

Installation of the soft X-ray quick XAFS system in the SR Center of Ritsumeikan University

Masashi Yoshimura¹, Kohji Nakanishi¹, Kei Mitsuhara², Toshiaki Ohta¹

1) The SR Center, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga, Japan

*2) Department of Physics, College of Science and Technology, Ritsumeikan University,
1-1-1 Noji-Higashi, Kusatsu, Shiga, Japan*

Abstract

The soft X-ray absorption fine structure (XAFS) is a powerful tool to analyze light elements in materials. The quick-scan XAFS (QXAFS) is a popular technique for time-resolved measurement in the hard X-ray XAFS. We installed a QXAFS system to the soft X-ray XAFS beamline (BL-13) in the SR Center and examined the performance of the system.

1. Introduction

X-ray absorption fine structure (XAFS) is an element-specific powerful technique for chemical analysis. In general, XAFS spectra are obtained by scanning X-ray energy step by step. Advent of synchrotron radiation drastically reduced the measuring time. To further reduce the measuring time, two kinds of method have been developed in the hard X-ray XAFS experiments. One is the energy-dispersive XAFS [1, 2] and another is the quick scan XAFS [3]. The former is a method to get a spectrum in a certain energy region simultaneously by using a curved crystal to produce polychromatic X-ray beams, focus them at the sample position and to disperse transmitted polychromatic X-rays at the position sensitive detector. With this method, we can obtain a XAFS spectrum in a second or shorter. However, this method needs a specific experimental setup, depending on the X-ray absorbing element. The latter is a method to scan X-ray energy continuously, detecting I_0 and I signals simultaneously. Different from the dispersive XAFS, drastic shortening of the measuring time is expected, but the experimental setup is just same as the conventional step-scan method and the two methods can be easily exchanged case by case.

These methods have been exclusively adopted in hard X-ray XAFS experiments, which use the transmission mode. In contrast, soft X-ray XAFS is in a quite different situation. In general, we cannot adopt the transmission mode because of low transmission of soft X-rays. Instead, electron yield and/or X-ray fluorescence yield mode are used, whose signal intensities are much lower than the case of the transmission mode in hard X-ray XAFS.

In recent years, strong demand for the secondary batteries with high performance accelerates the research for the new generation batteries which contain light elements such as sulfur, silicon and magnesium. Characterization of these elements during charge and discharge is a fundamental issue for the development and soft X-ray XAFS has turned to be a useful and powerful technique. In the SR center, soft X-ray XAFS beamlines, BL-2, 10, 11 and 13 are actively used for characterization of secondary batteries. Generally, it takes about 5 to 10 minutes to get one XANES spectrum of light elements by the conventional step scan mode. Shortening of the measuring time without sacrifice of S/N ratio is desirable especially for operando experiments to monitor spectral change during charge/discharge.

Adoption of the quick scan mode is one of the possible improvements to shorten the measuring time, although it is not sure whether the method is effectively used or not. Here, we installed the quick scan method in the soft X-ray XAFS beamline, BL-13. In this study, we report the characteristics, efficiency, and problems of soft X-ray quick XAFS.

2. Experimental

All the experiments were carried out at focusing soft X-ray XAFS beamline (BL-13) in the SR Center of Ritsumeikan University. The BL-13 is a new double crystal monochromatic soft X-ray beamline that was built in 2015 to share saturated users of existing soft X-ray XAFS beamline (BL-10) [3, 4]. Figure 1 shows the outline of BL-13, which consists of a Be foil to cut visible light, a toroidal Si mirror to make parallel beam, a Golovchenko-type double crystal monochromator, a focusing toroidal Si mirror, a Ni mesh to measure I_0 , and a measurement chamber. The energy range is between 1 keV and 5 keV, which is a little wider than BL-10. The X-ray absorption signal is measured with the total energy yield (TEY) using drain current of a sample, the partial fluorescence yield (PFY) using a Si drift detector (SGX Sortotec, SiriusSD) and a digital signal processor (DSP, DPX Mercury, XIA LLC). We use five kinds of crystal sets: KTP(011), InSb(111), Ge(111), Si(111), and Si(220) depending on the X-ray energy. The measurement chamber was kept in 10^{-6} Pa vacuum condition. Beam size at the sample position is 3.0 mm (H) \times 1.5 mm (V). A sample transfer system from a glove box without exposing in air was developed in the SR Center and installed in BL-13. This system is indispensable for the battery samples.

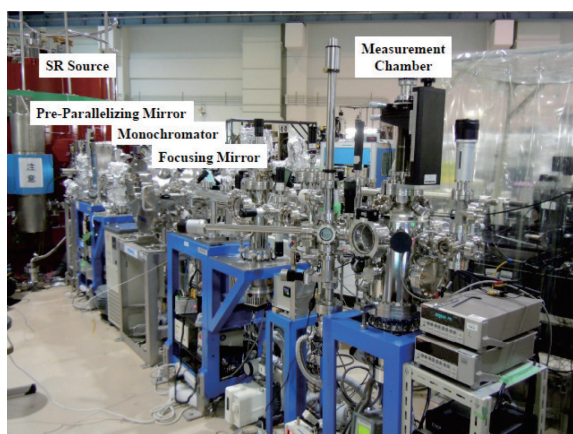


Fig. 1. Photograph of the double-crystal soft X-ray XAFS beamline (BL-13) at the SR center, Ritsumeikan University.

