BL36XU
RIKEN Materials Science II

1. Introduction

BL36XU is the RIKEN Materials Science II beamline constructed by the University of Electro-Communications, Institute for Molecular Science, and Nagoya University with the support of RIKEN and JASRI under a New Energy and Industrial Technology Development Organization (NEDO) program for the development of polymer electrolyte fuel cells (PEFCs). Construction was completed in November 2012, and user operations began in January 2013. BL36XU became a RIKEN beamline in March 2020 and serves users of RIKEN proposals (40–50% of beamtime), project proposals (NEDO PEFC project) (40–50%) and general proposals (5%).

BL36XU consists of an in-vacuum-type tapered undulator and two channel-cut monochromators having a channel-cut Si (111) crystal and a Si (220) crystal, which are tandemly arranged to cover an energy range from 4.5 to 35 keV [1]. The design of the synchrotron light source and X-ray optics is a SPring-8 standard. BL36XU provides time-resolved quick scan XAFS (QXAFS, time resolution of 10 ms), full-field/scanning XAFS imaging (spatial resolution of 100 nm–1 μm), XES (high-energy-resolution fluorescence detected XANES (HERFD-XANES) and resonant inelastic X-ray scattering (RIXS)), simultaneous time-resolved QXAFS/XRD, ambient-pressure HAXPES, and pink beam experiments under *in situ* experimental conditions.

Available X-ray detectors are fast ionization chambers, a 25-element Ge detector, a 4-element silicon drift detector, a 2-dimensional pixel array detector, and indirect X-ray imaging detectors. Equipment for controlling the sample environment are a cryostat (4 K-RT), reaction gas supply and removal equipment, a high-temperature gas cell (RT-1000 K), a fuel cell, and power generation equipment.

2. Recent activities

The following experimental equipment based on the time-resolved QXAFS measurement system were developed to accommodate new users of general proposals.

2-1. Sequential time-resolved QXAFS measurement system at two absorption edges

To measure *in situ* time-resolved XAFS spectra at two absorption edges during transient reactions of materials, a fast sequential time-resolved QXAFS measurement system was developed. Figure 1 shows the schematic layout of the measurement system. Three sets of I0, I1, and I2 ionization chambers to measure incident and transient X-ray intensities are filled with mixture gases suitable for transmission-mode XAFS measurement at each absorption edge. Also, two sample cells filled with samples of the optimal concentration for transmission-mode XAFS measurement at each absorption edge are prepared. The ionization chambers and sample cells are mounted on the translation stages and switched in position in conjunction with XAFS measurement at each absorption edge. The time resolution of the measurement was limited to 20 s by the time required to change the gap of the undulator. This measurement system enabled the study of local structural changes of mixed metal oxide clusters associated with CO_2 adsorption by the measurement of sequential time-resolved QXAFS spectra at the Ta L_I- and Nb K-edges.

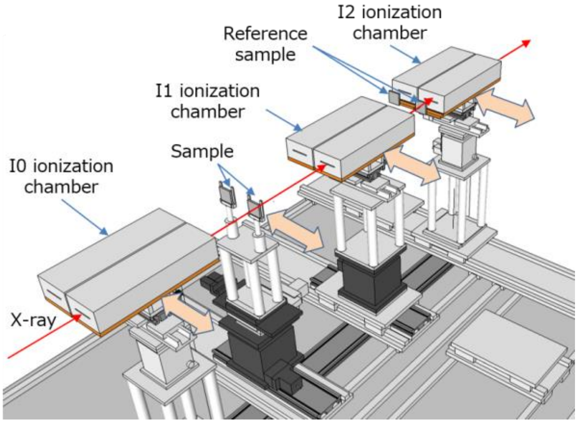

Fig. 1. Schematic of layout of sequential time-resolved QXAFS measurement system at two absorption edges.

2-2. Simultaneous time-resolved QXAFS/XRD measurement system combined with control system of pressure of gases and temperature

In 2016, we developed a simultaneous time-resolved QXAFS/XRD measurement system for the operando analysis of electrochemical reactions occurring in PEFCs [2]. Figure 2 shows the experimental setup of the measurement system. A minimum time resolution of 60 ms (20 ms QXAFS x2 + 20 ms XRD x1) was achieved using a high-speed direct servomotor-driven channel-cut monochromator controlled with a smooth waveform. Time-resolved QXAFS measurement using ionization chambers provides element-selective information on the dynamic transformations of the short-range local structures and chemical states of the surfaces of catalyst nanoparticles, and time-resolved XRD measurement using a 2-dimensional pixel detector (PILATUS 300K, Dectris) provides information on long-period ordered crystalline structures of nanoparticles. The results of the combined analysis of QXAFS and XRD data more directly and clearly clarified that the chemical reaction occurred in the sample materials than the results obtained from only QXAFS or XRD analysis.

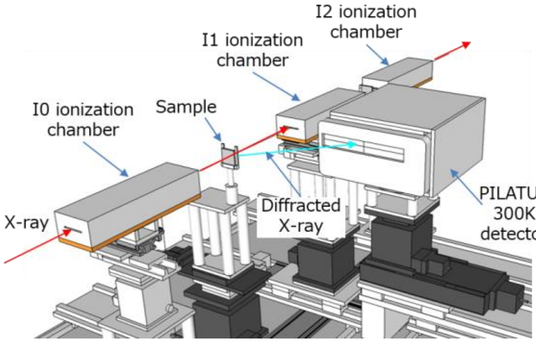

Fig. 2. Experimental setup of simultaneous time-resolved QXAFS/XRD measurement system.

In order to apply this measurement system for studying high-speed gas reactions of materials, we constructed a measurement system by combining it with a gas reaction control system developed for *in situ* powder XRD experiments by Kawaguchi at BL02B2 [3]. Figure 3 shows the experimental setup around the sample. The sample is installed in the capillary. The gas around the sample can be quickly switched within milliseconds by exhausting the gas in the capillary with a vacuum pump and introducing the reaction gas. The sample temperature can be controlled using hot N_2 gas flow devices between RT and 827 K. The measurement system was successfully adopted for studying topochemical redox reactions in layered perovskite oxide during adsorption/desorption processes by time-resolved Sr K-edge QXAFS/XRD measurements with a time resolution of 100 ms under 827 K.

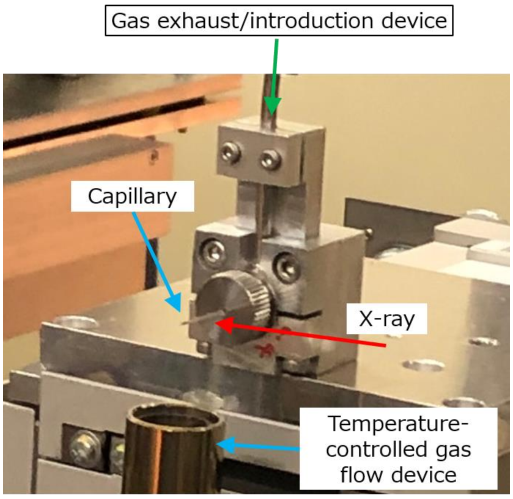

Fig. 3. Experimental setup around the sample.

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