Development of a new in-laboratory XAFS apparatus based on new concept

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In a conventional in-laboratory XAFS apparatus using conventional X-ray source, sealed tube or rotating anode, has been used. In which the X-ray source is fixed and the sample is moved (translated and rotated). Hence it has been difficult or required a complex method in order to put a heavy element, such as a cryogenic cooler, high temperature furnace and an in-situ reacting cell, at a sample position. Nowadays, there is a strong demand for obtaining dynamic information of a sample and in-situ observation becomes almost unavoidable. We have developed a compact X-ray tube and a new goniometer on which X-ray source is moved and monochromatic X-ray comes out of goniometer is fixed. Therefore it becomes easier to put a various cell at a sample position.

Keywords: in-laboratory XAFS, demountable tube

1. INTRODUCTION

It is no doubt that X-ray Absorption Spectroscopy plays a very important role in investigations of the local structure in various systems. It has been kept saying that in-laboratory and synchrotron radiation facilities are complement for XAFS study (Stern, E. A. Ed., 1980) and a lot of excellent work has been performed using in-laboratory apparatus (Tohji, K., Udagawa, Y., Tanabe, S. and Ueno, A., 1984, Tohji, K., Udagawa, Y., 1985). Nevertheless in-laboratory apparatus does not seems to be widely distributed as they predicted about 20 years ago. The main reason of preventing the spread of in-laboratory apparatus is thought to be, apart from its high price, the difficulty of operation. Most in-laboratory system uses a rotating anode X-ray source, which requires a lot of utility and need to maintain water seal, magnetic seal, etc. Also the goniometer occupied fairly large space, which against to the current trend of analytical equipment today. Present 3rd generation synchrotron radiation facilities provides highly bright X-ray source and a lot of advanced research requires more photons. On the other hand, there is increasing demand of “just” measuring XAFS spectrum as X-ray Absorption Spectroscopy becomes very popular, but most of synchrotron radiation facilities cannot satisfy such requirement. We have looked the current in-laboratory apparatus again carefully and developed the new XAFS apparatus for anyone use.

2. HARDWARE DESIGN CONSIDERATION

A lot of effort has been paid for measuring XAFS spectra with conventional X-ray source. Some modified a commercial diffractometer and some designed original apparatus for XAFS measurement. On the other hand, more than 60 sets of commercial in-laboratory apparatus were sold in last two decade. We have surveyed the performance of those apparatus. Then we determined specification of the new in-laboratory XAFS apparatus.

2.1 X-ray source

Many in-laboratory XAFS systems employ a rotating anode based X-ray source, but do not operate the maximum power in most case. Tube voltage is set to about twice of absorption edge energy of examined atom so that not to raise second harmonics. For the case of transition metals, tube voltage is usually set 10-20kV. Tube current is subordinate to tube voltage. When tube voltage is low, tube current cannot reach its maximum value for technical reason. Even though, it is not difficult to set tube current 100 mA at 20kV for any rotating anode X-ray generator. Combined with “linear spectrometer” more than 300k photons per second would be obtained and that can easily saturate a slow detector like SSD. For transmission measurement, the power of rotating anode X-ray source is not necessary. On the other hand, its power is not enough to measure very diluted system in fluorescence mode.

Some in-laboratory XAFS systems employ sealed tube. The maximum tube current is limited to 50mA at any tube voltage. Although transmission measurement is possible with this tube current, a sealed tube contains serious problem for XAFS measurement. The tungsten deposition onto the target produce tungsten L series characteristic line at energy range of 7-12keV and they degrade XAFS spectra of transition metals. It is unavoidable and it cannot be polished like in the case of rotating anode. Neither of using a material other than the tungsten, LaB6 for rotating anode generator, is yet achieved for sealed tube. The only way of vanishing tungsten contamination is replace the tube.

We have developed a new demountable tube generator. The new tube can use both W and LaB6 for filament. The operating voltage and current is 10-40kV and 10-100mA respectively.