3. Results and Discussion

A procedure of the step-scan mode is as follows: start changing the Bragg angle of the double crystal monochromator, stop changing at a certain angle with feedback control, then collect I_0 and I signals during a certain dwell time using by counter. The step-scan repeats this process until the end of scanned energy. This method has some dead time at angle change and feedback adjustment, and that signal collection is not parallel with energy change. On the other hand, in the quick-scan mode, the XAFS signals were collected in parallel with energy change. The energy was changed continuously without stopping step by step. The

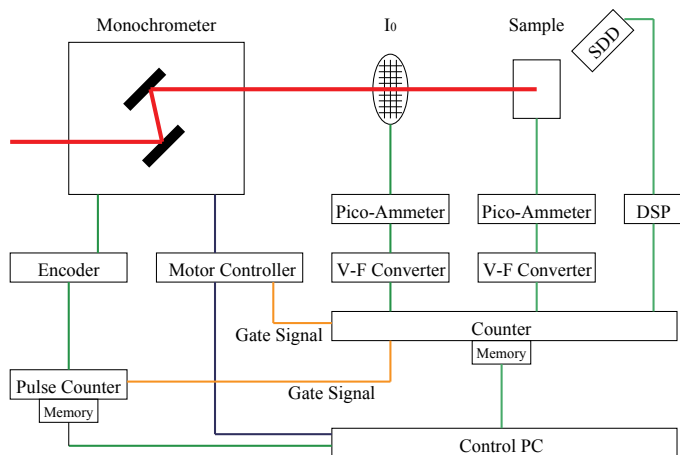


Fig. 2. Schematic diagram of an introduced QXAFS system. The total electron yield is measured by a sample drain current. The fluorescence yield is detected by a silicon drift detector. An I_0 current is obtained by drain current of Ni mesh. The measurement timing was synchronized by an internal clock of a counter.

method reduces the dead time in the step-scan mode. Figure 2 shows the Quick XAFS system in BL-13. The TEY, PFY, and incident photon intensity (I_0) were measured by pico-ammeter (KEITHLEY, 6514), DSP, and counter (TSUJI, NCT08). The energy was translated from the Bragg angle of the double crystal monochromator by an angle encoder. In the step-scan mode, we read an angle value at each point from the encoder to computer. However, in the quick-scan mode, we introduced a counter (HEIDENHEIN, EIB741) that has internal memory and high-speed logging. A control software was updated to support both step-scan and quick-scan modes. Measurement parameters of QXAFS are start energy, end energy, number of measurement points, and sweep speed of the monochromator. Prior to the measurement, the goniometer angle was moved to a lower energy than the start energy to avoid gear backlash. Then the goniometer starts rotation until it reaches the end energy. A gate signal was sent from the motor controller to counter when the goniometer rotates across the start energy angle. The gate signal was kept “on” until the goniometer reaches the end energy. The counter starts data collection which is stored in its internal memory. The collection timing is determined by internal clock of the counter using preset interval and exposure time. The counter sends a timing pulse to the encoder’s counter of the monochromator. The encoder’s counter reads the goniometer angle synchronously with the timing pulse. The collected values were kept temporary in the internal memory. The values read to computer in that the double crystal angle return to start position after finished measurement.

We demonstrated S K-edge XAFS measurement of K_2SO_4 using step-scan and quick-scan modes. The quick-scan experiment was performed with two kinds of sweeping speed. Figure 3 shows S K-edge XAFS spectra of K_2SO_4 with the step-scan and quick-scan modes. The scan range was from 2300 eV to 3200 eV. The quick-scan mode digitized the whole energy range into 1200 points. The sweeping speeds were 0.5 eV/s and 3.0 eV/s at 2482 eV,

