New XAFS beamline BL36XU for catalytic reaction dynamics for fuel cells

Recently, the development of a low carbon society has become a countermeasure against problems of global climate warming or exhaustion of resources. Fuel cells that generate electricity from hydrogen and oxygen are one of the most promising technologies for green energy creation. Crucial issues to be resolved for developing next-generation polymer electrolyte fuel cells (PEFCs) are the improvement of activity, achievement of high durability, and reduction in the cost of Pt/C cathode catalysts. A schematic drawing of PEFC is shown in Fig. 1. To use PEFCs particularly in automobiles, it is necessary to clarify the dynamic aspects of structures and electronic states, the kinetics/dynamics of the cathode catalysts in membrane electrode assemblies (MEAs), and chemical reaction mechanisms at cathode catalyst surfaces under PEFC operating conditions and in deterioration processes.

Temporally and spatially resolved X-ray absorption fine structure (XAFS) techniques are very powerful in the investigation of the structure and chemical states of nanoparticle catalysts under *in situ* working conditions, especially in such complex systems as PEFCs. To investigate the elementary steps in the practical catalytic reaction mechanism and deterioration process of PEFCs in real time, XAFS measurements with time resolutions of 100 μs to 1 s are required. Also, the catalyst layer of MEAs is a microscopically heterogeneous dispersed system consisting of a spatially complex mixture of catalyst, support, ionomer and water, and requires spatial resolutions of 100 nm to 10 μm for XAFS measurements. However, there was no beamline capable of conducting the XAFS measurements with such high time and spatial resolutions.

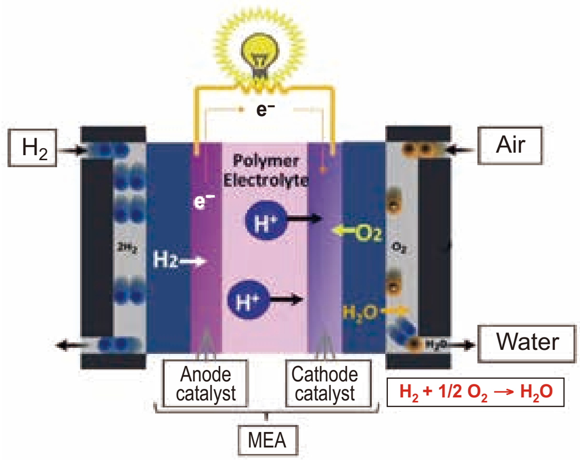

Fig. 1. Schematic drawing of PEFC.

Therefore, we constructed a new XAFS beamline **BL36XU** [1] under a New Energy and Industrial Technology Development Organization (NEDO) program, which provides highly temporally and spatially resolved XAFS methods specialized for the structural and electronic analyses of the dynamic events on the cathode catalysts in PEFC MEAs. The target specifications of BL36XU are as follows: time resolutions of 800 μs by quick XAFS and 100 μs by energy dispersive XAFS (DXAFS), a two-dimensional in-plane spatial resolution of 200 nm, and a 3-dimensional resolution of 1 μm for MEA samples. The energy range is from 4.5 to 35 keV, which covers absorption edges of almost all metal elements used for the PEFC catalysts.

Figures 2 and 3 show the schematic layout and arrangement of the main components of the beamline, respectively. The design of the synchrotron light source and optics is a SPring-8 standard, and results in both quick XAFS measurements with 10 ms time resolution and spatially resolved measurements using 100-nm-order X-ray beams. The light source is an in-vacuum-type tapered undulator for adjusting the energy width of an X-ray suited for quick XAFS and DXAFS measurements. The hutches consist of one optics hutch and one experimental hutch. The experimental hutch is located 77 m from the light source to obtain a high reduction ratio of the focusing mirror.

The main X-ray optics consists of four mirrors and two monochromators. The mirrors are used for two-dimensional focusing of X-rays on the 100 μm level and higher harmonics rejection. Two servo-motor-driven compact monochromators [2] with a channel-cut Si (111) crystal for 4.5 – 28 keV and a Si (220) crystal for 7–35 keV are tandemly arranged to realize 10-ms-time-resolved quick XAFS measurements.

