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SPring-8 BL36XU: Catalytic Reaction Dynamics for Fuel Cells

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Abstract. A tapered undulator beamline BL36XU was constructed at SPring-8 to conduct structural and electronic analysis of dynamic events on polymer electrolyte fuel cell (PEFC) cathode catalysts for the development of next-generation PEFCs. BL36XU provides various time and spatially resolved XAFS techniques in an energy range from 4.5 to 35 keV for investigating PEFCs under the operating conditions. In addition, we developed in-situ complementary measurement systems, such as in-situ time-resolved XAFS/XRD and ambient pressure HAXPES systems. This report describes the performance and present status of the BL36XU.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have extensively been studied as a next-generation clean energy supply source. Stationary fuel-cell cogeneration systems and fuel-cell vehicles have been launched on the market in Japan, but various problems have to be solved to spread them widely. Crucial issues for widely spread commercialization of fuel-cell cars are an increase of activity, much improvement of durability and reduction in the cost. To solve these problems and to elucidate the oxygen reduction reaction mechanism and the degradation process of cathode catalysts, we constructed a high time- and spatially resolved XAFS beamline BL36XU at SPring-8. The time scale of milliseconds to seconds is necessary to study the structural kinetics of the catalytic reactions in PEFCs, and the spatial resolution of 100 nm is necessary to observe the spatial distribution of catalyst in PEFCs during the deterioration process.



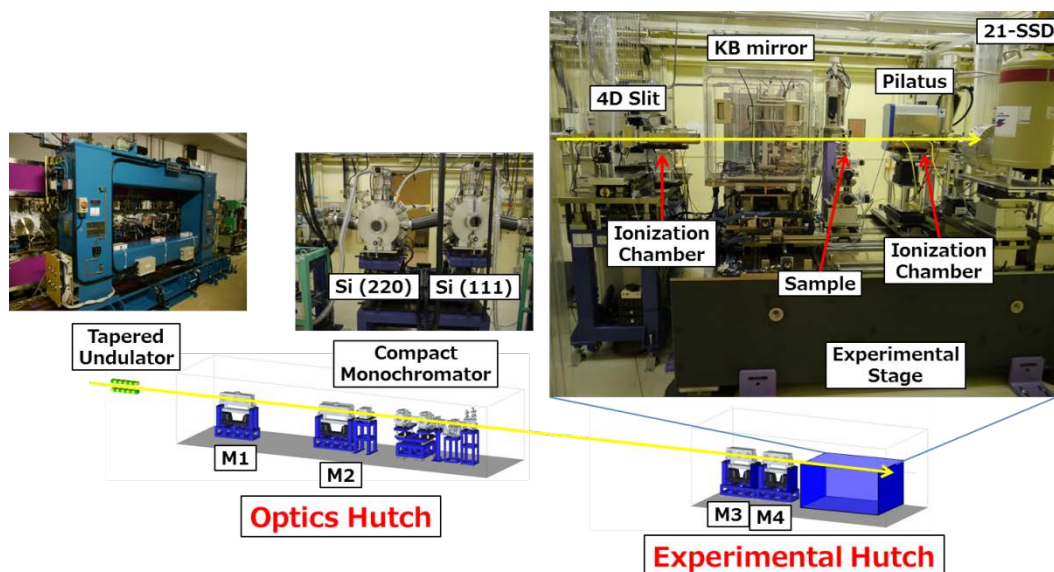


Figure 1. Layout of BL36XU.

The BL36XU construction was completed in November 2012 and made available to users in January 2013. The outline and design of the BL36XU are described in a previous report [1]. Figure 1 shows a schematic layout of BL36XU. It consists of a SPring-8 standard tapered undulator, front-end section, one optics hutch, and one experimental hutch. The main X-ray optics consists of two servomotor-driven monochromators and four mirrors. The main measurement system and performance specifications are described below.

2. Time-resolved measurements

Three types of time resolved XAFS systems were developed and installed at BL36XU corresponding to the time resolution, sample, and measurement condition using quick XAFS (QXAFS) and energy dispersive XAFS (DXAFS) techniques.

