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 (10%).

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 two-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

2-1. Simultaneous time-resolved fluorescence-mode QXAFS/XRD measurement system

In 2016, we developed a simultaneous time-resolved transmission-mode QXAFS/XRD measurement system for the *operando* analysis of chemical reactions [2]. The transmission-mode QXAFS measurement system using fast ionization chambers can be employed only for concentrated samples. To realize the measurement of dilute samples, we developed a time-resolved QXAFS measurement system in fluorescence mode.

Figure 1 shows the experimental setup of the measurement system. Fluorescence X-rays from the sample were detected using a two-dimensional pixel detector (Eiger 1M, Dectris) with a high-speed frame rate, the maximum frame rate of which is 3 kHz. A Soller slit and a filter were placed between the sample and a two-dimensional pixel detector to improve the signal-to-noise ratio of the XAFS spectrum by removing background X-ray scattering from the sample. The time-resolved XRD measurement was conducted using a two-dimensional pixel detector (PILATUS 300K-W, Dectris). 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 provides element-selective information on the dynamic transformations of the short-range local structures and chemical states of samples, whereas time-resolved XRD provides information on long-period ordered crystalline structures.

The measurement system expands the research target for dilute samples, which was successfully adopted for studying topochemical redox reactions in layered perovskite oxide during adsorption/desorption processes with a time resolution of 100 ms combined with a high-speed gas reaction control system.

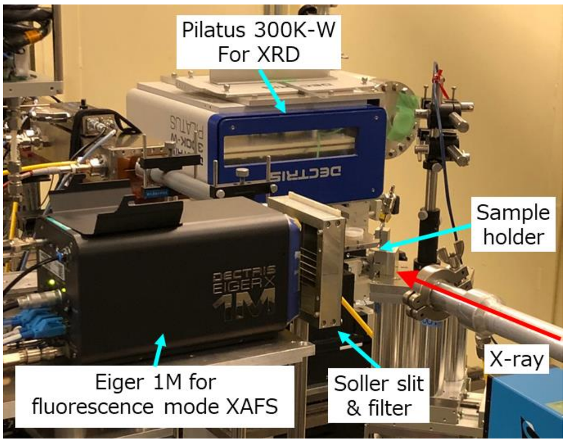

Fig. 1. Experimental setup of simultaneous time-resolved fluorescence-mode QXAFS/XRD measurement system.

2-2. *In situ/Operando* XES measurement system

We conducted the following improvement on the *in situ/operando* XES measurement system for measuring HERFD-XANES and RIXS of the catalyst nanoparticles under operating conditions. Figure 2 shows a schematic layout of the XES/XAFS/XRD measurement system [1]. Eight sets of spherically bent Ge (660) and Si (933) analyzer crystals (Johan type, R=820 mm) (Saint-Gobain Co.) are installed for HERFD-XANES and RIXS measurements at the Pt L_{III}-edge, respectively. The X-rays diffracted by the analyzer crystals were measured using a two-dimensional X-ray pixel array detector (Merlin Quad, Quantum detector Co.) [1]. In 2021, we developed a semi-automatic adjustment system for the diffraction angle of analyzer crystals, which drastically reduced the adjustment time from 5 hours to 1 hours.

We constructed an on-site SO_2 poisoning system in the experimental hutch of BL36XU. Figure 3 shows a schematic layout of the system, which consists of a gas cylinder cabinet, gas lines, humidifying gas supply devices, and a reaction cell dedicated to SO_2. The system was successfully adopted for studying the sulfur poisoning mechanism on a Pt cathode catalyst in PEFCs by XES measurement under operation conditions.

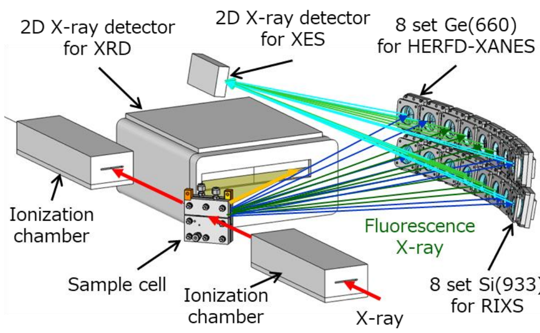

Fig. 2. Schematic layout of XES/XAFS/XRD measurement system.

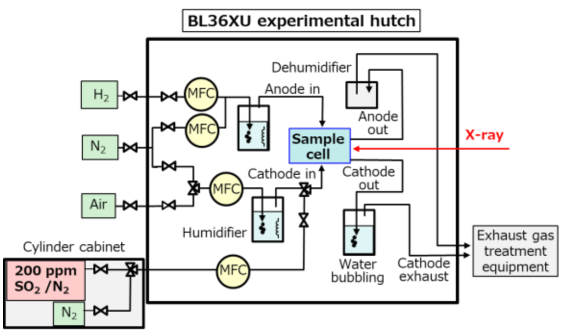

Fig. 3. Schematic layout of on-site SO_2 poisoning system.

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References:

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[2] Sekizawa, O. et al. (2017). *ACS Sustainable Chem. Eng*. **5**, 3631–3636.