New XAFS beamline for structural and electronic dynamics of nanoparticle catalysts in fuel cells under operating conditions

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Abstract. We are currently constructing a new X-ray absorption fine structure (XAFS) beamline BL36XU at SPring-8 dedicated for the structural and electronic analysis of the dynamic events on polymer electrolyte fuel cell (PEFC) cathode catalysts for the development of next-generation PEFCs. To investigate the cathode catalyst nanoparticles in PEFCs under the operating conditions, the beamline is designed to provide time- and spatially resolved XAFS techniques having a time resolution of 100 μs, spatial resolution of 200 nm, and depth resolution of 1 μm. We report the outline and design of the new beamline.

1. Introduction

Recently, the development of a low carbon society has become a countermeasure against problems of global 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 for developing next generation polymer electrolyte fuel cells (PEFCs) are improvement of activity, high durability, and reduction in the cost of cathode catalysts. To make PEFCs reality particularly in automobiles, it is necessary to clarify the dynamic aspects of structures and electronic states, and their kinetics/dynamics of cathode catalysts in membrane electrode assemblies (MEAs), and chemical reaction mechanisms at cathode catalyst surfaces under PEFC operating conditions and in the deterioration processes.

Time- and spatially resolved X-ray absorption fine structure (XAFS) techniques are very powerful for investigation of the structure and chemical states of nanoparticle catalysts under in-situ working conditions. To clarify 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 is required. Also, the catalyst layer of MEAs is a micro-heterogeneous dispersed system consisting of a spatially complex mixture of catalyst, support, ionomer, and water, which requires spatial resolutions of 100 nm to 10 μm for XAFS measurements. However, there is no beamline capable of conducting XAFS measurements with such high time and spatial resolutions.
Therefore, we started to construct a new XAFS beamline BL36XU at SPring-8, which provides high time- and spatially resolved XAFS methods specialized for the structural and electronic analysis of the dynamic events on the cathode catalysts in PEFC MEAs.

2. Light source and optics

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 2-dimensional in-plane spatial resolution of 200 nm, and 3-dimensional resolution of 1 μm for membrane electrode assembly (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.

Figure 1 is a schematic arrangement of the beamline. The design of the synchrotron light source and optics is a SPring-8 standard, which results in both quick XAFS measurements with 10-ms time resolution and spatially resolved measurements using 100-nm-order X-ray beams [1]. The light source is an in-vacuum type tapered undulator to adjust the energy width of an X-ray suited for quick XAFS and DXAFS measurements. The hutchs consist of one optics hutch and one experimental hutch. The experimental hutch is located 77 m far from the light source to obtain a high reduction ratio of the focusing mirror, which was designed for spatially resolved XAFS using a 100-nm focused beam.

The main X-ray optics consists of four mirrors (M1, M2, M3, and M4) and two monochromators. The M1 is a liquid-nitrogen cooled horizontal deflection flat mirror, and M2 is a water-cooled spherically bent flat mirror for horizontal focusing. The M1 and M2 are placed apart at a distance of 7.5 m with a glancing angle of 2 mrad to separate reflected X-rays by 30 mm in the horizontal direction from high energy X-rays and gamma-rays emitted from the light source. This configuration enables the rejection of the high energy components by a gamma-ray stopper and downsizing of the monochromator. The downstream mirrors, M3 and M4, are water-cooled spherically bent flat mirrors for vertical focusing and higher harmonics rejection. The M1 and M2 are 1000 mm long, and M3 and M4 are 700 mm long. The substrates of the mirrors are Si. The coatings are stripes of Pt and Rh, which are switched depending on the energy region of the XAFS measurement.

Servomotor-driven compact monochromators located downstream of the M2 mirror results in 10-ms time-resolved quick XAFS measurement [2]. To cover a wide energy range, two monochromators having a channel-cut Si (111) crystal for 4.5-28 keV and a Si (220) crystal for 7-35 keV are tandemly arranged. The crystals are cooled with liquid nitrogen. The monochromators can be switched using vertical translation stages while maintaining a vacuum.

Figure 1. Schematic of the new beamline BL36XU.

3. XAFS measurement system

3.1. Time-resolved XAFS

3.1.1. Quick XAFS. Figure 2 is a schematic drawing of a 10-ms time-resolved QXAFS measurement system using servomotor-driven monochromators. The X-ray detectors are fast response ionization
chambers having narrow gap electrodes for transmission-mode measurements and a Si PIN photodiode (Hamamatsu photonics, S3584-09) for fluorescence-mode measurements. This system is a base system for XAFS measurements of this beamline. For long measurements, the step-scan XAFS method is applied, and the undulator gap is not tapered and is adjusted to maximize X-ray flux at each measurement point.

