X-ray beam on the monochromator surface, is corrected in considering the geometrical arrangement of the monochromator. The data analysis system has been also developed to find automatically the energy of the absorption edge, and thus the chemical species are possible to be mapped on the basis of the XANES feature in the wide area of 4.8 mm(H) \times 3.6 mm(V) with the maximum resolution of $2.5 \times 2.5 \mu\text{m}^2$. This system is expected to become a powerful tool to analyze the spatial distribution of the chemical species for many heterogeneous materials, especially for the heterogeneous catalysts and the battery electrode samples.

1. Introduction

Identification of chemical species is the most fundamental to clarify the chemical function and reactivity. In addition, the equilibrium and the kinetics of chemical reactions at solid surface must be influenced by the particle size and surface condition [1,2]. The understanding of feature of active species in small regions is very important to improve the performance of heterogeneous sample, such as lithium ion secondary batteries (LIB) and catalysts. Demand for the spatially resolved measurement is large in the field of electrochemistry and catalysis chemistry. Although the atomic distribution can be analyzed by a combination of the scanning electron microscope (SEM) and the X-ray fluorescence (XRF) analysis, we cannot obtain the distribution of chemical species.

X-Ray absorption fine structure (XAFS) method is a powerful tool to analyze the local structure and electronic state of the objective element. The micro XAFS method is operated using microbeam X-ray to investigate microscopic region in a sample. The microbeam is normally generated by the Kirkpatrick-Baez focusing optics or zone plate focusing system, and the spatial resolution reaches the sub- μm order in such cases. This method can obtain the XAFS spectrum at a specific small region, however the enormous number of XAFS scan (for example, a million times of measurement needs to examine an area of a few cm^2 with the $10\ \mu\text{m} \times 10\ \mu\text{m}$ microbeam X-ray) is necessary to cover the objective area. Thus, we have developed the imaging XAFS method using a 2-dimensional detector for mapping the distribution of chemical species at a large area (order from mm^2 to cm^2).

We have previously reported about the one-dimensional imaging XAFS system using the photodiode array (PDA) linear detector [3]. In this report, the detail system configuration will be presented for a new 2-dimensional imaging XAFS system using complementary metal-oxide semiconductor (CMOS) image sensor. The 2-dimensional XAFS imaging system in the transmission mode is applied to the LIB cathode sample to visualize the spatial distribution during electrode reactions.

2. Imaging XAFS Measurement System

The 2-dimensional XAFS imaging system have been constructed at BL-4 of the SR center. Figure 1 shows the schematic diagram of the measurement system in the experimental hutch of BL-4. The transmitted X-ray is measured by the 2D X-ray detector (Flash 2.8, Hamamatsu Photonics). The 2D detector consists of a CMOS image sensor, a zooming optics of visible light, and a scintillator. The P43 (Tb^{3+} -doped $\text{Gd}_2\text{O}_2\text{S}$, $10\ \mu\text{m}$ thickness) was used as scintillator to convert X-ray to the visible light. The zooming optics expands the image at the scintillator with the fixed expansion ration of 1.45. The scintillator and zooming optics are located in a box to shield from the visible light, and the box is equipped with an X-ray

window of the aluminum-deposited mylar film. The CMOS image sensor has the matrix arranged 1920×1440 CMOS elements and the actual size of one element is $3.63 \mu\text{m} \times 3.63 \mu\text{m}$. Thus the area of $4.8 \text{ mm} \times 3.6 \text{ mm}$ is covered as the field of vision with the maximum spatial resolution of $2.5 \times 2.5 \mu\text{m}^2$. The A/D converter of the image sensor has the dynamic range of 12-bit. The non-focused X-ray beam at BL-4 (normally $4 \text{ mm(H)} \times 3 \text{ mm(V)}$) is irradiated to the CMOS detector.