2.1. Quick XAFS measurement system

A QXAFS system using direct-drive servomotor-driven Si channel-cut crystal monochromators with a minimum time-resolution of 10 ms [2] is a base system for XAFS measurements at BL36XU. Two monochromators consisting of Si(111) and Si(220) crystals were installed for covering an energy range from 4.5 to 35 keV. This system has been used for 20-ms time-resolved QXAFS measurements conducted for PEFCs under various operating conditions [3-5]. Figure 2 shows the Pt L_3 -edge EXAFS spectra of a PEFC Pt/C catalyst under the operating conditions at the BL36XU. The minimum Pt concentrations to measure good quality XANES and EXAFS spectra with 20-ms time resolution is

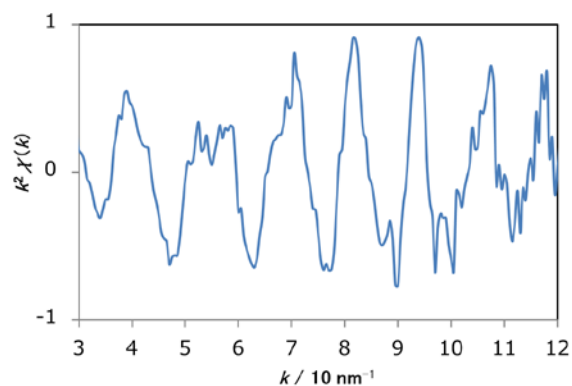


Figure 2. k^2 -weighted Pt L_3 -edge EXAFS oscillation of PEFC ($0.5 \text{ mg}_{\text{Pt}}/\text{cm}^2$) by 20 ms time-resolved QXAFS.

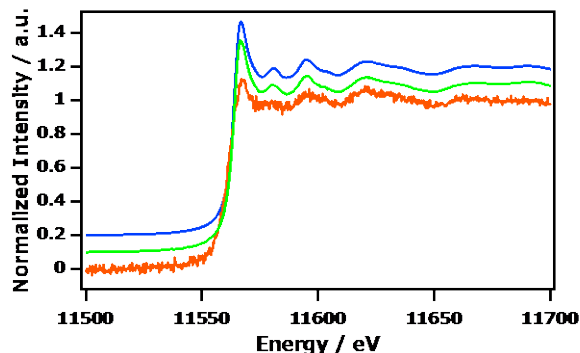


Figure 3. Pt L_3 -edge XANES spectrum of Pt foil measured by step scan (blue), QXAFS (green) and DXAFS (red) techniques. Measurement times; 12 min, 20 ms and 100 μs , respectively.

ca. 0.1 and 0.5 mg_{Pt}/cm², respectively

Another faster QXAFS system consists of a galvano motor driven monochromator [6], which enables a time resolution of milliseconds and is used to observe fast elementary steps in real PEFCs.

2.2. Energy dispersive XAFS measurement system

The fastest measurement system is a DXAFS system with a minimum time resolution of 100 μ s, which is especially used for model samples of PEFCs with high catalyst concentrations to obtain information on the faster elementary steps in a cathode catalytic reaction. Figure 3 shows the Pt L_3 -edge DXANES spectra of Pt foil together with step scan XANES and QXANES spectra.

3. Spatially resolved XAFS

Membrane electrode assembly (MEA) of PEFCs has multi-layered structures consisting of anode catalyst layer, polymer electrolyte membrane and cathode catalyst layer. The electrochemical reactions occur at the cathode catalyst layer with spatially heterogeneous distribution, so spatial distribution and morphology of cathode nanoparticles must be investigated. Two types of two-dimensional imaging XAFS methods were installed in BL36XU depending on the catalyst concentration in MEAs: a fast scanning microscopic XAFS system and an imaging QXAFS system. An in-situ X-ray computed laminography (XCL) XAFS measurement system was developed and installed as a three-dimensional microscopic XAFS.

3.1. Fast scanning microscopic XAFS systems

A fast scanning microscopic XAFS system [7] using Kirkpatrick-Baez (KB) mirrors (JTEC Co.) was developed with a minimum spatial resolution of 100 nm. Two sets of KB mirror systems were installed to cover an energy range from 4.5 to 35 keV: one has Rh-coated mirrors, and the other has Pt-coated mirrors. Both mirror systems can be automatically switched using motorized stages. Figure 4 shows focused beam profiles. For example, the X-ray flux is 2×10^{10} photons/s with a beam size of 200 nm \times 200 nm at 12 keV. This system has been used for 2D chemical state imaging of dilute samples, such as a sliced MEA sample [8] and single-catalyst particle [9].

