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 and CREST Innovative Measurement and Analysis projects) (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 synchrotron light source and X-ray optics have a SPring-8 standard design. 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, and pink beam experiments under *in situ* experimental conditions.

Available X-ray detectors are fast ionization chambers, a four-element silicon drift detector, a two-dimensional pixel array detector, and indirect X-ray imaging detectors. Equipment for controlling the sample environment includes 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. *In situ/operando* time-resolved HERFD-QXANES measurement system

HERFD-XANES is a powerful technique for analyzing the chemical state of materials. We constructed a time-resolved HERFD-quick scan XANES (HERFD-QXANES) measurement system for transient reaction analysis. The fluorescence X-rays from the sample were diffracted from Johan-type analyzer crystals and detected by a fast X-ray imaging camera, AdvaPIX TPX3 (Advacam), positioned on a Rowland circle (Fig. 1). The mechanical minimum time resolution of the system is 20 ms/spectrum, which is restricted by the scan speed of the direct servomotor-driven channel-cut crystal monochromator. The actual time resolution is determined by the quality of the HERFD-XANES spectra, depending on the intensity of the fluorescence X-ray diffracted by the analyzer crystal.

We applied this system to the analysis of the dynamics of CeO_2-supported Pt nanoparticles in the CO oxidation reaction [2]. Figure 2(a) shows 100 ms Pt L_{III}-edge time-resolved i*n situ* HERFD-XANES spectra of Pt/CeO_2 taken between 3 and 15 s during the CO oxidation process. Figure 2(b) shows the

time course of the fractions of CO-adsorbed Pt, bare Pt, and oxidized Pt during the CO oxidation process over Pt/CeO_2, which was obtained by the linear combination fitting analysis of HERFD-QXANES spectra.

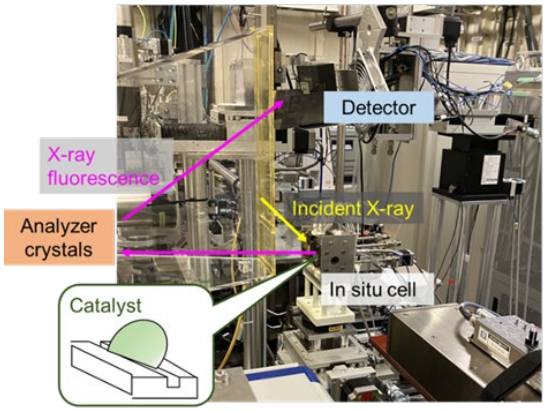

Fig. 1. Experimental setup of *operando* time-resolved HERFD-QXANES.

2-2. *In situ/operando* time-resolved pump-probe HERFD-XANES/XRD measurement system

We constructed a time-resolved pump-probe HERFD-XANES/XRD measurement system for repeatable reaction analysis. The time-resolved high-energy-resolution fluorescence X-ray intensity was measured at each energy of the XANES spectra.

We applied this system to the study involving the cyclic voltammetry (CV)-synchronized operando analyses of adsorbed structures and bonding states of active oxygen species on Pt nanoparticle electrocatalysts in a polymer electrolyte fuel cell (PEFC) [3]. Figure 3 shows 2D maps (a, b) of operando time-resolved Pt L_{III}-edge HERFD-XANES spectra [μ(E)] and HERFD-

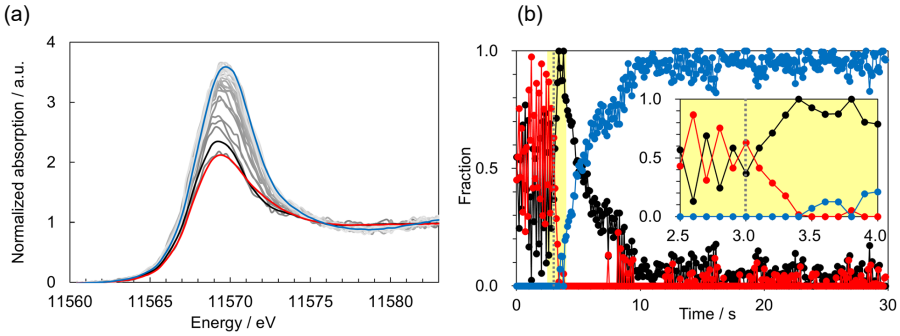

Fig. 2. (a) Time-resolved HERFD-QXANES spectra and (b) time course of fraction of reaction species. CO-adsorbed Pt (red), bare Pt (black), and oxidized Pt (blue).

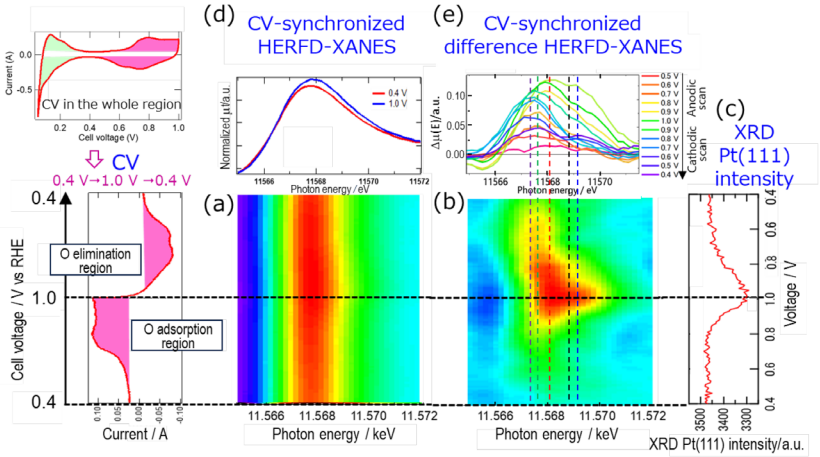

Fig. 3. CV-synchronized time-resolved HERFD-XANES spectra and XRD Pt(111) integrated intensity.

XANES difference spectra [μ(E) − $\mu_{0.4V}$(E)], respectively, and operando XRD Pt(111) integrated intensities (c) for Pt nanoparticles in a membrane electrolysis assembly (MEA), synchronizing with CV (0.4→1.0→0.4 V). In this study, the specific oxygen adsorption configurations of oxygen species adsorbed on Pt nanoparticles during the CV process were revealed by theoretical spectral calculation using FDMNES and cell-voltage-dependent stability calculation by DFT.

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Reference:

[1] Uruga, T. et al. (2019). *Chem. Rec*. **19**, 1444.

[2] Ohyama, J. et al. (2025). *Catal. Sci. Technol.* **15**, 2544.

[3] Miwa, H. et al. (2025). *ACS Catal.* **15**, 9856.