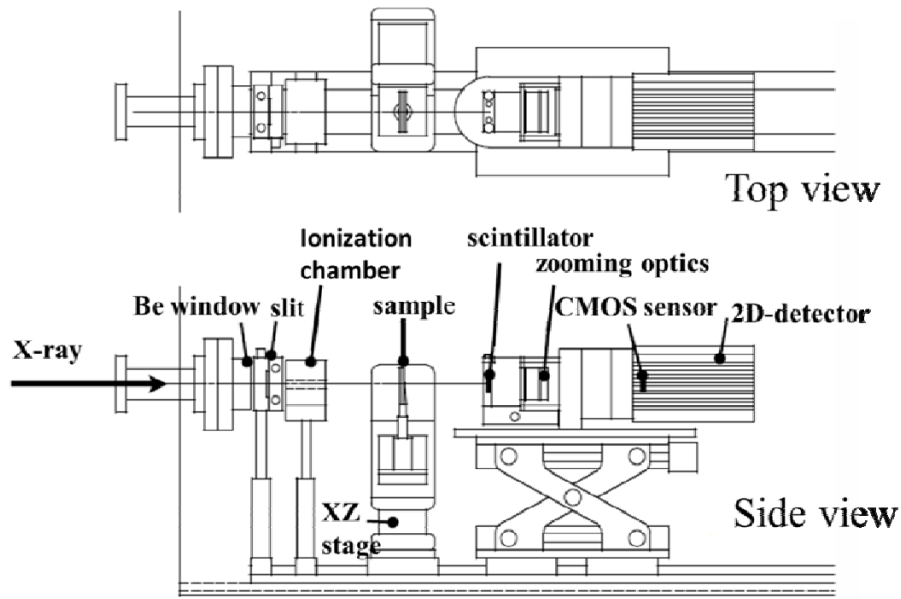


Figure 1. Schematic diagram of 2D XAFS imaging system.

3. Imaging XAFS Spectra and Energy Correction

The raw data of the 2D imaging XAFS system is composed of a 3-dimensional array of the transmitted X-ray intensities, $I(E', x, y)$, where E' is the apparent X-ray energy calculated by the monochromator angle and (x, y) is the coordinate at the detector surface. The X-ray absorbance μt is given by eq. (1),

$$\mu t(E', x, y) = \ln \frac{I_0(E')}{I(E', x, y)} \quad (1)$$

where $I_0(E')$ is the intensity detected by the ionization chamber. When the values of incident X-ray intensity are separately measured using the 2D detector, this term is replaced with $I_0(E', x, y)$. The XAFS spectrum for a specific area can be obtained by integrating $\mu t(E', x, y)$. However, because there is a vertical energy variation in the incident X-ray beam, it is

necessary to correct the apparent X-ray energy E' into the real energy E measured at one CMOS element. The incident angle to the monochromator crystal surface depends on the distance (y) from the horizontal plane. When the angle between the monochromator crystal surface and the horizontal plane is the Bragg angle θ , the difference of the incident angle ($\Delta\theta$) from θ is geometrically derived at y as eqs. (2) and (3) for the Golovchenko-type monochromator,

$$\Delta\theta = \tan^{-1} \frac{y - y_0}{L} \quad (2)$$

$$L = L_0 + \frac{D}{\sin 2\theta} - \frac{D}{\tan 2\theta} \quad (3)$$

where y_0 denotes the vertical position of the horizontal plane, L is the distance from the light source to the detector, L_0 corresponds to L when $\theta = 45^\circ$, and D is the height difference between the incident and exited X-ray beams of the monochromator. The real X-ray energy, E / eV, at the position y is then given by eq. (4),

$$E = \frac{12398.52}{2d \sin(\theta + \Delta\theta)} \quad (4)$$

where $d / \text{\AA}$ is the lattice spacing of the monochromator crystal.

Figure 2 shows the XAFS spectra of the Co foil measured using the newly developed 2D-imaging XAFS system. The μt values at three different areas are plotted versus the apparent E' value in Fig. 2(a), and it is clearly observed that the absorption edge is different in the three spectra and that the edge energy at upper area is higher than that at lower area. The XANES corrected spectra using eqs. (2)–(4) are shown in Fig. 2(b). The real energy E is reasonably corrected by introducing the term of $\Delta\theta$. We have developed the analysis program to correct automatically the energy shift and to analyze every spectrum at all detector elements. The absorption edge energy, E_0 , can be estimated as the energy at the maximum of the first derivative function of μt , and the E_0 value is used as the measure of the chemical state analysis. In addition, the content of the absorbing atom can be measured by the absorbance difference, $\Delta\mu t$, between the pre- and post-edge regions. The analysis program can draw the 2D map for the chemical state of the absorbing atom by changing the color and the brightness according to the E_0 and $\Delta\mu t$ values.

