Development of Fast Scanning Microscopic XAFS Measurement System

T. Tsuji¹, T. Uruga¹, ², K. Nitta¹, N. Kawamura¹, M. Mizumaki¹, M. Suzuki¹, ³, O. Sekizawa², N. Ishiguro¹, M. Tada³, H. Ohashi¹, H. Yamazaki¹, ³, H. Yumoto¹, ³, T. Koyama¹, ³, Y. Senba¹, ³, T. Takeuchi¹, ³, Y. Terada¹, ³, N. Nariyama¹, ³, K. Takeshita¹, ³, A. Fujiwara¹, S. Goto¹, ³, M. Yamamoto¹, ³, M. Takata¹, ³, and T. Ishikawa¹, ³

¹ JASRI/Spring-8, Sayo, Hyogo 679-5198, Japan
² The Univ. of Electro-Communications, Chofu, Tokyo 182-8585, Japan
³ Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444-8585, Japan
4 RIKEN Harima Institute, Sayo, Hyogo 679-5148, Japan

E-mail: t.tsuji@spring8.or.jp

Abstract. We have developed a fast scanning microscopic X-ray absorption fine-structure (XAFS) measurement system using a 100–300 nm focused X-ray beam at the BL39XU nano-scale analysis station at SPring-8. This system provides two-dimensional XAFS images constructed from X-ray fluorescence (XRF) images measured by fast continuous 2-dimensional scanning at all XAFS measurement energies. High-quality XAFS spectra at each position were obtained by correcting shift in the XRF images. We applied our proposed method to measuring single catalyst particles, and succeeded in measuring the microscopic x-ray absorption near-edge structure (XANES) images that were 2–4 μm square with a spatial resolution of 300 nm.

1. Introduction

It is essential to measure single particles or single cells of devices and not their averages to investigate the dynamic aspect of structures and electronic states of nano/meso-scale particle-based functional materials and devices. We need to carry out measurements with a spatial resolution of less than the size of the subject to do this. We previously conducted μ-XAFS measurements of single catalyst particles using an X-ray μ-beam of 800–1000 nm at SPring-8 [1]. Nano-scale analysis stations were recently constructed at beamline BL37XU and BL39XU at SPring-8 in 2011 [2]. These stations supply high flux 100-nm focused X-ray beams, which enable spatially resolved measurements of the internal electric state and structure of meso-scale particles and device cells to be conducted.

Full-field measurements are generally more effective for site-dependent studies than point-by-point measurements, since the former can be conducted with almost no time lag when different sites are measured, and in many cases there is no information about the sites of specific points in the samples. It is also not easy to conduct μ-XAFS measurements at fixed points because of shift in the position irradiated by X-ray beams due to vibration and/or thermal drift in the focusing devices and sample.
stages during XAFS measurements. This is more serious when carrying out measurements with smaller X-ray beams.

Therefore, we developed a system for fast two-dimensional scanning microscopic XAFS measurements and its design and some preliminary experimental results are presented in this report.

2. Experimental and data correction method

The measurements were conducted at the BL39XU nano-scale analysis station at SPring-8 (8 GeV, 100 mA) [2]. The X-rays were monochromatized by using an Si (111) double crystal monochromator. Incident X-rays were focused with an Rh-coated Kirkpatrick-Baez mirror (KB mirror). The focused beam was 300 (H) × 260 nm (V). The beam flux incident on the sample was \(8 \times 10^9\) photons/sec at 5.8 keV.

Figures 1 and 2 have schematics of the scanning method and proposed system for fast scanning microscopic XAFS measurements. The sample holder is mounted on a 2-axis piezo positioning stage (PI, P-541.2DD) to continuously scan the sample position. The maximum scanning speed of this piezo stage is about 500 Hz with the load of the sample holder (about 1 kg in weight). Piezo stage scanning is controlled with an analog voltage wave generated by a function generator (Fig. 2 (b)). The voltage waveforms applied to the X and Z piezo stages are programmed with a PC for scanning along the route in Fig. 1. Fluorescence X-rays from the sample are measured with a four-element silicon drift detector (SDD) (Vortex, ME4) and the X-ray intensity incident on the sample is measured with an ionization chamber (IC) (Oken, S-1194A1). The output voltages of the IC and the piezo stage’s 2-axis sensor are stored in ADC memory. The output signals of the SDD are stored in the memory of a digital X-ray processor (DXP) (XIA, DXP-XMAP). Data storage in the ADC and DXP is synchronized with a trigger signal from the PC. Storage data sets are transferred to the PC’s hard disk after each XRF measurement, thus enabling us to obtain fast 2-dimensional XRF images. Spatially resolved XAFS
images can be obtained by carrying out these measurements at each energy point of the XAFS measurements.

