BL36XU

(Catalytic Reaction Dynamics for Fuel Cells)

1. Introduction

BL36XU at SPring-8 supports the development of next-generation polymer electrode fuel cells (PEFCs). Advanced SR X-ray–based analysis systems to study PEFCs are developed under a New Energy and Industrial Technology Development Organization (NEDO) program [1]. BL36XU construction was completed in November 2012, and user operations began in January 2013. In October 2016, simultaneous/sequential multi-analysis systems became available to users.

The performance of PEFC is highly sensitive to the sample conditions such as humidity, temperature, gas pressure, and contamination of an Membrane Electrode Assembly (MEA). Simultaneous or sequential measurements using multi-analysis methods on a point fixed in the sample provide more reliable information about the complex reaction occurring in a PEFC under voltage operations than measurements at different points [2]. Here, we describe *in situ/operando* multi-analytical advanced SR-based systems for PEFCs developed at BL36XU.

2. *In situ/operando* simultaneous HERFD-XANES/XRD measurement system

The changes in the electronic structure and chemical adsorption species at the surface of Pt nanoparticles during PEFC operations are crucial events that affect the catalytic activity and durability. Because *in situ* observations have not been achieved, the origin and key factors of Pt cathode catalysis in PEFCs have yet to be addressed.

To investigate these issues, we developed an *in situ/operando* simultaneous high-energy resolution fluorescence detection XANES (HERFD-XANES)/XRD measurement system (Fig. 1). This can measure Pt, including cathode catalyst nanoparticles in PEFCs under operating conditions. Sixteen sets of spherically bent Ge(660) analyzer crystals (Johan type, R=820 mm; Saint-Gobain) are installed for HERFD-XANES measurements at the Pt L_{III}-edge. A two-dimensional X-ray pixel array detector (Merlin Quad; Quantum Detector) detects X-rays diffracted by the analyzer crystals. The energy resolution of the system is 1.2 eV at 12 keV. Figure 2 shows the preliminary results of the *in situ* Pt L_{III}-edge HERFD-XANES and RIXS for the Pt/C cathode catalyst in a PEFC. With the HERFD-XANES method, the measured specific fine XANES spectra depend on the PEFC voltage by reducing the effect of the core-hole lifetime broadening. Theoretical calculations are in progress.

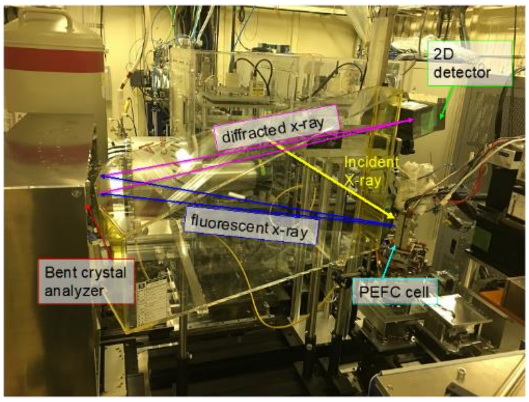

Fig. 1. *In situ/operando* simultaneous HERFD - XAFS/XRD measurement system [2].

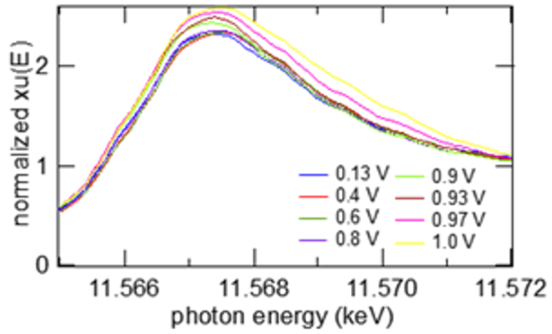

Fig. 2. *In situ* Pt L_{III}-edge HERFD-XANES spectra of PEFC depending on voltage load on the electrodes [2].

3. Sequential *in situ/operando* multi-analytical SR X-ray–based systems

The electrochemical reaction of practical PEFCs occurs in MEAs. We developed a sequential *in situ/operando* multi-analytical measurement system by combining several *in situ/operando* systems. To obtain reliable information, the sample was measured at the same point.

Figure 3 shows a schematic of this system. X-ray optics and detectors were automatically switched using motorized stages. We used this system to investigate the degradation process. Sequential *operando* measurements of time-resolved simultaneous XAFS/XRD and full-field XAFS-CT imaging were conducted at the same point in an MEA after the aging treatment and accelerated degradation test (ADT) cycles of PEFCs. Figure 4 shows the transient quick scan XAFS (QXAFS) response and *in situ* CT-XAFS imaging of the Pt/C cathode catalyst in the MEA conducted at the same point after the aging treatment. *In situ* time-resolved QXAFS yields information about the change in the oxygen reduction reaction dynamics. Additionally, *in situ* XAFS imaging after ADT cycles provides three-dimensional imaging of the content and chemical state of Pt cathode catalyst in an MEA, which is useful for investigating the spatially and temporally heterogeneous transient process occurring in practical PEFCs. The results will be presented elsewhere.

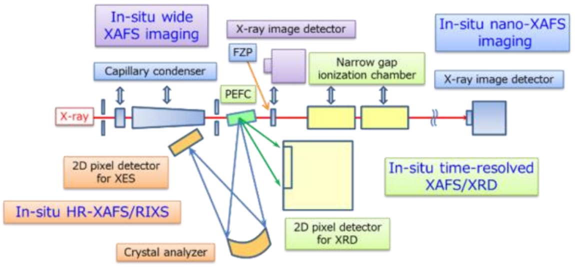

Fig. 3. Schematic of sequential *in situ/operando* multi-analytical measurement system for PEFCs [2].

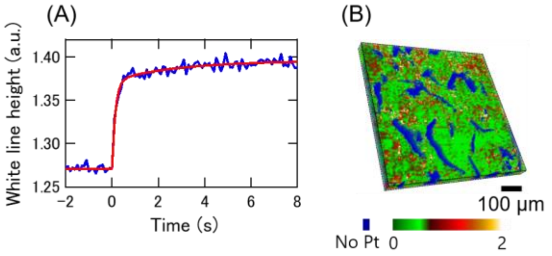

Fig. 4. (A) Transient white line peak response of Pt L_{III}-edge QXANES response at a time resolution of 100 ms under fast potential changes from 0.4 V to 1.0 V. (B) Three-dimensional images of the Pt valence in cathode catalyst layer at a cell potential of 1.0 V after an aging treatment [2].

Acknowledgments

This work was supported by the NEDO of Japan.

Yasuhiro Iwasawa[*1], Kotaro Higashi[*1], Tomohiro Sakata[*1], Tomoya Uruga[*1, 2], Oki Sekizawa[*1, 2], Mizuki Tada[*3], and Toshihiko Yokoyama[*4]

[*1] The University of Electro-Communications

[*2] JASRI
[*3] Nagoya University
[*4] Institute for Molecular Science

References:

[1] O. Sekizawa et al., *J. Phys: Conf. Series* **430**, 012020 (2013).
[2] T. Uruga et al., *The Chem. Rec.* **19**, 1444 (2019).