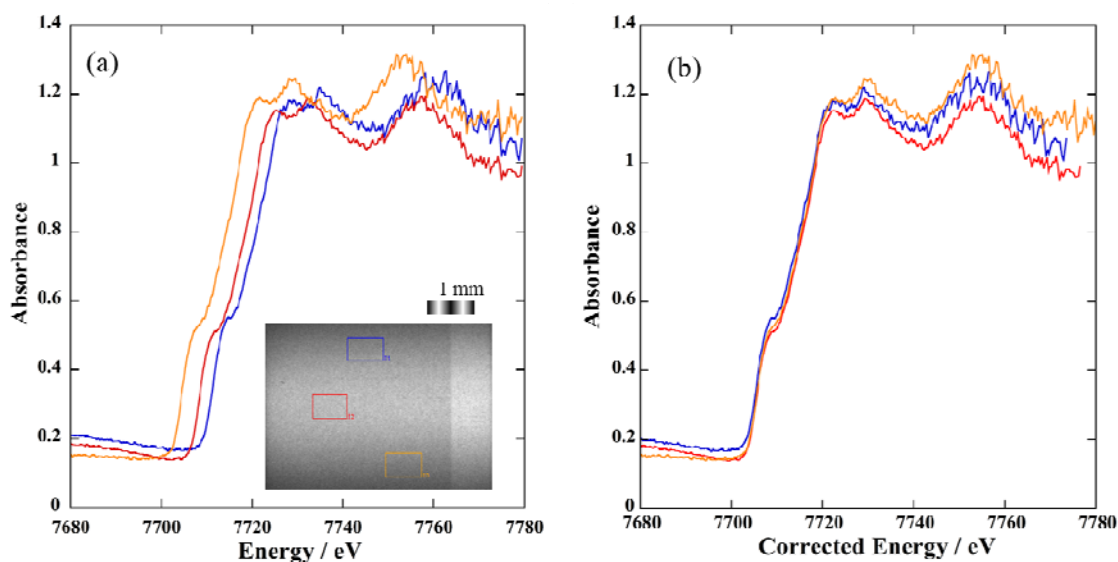


Figure 2. (a) XANES spectra of Co foil without energy correction and (b) XANES spectra corrected for the energy shift by the vertical position on the detector.

4. Application to LIB Cathode Sample

The 2D-imaging XAFS measurement system has been applied to analyze the distribution of chemical species on the LIB cathode material. The lithium iron phosphate (LiFePO_4) is one of the candidate materials for the next generation LIB, and we have thus measured the 2D-imaging XAFS spectra at the vicinity of the Fe K edge for the actual cathode sample (Fig. 3(a)). Figure 3(b) shows an example of the XAFS imaging map of the Fe species for the 50 % charged LIB cathode. The absorption edge is shifted to a higher energy by charging the LIB, because the ratio of the Fe(III) species is increased. In Fig. 3(b), the Fe species with the lower oxidation state (Fe(II)) is drawn by the blue color and that with high oxidation state (Fe(III)) is by red. The XANES spectra of each area plotted in Fig. 3(c) show the actual edge shift, indicating that the Li^+ ion is dissociated at the position of red pixels. The yellow pixel indicates that the absorption edge energy is intermediate between those of the Fe(II) and Fe(III) species.

Fig. 3 shows that the area ratio of red and blue pixels is almost consistent with the state of charge of the actual battery. This finding strongly suggests that the delocalization of the Li^+ defects is very slow in the LiFePO_4 cathode. The slow migration of the Li^+ ion may be ascribed by the olivine crystal structure [4]. The heterogeneous distribution of the Fe species shown in Fig. 3(b) indicates that there must be some factors to occur the electrochemical reaction in advance, which are crucial aspects to improve the battery performance.