The data points of 2D XRF images obtained by continuously scanning with the piezo stage are on an unequally-spaced grid. Consequently, all measured 2D XRF data are linearly interpolated at equally spaced positions. The position of the focused X-ray beam on the sample also slightly shifts at the same position of the piezo stage during the XAFS measurements due to the displacement of the X-ray optics and/or sample stages. The shift in interpolated XRF image data are corrected by calculating the shift of the center of gravity coordinates for particle-like samples or by finding a peak for the cross-correlation function of XRF data and that of the reference.

3. Results

Figure 3 shows a linearly interpolated 2D XRF image of the Ce-Lα fluorescence of a single particle of catalyst mounted on an SiC membrane that was 1000 nm thick. The sample was a Pt/CeZrOₓ catalyst, and its particles were 1.0 (H) × 1.3 μm (V) in size. The scanning area was 3.5 (H) × 3.4 μm (V), and there were 36 × 33 scanning points. The total time for the measurements was 30 sec. High speed continuous 2D scanning was achieved by using the piezo stage while continuously storing the output of the high accuracy position encoder. This measurement system combined with a high flux focused X-ray beam at the BL39XU nano-scale analysis station rapidly provided high S/N ratio 2D XRF images with a spatial resolution of 100–300 nm.

Figure 3. Linearly interpolated Ce-Lα XRF image of single particle catalyst. Incident X-ray energy: 5.8 keV.

Figure 4. Ce Lα XRF images (a) (incident X-ray energy: 5.73 keV), and Ce L₃-XANES spectra at point A before and after correction of shift in center of gravity.
Figure 4 (a) shows Ce Lα XRF image. Figure 4 (b) shows the Ce L_3-edge XANES spectra at point A in Fig. 4 (a) before and after correction of shift in center of gravity. The scanning area of the XRF image was 2.9 (H) × 1.8 μm (V) and its pitch was 300 (H) × 260 nm (V). There were 10 × 7 scanning points and the XRF images were measured at 280 energy points. The time to measure one XRF image was 30 sec and that to measure the XANES spectrum was 140 min. The shift in the field of view of the XRF images was corrected by estimating the shift in the center of gravity of the particles in the selected area. Figure 5 shows the shift in position of the center of gravity of the particles in the XRF images. The maximum deviations were about 200 nm (H) and 110 nm (V), and the standard deviations were 33 nm (H) and 22 nm (V). Here, the quality of the XANES spectra was only slightly improved by this correction (Fig. 4 (c)) as the shift in the XRF images was relatively small. The time to measure the XANES of one area of 300× 260 nm (V) was 2 min. A reduced spatial resolution of 1/3 and measurement time of 1/20 were achieved using this measurement system in comparison with our previous studies on similar samples [1]. In addition, it was possible to rapidly obtain spatially resolved information about local structures and chemical states in areas that were several micrometers square of meso-scale samples.

Figure 5. Shift in center of gravity of particle (a) horizontally and (b) vertically around point A in Fig. 4 (a).

4. Summary
We developed a fast system for scanning microscopic XAFS measurements with a spatial resolution of 100–300 nm at the BL39XU nano-scale analysis station. This system of measurement rapidly provided 2D XAFS spectra images. We expect to be able to apply this method to in-situ temporally and spatially resolved XAFS measurements of meso-scale samples in the near future.

5. Acknowledgments
This research was carried out with the approval of SPring-8 (Nos. 2011A2060, 2011B1889 and 2011B2100). It was also supported in part by the Polymer Electrolyte Fuel Cell program by the New Energy and Industrial Technology Development Organization (NEDO) of Japan and by the “Low-Carbon Research Network (LCnet)” funded by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References
[1] Tada M, Ishiguro N, Uruga T, Tanida H, Terada Y, Nagamatsu S, Iwasawa Y, and Ohkoshi S 2011 Phys. Chem. Chem. Phys. 13 14910–14913
[2] Koyama T, Yumoto H, Terada Y, Suzuki M, Kawamura N, Mizumaki M, Nariyama N, Matsushita T, Ishizawa Y, Fukuoka Y, Ohata T, Yamazaki H, Takeuchi T, Senba Y, Matsuzaki Y, Tanaka M, Shimizu Y, Kishimoto H, Miura T, Kimura H, Takeshita K, Ohashi H, Yamamoto M, Goto S, Takata M, and Ishikawa T 2011 Proc. of SPIE 8139 81390I