2.2 Goniometer

Many systems have been proposed for in-laboratory XAFS apparatus (Nomura, M., 1981, Shuvaev, A.T., Helmer, B.Yu., Lyubeznova, T.A., Shuvaeva. V.A. 1999, Taguchi, T., Xiao, Qi-Fan, Harada, J. 1999). The easiest method to measure XAFS spectra with conventional X-ray source is to use flat crystal and a position sensitive detector (such as X-ray film, PSPC, photodiode array, etc.). Modifying a powder diffractometer and use it with flat crystal or bent crystal at sample position is commonly seen. (Nomura, M., 1981) Among of many systems proposed, so-called “linear spectrometer” is most reliable and it utilizes dispersed X-rays from the conventional X-ray tube very efficiently. The “linear spectrometer” moves along a complicated track and it requires large area if it covers wide scanning angle. The common range of scanning angle of “linear spectrometer” is 30 to 120 degree in 2-theta. Table 1 shows the number of atoms of which k absorption edge can be measured in different 2-theta range using different monochromator crystal. As 2-theta angle goes higher, the number of atoms can be measured decrease. Almost 90% of atoms involved the range of 30 to 90 degree. Furthermore the number of photons one can get decrease as 2-theta angle gets higher. The lowest 2-theta angle is determined by physical size of each component. From above consideration, we decided setting the highest 2-theta angle 90 degree is quite adequate.

2.3 Detector

Inserting a specimen in X-ray path and taking out in front of X-ray detector and measure the X-ray intensity each time gives absolute absorption, but this method takes twice the time than the simultaneous detection. We employed gas proportional counter for Io detection and NaI(Tl) scintillation counter to detect transmitted X-ray for its ease of use and maintenance free. Both detectors are equipped with high-speed electric circuit and can count up to 1,000,000 cps and 700,000 cps with 1 percent linearity. The scintillation counter can be used for fluorescence detection.

3. PERFORMANCE

According to the design consideration described in previous section, we have developed a new in-laboratory XAFS apparatus (Figure 1). The compact vertical type goniometer mounted a newly developed 3kW demountable tube. The X-ray source and monochromator crystal move along Rowland circle of 320mm in radius. The direction and point where monochromatic X-ray is emitted are utterly fixed, which has never been achieved by any in-laboratory apparatus. Some preliminary DATA taken with this apparatus is shown below.

Figure 2 shows the XANES spectra of Cu foil. The top spectrum is measured with a rotating anode X-ray generator (RAG). Middle and bottom spectra are measured using the demountable tube generator (DTG). The top and middle spectra are measured at the same condition. Only the difference is the X-ray source type. Comparing those two spectra, one can tell the energy resolution of middle is better than top since the dip at around 9005 eV is not clear in top spectrum. Although the vibration of a rotating anode is quite small (a few micron (Stern, E. A. Ed., 1980)), oscillation of target enlarges the nominal source size and affect to the energy resolution. Because there is no vibration, nor oscillation on the demountable X-ray tube, obtained spectrum shows better energy resolution than with rotating anode generator under the same condition. The bottom spectrum of Figure 1 is measured with higher order reflection and 1s-3d oriented structure is clearly observed.

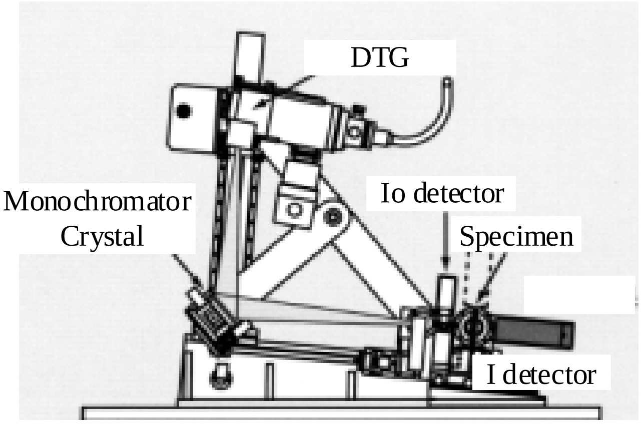
Figure 3 shows EXAFS spectrum of MoS_2. The total DATA acquisition time for this spectrum was just above 12 hours with Ge(840) monochromator crystal (440 sampling points, 100 sec/point). k^3 weighted $\chi(k)$ more than 16 $Å^{-1}$ can be useable for FOURIER Transform.