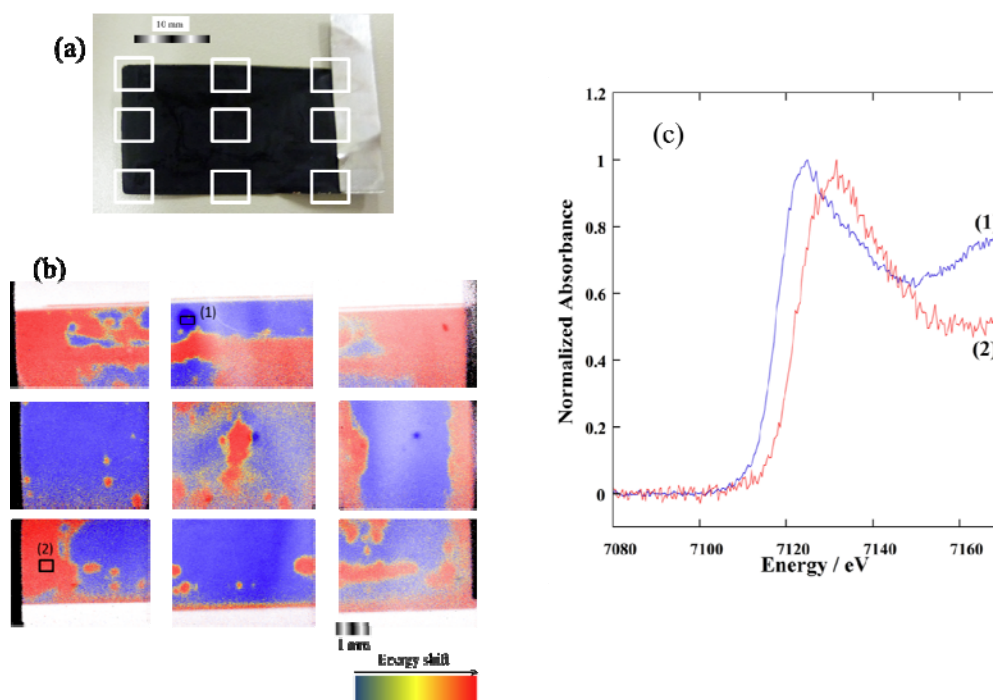


Figure 3. The optical image of the LiFePO_4 cathode (a), the mapping images of the chemical species for the 50 % charged LiFePO_4 cathode (b), and the typical XANES spectra of two areas marked in (b) (c).

5. Conclusion

The 2D XAFS imaging system has been newly developed at the BL-4 of the SR Center. The X-ray energy shift due to the vertical divergence of the X-ray beam is corrected based on the geometrical configuration of the monochromator. The chemical state of X-ray absorbing atoms over an area of a few mm^2 can be analyzed by the 2D-imaging XAFS system with the maximum spatial resolution of $2.5 \times 2.5 \mu\text{m}^2$. Chemical state mapping of the Fe species in an actual LIB cathode has been performed for a LiFePO_4 cathode. The XAFS imaging map reveals that the Fe oxidation state has a heterogeneous distribution in a 50 % charged cathode. The knowledge on this phenomenon is extremely important for the research and the development of the present and next generation secondary batteries.

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Reference

- [1] Y. Seo, Y. Jung, Wang. Y, I. Jang, and T. Lee, *Int. J. Hydrogen Energy*, **36**, 94-102 (2011).
- [2] I. Hwang, C. Lee, J. Kim, and S. Yoon, *Mater. Res. Bull.*, **47**, 73-78 (2012).
- [3] M. Katayama, K. Sumiwaka, M. Sato, K. Ozutsumi, and Y. Inada, *Memoirs of the SR Center*, **13**, 16-21 (2011).
- [4] A. Yamada, H. Koizumi, S. Nishimura, N. Sonoyama, R. Kanno, M. Yonemura, T. Nakamura, and Y. Kobayashi, *Nature Materials*, **5**, 357-360 (2006).