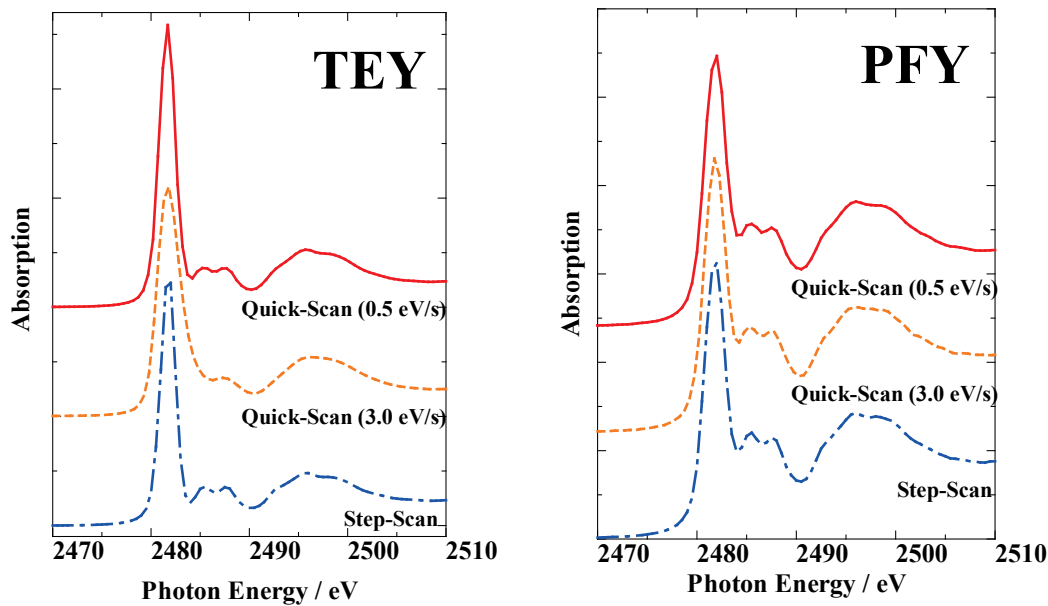


Fig. 3. Observed S K-edge XANES spectra of K_2SO_4 ; a comparison among two quick-scan modes and step-scan mode using the TEY mode (left) and PFY mode (right). The quick-scan modes were carried out with fast (3.0 eV/sec at 2482 eV) and slow (0.5 eV/sec at 2482 eV) sweep speed modes.

whose measurement times were 40 minutes and 6 minutes, respectively. On the other hand, the step-scan divided the energy range to 7 blocks and 440 points, and the measurement time was 50 minutes. The equivalent TEY and PFY spectra were obtained by the step-scan and low speed quick-scan modes. The equivalent PFY spectrum was also obtained by the high speed quick-scan mode. However, the TEY spectrum shows that the main peak at 2482 eV is broadened and the double peak between 2484 eV and 2489 eV was smeared out. It is possible that the powder sample of K_2SO_4 was charged up to some extent and this affect the TEY spectrum when the scan speed is too high to keep the equilibrium of the space charge. We measured the transient response of TEY and PFY from Al_2O_3 after the X-ray beam turned off. As shown in Fig. 4, it took about two seconds for the sample current settled down to zero after X-ray turned off. The fast quick-scan TEY spectrum was deformed because the energy-changing rate was too fast for the sample current to follow. The result indicated that the deformation of the TEY spectrum takes place for highly charged-up sample with high-speed scan.

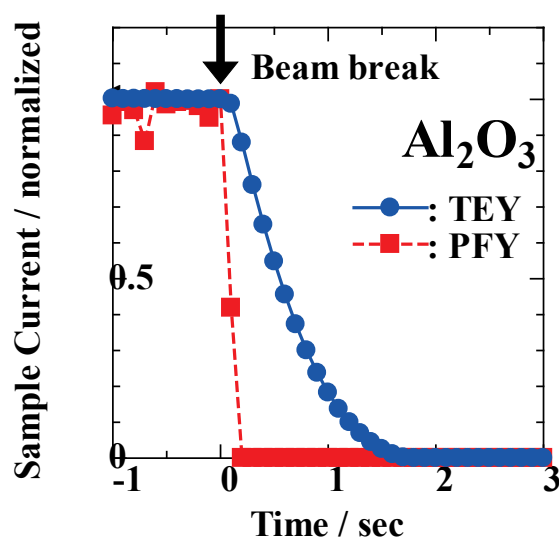


Fig. 4. Change in a sample current, and the fluorescent X-ray intensity after the shutout of the incident X-ray. The incident X-ray was cut-off at 0 sec point. The intensities were measured every 0.1 sec.

4. Conclusions

We introduced Quick XAFS system to soft X-ray XAFS beamline for time-resolve chemical analysis method. A XAFS spectrum was obtained faster by the quick-scan mode than by the step-scan mode. However, the TEY spectrum was deformed when we use high-speed energy sweep. We have to consider the experimental conditions depending on the sample nature.

Acknowledgement

This research was supported by NEDO Research & Development Initiative for Scientific Innovation of New Generation Batteries II (RISINGII).

References

- (1) T. Matsushita and R. P. Phizackerley, *Jpn. J. Appl. Phys.* **1981**, 20, 2223.
- (2) Y. Inada, Y. Niwa, M. Nomura, *Journal JSSRR*, **2007**, 20, 242.
- (3) R. Frahm, *Nucl. Instrum. Methods A*, **1988**, 270, 578.
- (4) K. Nakanishi, S. Yagi, and T. Ohta, *AIP Conference Proceedings*, **2010**, 1234, 931.
- (5) K. Mitsuhashi, T. Yaji, and T. Ohta, *MEMOIRAS OF THE SR CENTER RITSUMEIKAN UNIVERSITY*, **2015**, 17, 69.