For 800-μs time-resolved QXAFS measurement, the servomotor-driven monochromator is removed from the beam axis, and instead a newly developed galvano scanner motor driven monochromator is set [3]. The monochromator has a compact Si crystal (less than 30(L)×15(H)×13(W) mm) installed in a He chamber and has no active cooling devices to lower the rotational inertia for fast angle scanning. Calculation by the synchrotron radiation calculation code SPECTRA [4] showed that the heat load of the undulator radiation on the monochromator crystal can be reduced to less than 10 watts by rejecting higher harmonics and low energy parts using the M3 and M4 mirrors and an absorber, respectively, and by limiting incident beam size using the front end slit. This heat load is acceptable for maintaining the Bragg condition of the crystal. This system results in fast quick XAFS measurements, but causes a slight loss of beam flux. To cover a wide energy range, three monochromators, each having Si (111) for 4.5-8 keV, Si (111) for 7-14 keV, and Si (220) for 12-35 keV, will be installed in the experimental hutch and switched using a vertical translation stage.

![Figure 2. Schematic of the 10-ms time-resolved QXAFS optics and measurement system.](image)

3.1.2. DXAFS. Figure 3 is a schematic drawing of a 100-μs time-resolved DXAFS optics and measurement system. DXAFS method will be especially used for model samples of PEFC with high catalyst concentration to obtain information on the faster elementary steps in a cathode catalytic reaction if anything. The X-ray beam incident on the bent crystal polychromator placed in the experimental hutch is expanded in the horizontal direction by the M2 mirror to achieve the energy band required for DXAFS measurement. To cover a wide energy range, two types of polychromator configurations, i.e. Bragg configuration for 4.5-12 keV and Laue configuration for 12-35 keV, will be installed. The polychromator consists of a common elliptical bender and two exchangeable crystalline holders for each configuration (Toyama). The crystalline holders are cooled with water. The position-sensitive X-ray detector is a fast 2-dimensional X-ray imaging detector that is composed of a visible light conversion unit called an imaging unit (Hamamatsu Photonics, AA40), which converts the incident X-rays to visible light by a crystalline scintillator (YAP: Ce), and a high-speed CMOS camera (Phantom, V711, maximum frame rate: > 10^4 fps, full well capacity: 23000 e).

![Figure 3. Schematic of the DXAFS optics and measurement system.](image)
3.2. Spatially resolved XAFS

3.2.1. Two-dimensional imaging XAFS. Two types of 2-dimensional imaging XAFS methods will be available in BL36XU depending on the catalyst concentration in MEAs. For high concentration samples, the transmission microscopic XAFS method will be used. X-ray images transmitted through the sample are measured using a 2-dimensional X-ray imaging detector consisting of an imaging unit having a magnification ratio of 50 (Hamamatsu Photonics, AA50) and a low noise CMOS camera (Hamamatsu photonics, Orca flash 4.0). The expected field of view and spatial resolution are about 300×300 μm and 1×1 μm, respectively.

   For low concentration samples, a newly developed fast scanning microscopic XAFS method will be used [5]. In this method, 2-dimensional X-ray fluorescence (XRF) images are measured by fast scanning of a sample using a high-speed piezo positioning stage (PI, P-541.2DD) at each energy point of the XAFS measurement; as a result, a 2-dimensional fluorescence XAFS image is obtained. The designed field of view and spatial resolution is 40×40 μm and 200×200 nm, respectively. The X-ray beam is focused at the sample using a Kirkpatrick-Baez (KB) mirror (JTEC). To cover a wide energy range, two sets of KB mirror systems will be installed, one is Rh coated with a glancing angle of 4 mrad for 4.5-15 keV and the other is Pt coated with a glancing angle of 2 mrad for 15-30 keV. The two KB mirror systems are switched over using horizontal translation stages. Fluorescence X-rays from the sample are detected using a 4-element silicon drift detector (Vortex, ME4) or 21-element Ge detector (Canberra).

3.2.2. Depth-resolved XAFS. An exit angle-resolved fluorescence-yield XAFS method [6] will be used as a depth-resolved XAFS method. Fluorescence X-rays are detected using a 2-dimensional pixel detector (DECTRIS, PILATUS 300 K-W). The depth-resolution of this method highly depends on the flatness of the sample surface and thickness of the cap layer. Therefore, it may be suitable for flat model samples rather than real PEFC samples. We are currently developing a depth-resolved XAFS method applicable for real PEFC samples.

4. Conclusion

We described the design of the new XAFS beamline BL36XU at SPring-8 to investigate dynamic reactions on cathode catalyst nanoparticles distributed in MEAs of PEFC using newly-developed high time- and spatially resolved XAFS techniques. BL36XU will be commissioned from Oct. 2012, and opened for users in Jan. 2013.

5. Acknowledgments

We thank Drs. T. Nonaka and K. Dohmae (Toyota Central R&D Labs) for their helpful discussion. Part of this work was conducted with the approval of SPring-8 Nos. 2011A2060 and 2011B2100. This work was supported by New Energy and Industrial Technology Development Organization (NEDO), Japan.

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