As energy goes below 7keV, absorption by air becomes considerably large. About 140mm Air makes X-ray intensity half at 5keV. Evacuating X-ray path or replacing with He would be a method to increase X-ray intensity at low energy region, but that method requires troublesome attachment. Figure 4 shows TiO2 EXAFS spectrum measured in air and it took about 8 hours (280 sampling points, 100 sec/point).

4. SUMMARY AND CONCLUSION

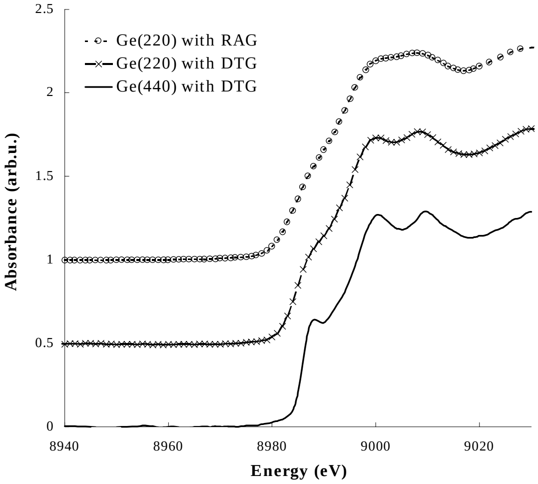
We have developed a new in-laboratory XAFS apparatus considering the ease of usage. The apparatus showed good performance at energy range of 5 to 25keV and would be a powerful tool for the development of catalyst, Li ion battery. This could be used for sample screening of synchrotron radiation experiment and help to save time and cost.

Figure 1



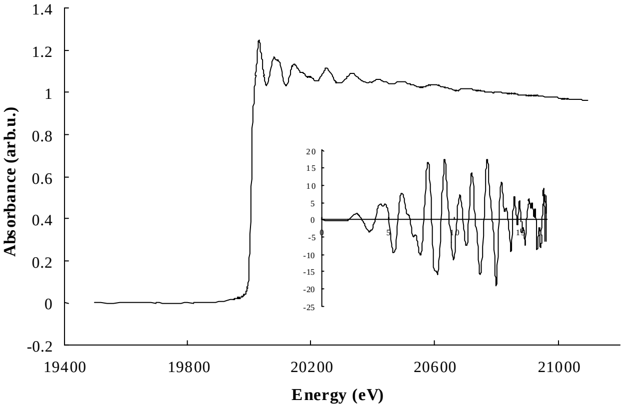
Schematic diagram of the new apparatus

Figure 2



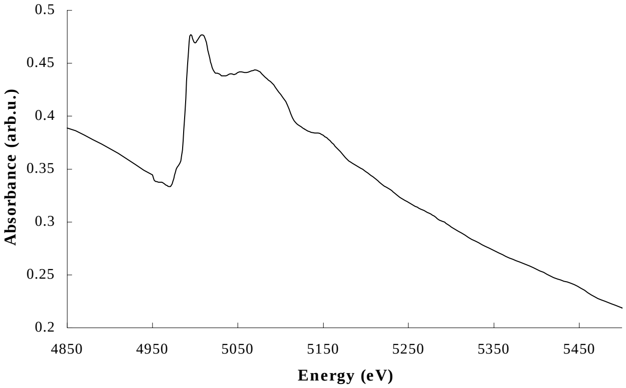
Cu foil XANES with a demountable tube and rotating anode

Figure 3



MoS_2 EXAFS and $\chi(k)\times k^3$

Figure 4



TiO$_2$ EXAFS

Table 1

	30-60	60-90	90-120
Ge(111)	7	3	1
Ge(220)	9	4	1
Ge(400)	10	4	2
Si(400)	10	5	2

Number of atoms covered with various monochromator crystals

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