3.2. Imaging QXAFS measurement system

Imaging QXAFS enables time- and spatially resolved QXAFS by measuring transmitted X-ray images by a high-resolution X-ray imaging detector consisting of an imaging unit (Hamamatsu Photonics K.K., AA50) and a low noise CMOS camera (Hamamatsu photonics K.K., ORCA-Flash 4.0). The field of view depends on magnification of lens (266 μ m \sim 1 mm), and maximum spatially resolution is 1 μ m. This system is used for high concentration samples. The time-resolved imaging QXAFS spectra can be measured with a minimum time resolution of one minute.

3.3. Laminography XAFS measurement system

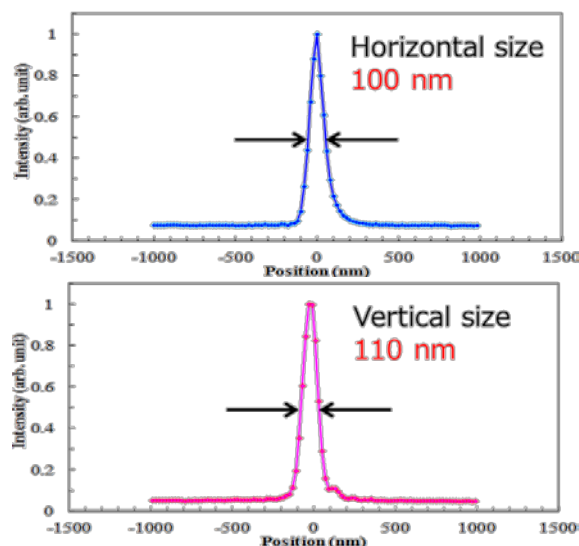


Figure 4. Profile of focused X-ray beam by KB mirror at X-ray energy of 25 keV.

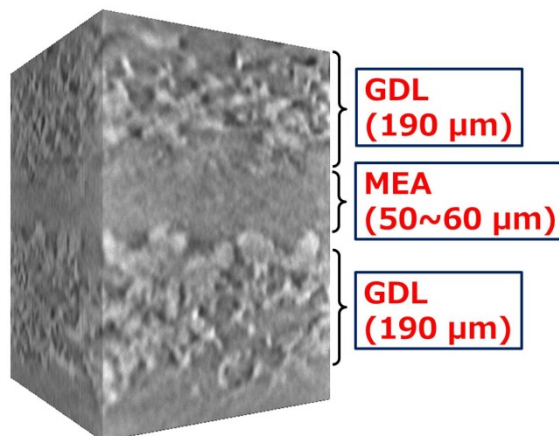


Figure 5. Reconstructed image of PEFCs.

An in-situ 3D imaging XAFS system was developed using XCL, which is suitable for 3D imaging of laterally extended planar objects such as PEFCs [10, 11]. The inclination angle of the rotational axis is set to 30 degrees and measures transmitted X-ray images by using a position sensitive detector. Figure 5 shows a reconstructed image of PEFC by XCL. 3D reconstruction was conducted using a filtered back projection method considering the inclination of the rotational axis. Each part of the MEA and gas diffusion layer (GDL) can be clearly seen.

4. Complementary measurement systems

4.1. Time-resolved X-ray diffraction

To obtain complementary structural information of the crystalline part in catalyst particles, an in-situ 20 ms time-resolved X-ray diffraction (XRD) measurement system was installed. Diffracted X-rays are detected using a two-dimensional pixel detector (DECTRIS Ltd., PILATUS 300K-W). This system can be coupled with a time-resolved XAFS measurement system using the same PEFC, which enables sequential time-resolved QXAFS/XRD measurement with time resolution of tens milliseconds by fast control of the QXAFS monochromators.

4.2. Ambient pressure hard X-ray photoelectron spectroscopy

An ambient pressure hard X-ray photoelectron spectroscopy (AP-HAXPES) system (VG Scienta Ltd., R4000 HiPP-2) was developed for investigating the electronic states of metal and light elements in catalysts under a maximum pressure of 5,000 Pa. This system has been applied for measuring PEFC cathode catalysts under operating conditions [12].

5. Conclusion

BL36XU is a high time- and spatially resolved XAFS measurement system under PEFC operating conditions. We have proceeded to elucidate the oxygen reduction reaction mechanism and degradation process of the cathode catalysts by complementary uses of XAFS, XRD, and HAXPES techniques.

6. Acknowledgement

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