For 800-μs-time-resolved quick XAFS measurement, the servo-motor-driven monochromator is removed from the beam axis, and instead, a newly developed galvano scanner motor driven monochromator [3] is set in the experimental hutch. The monochromator has a compact channel-cut Si crystal installed in a He chamber and has no active cooling devices for reducing the rotational inertia for fast angle scanning. The heat load of the undulator radiation on the monochromator crystal can be reduced to less than 5 W by rejecting higher harmonics using the mirrors and by limiting the incident beam size using the front-end slit.

A 100-μs-time-resolved DXAFS method is especially used for model samples of PEFC with

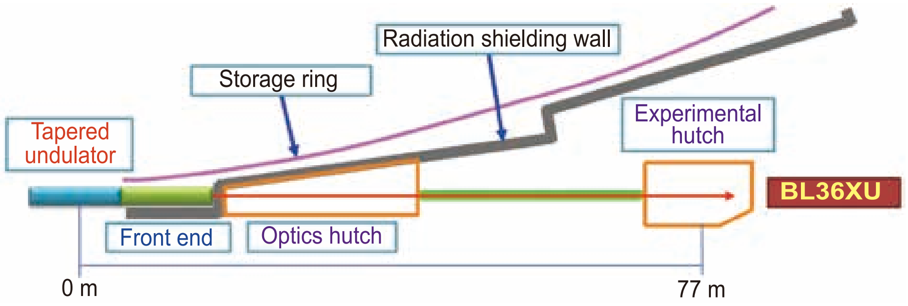

Fig. 2. Layout of BL36XU.

high catalyst concentration to obtain information on the faster elementary steps in a cathode catalytic reaction. To cover a wide energy range, two types of polychromator configuration, i.e., Bragg configuration for 4.5 – 12 keV and Laue configuration for 12-35 keV, are installed.

Two types of 2-dimensional imaging XAFS methods are available in BL36XU depending on the catalyst concentration in MEAs. For high-concentration samples, the transmission microscopic XAFS method is used. X-ray images transmitted through the sample are measured using a 2-dimensional X-ray imaging detector. The field of view and spatial resolution are about 500 × 500 μm^2 and 1 × 1 μm^2, respectively. For low-concentration samples, a fast scanning microscopic XAFS system [4] is installed. In this method, 2-dimensional X-ray fluorescence images are measured by fast scanning of a sample at each energy point of the XAFS measurement. The X-ray beam is focused to about 100 × 100 nm^2 at the sample using a Kirkpatrick-Baez mirror.

A laminography XAFS measurement system based on that developed at BL47XU [5] is installed for measuring a 3D XAFS image of the MEA of PEFCs. X-ray laminography is a 3D image reconstruction method applicable for to membrane samples. The 3D X-ray laminography images are measured at each energy point of the XAFS measurement to obtain a 3D XAFS image. The field of view and spatial resolution are about 500 × 500 × 500 μm^3 and 1 × 1 × 1 μm^3, respectively.

The beamline commissioning was finished at the end of 2012 and BL36XU was opened for user experiments in Jan. 2013.

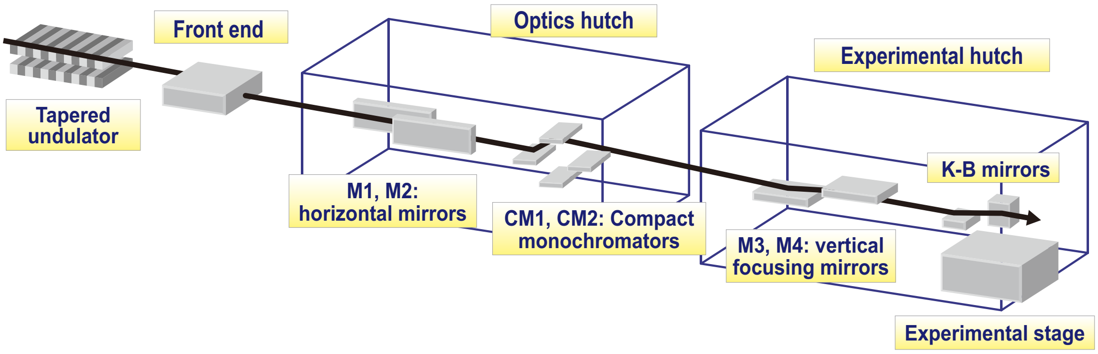

Fig. 3. Arrangement of main components of BL36XU.

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