

# Recent progress in advanced SR characterization of fuel cells at SPring-8

## 1. Introduction—a central base for SR research on fuel cell science and technology

The recent progress in the advanced SR characterization of new materials and functions, particularly the dynamic catalysis and degradation of polymer electrolyte fuel cells (PEFCs) at SPring-8, promises well for the rational development of next-generation PEFCs with high performance and remarkable long-term durability. This can bring about their commercialization for a wide range of fuel cell vehicles (FCVs) such as automobiles, taxis, buses, trucks, and forklifts. Recent reports of cars powered by hydrogen fuel cells have captured the world's imagination with the hope of a clean energy source to mitigate environmental issues. The FCV is itself a clean power generator, making it entirely different from electric cars that need great amounts of external electric power. A hydrogen and fuel cell society is a major and long-term challenge requiring close academia–industry–government cooperation.

The synchrotron facility, which has various beamlines for frontier, interdisciplinary, and emerging area research involving diverse, multi-axial and cross-disciplinary views, is a scientific base resembling a planetary projector which provides stellar achievements in modern science and technology for the Future Earth, Society 5.0, and SDGs. This review summarizes the recent progress in advanced SR analysis techniques for PEFCs and the findings and discoveries achieved mainly at beamline BL36XU with the world's only *in situ* and *operando* simultaneous and sequential multi-analysis systems, which have been constituted from high-performance time-, space- and energy-resolved techniques such as XAFS,

high-energy resolution fluorescence detected (HERFD)-XANES, resonant inelastic X-ray scattering (RIXS), nano-focused XAFS, three-dimensional (3D) computed tomography (CT)-XAFS imaging, XRD, and ambient pressure (AP)-HAXPES under PEFC working conditions.

Before the *in situ* time-resolved XAFS study on a Pt/C cathode catalyst in a PEFC under operating conditions conducted by Tada *et al.* at BL01B1 in 2007 [1], there had been no reports on the full exploration and determination of the elementary reaction steps or the kinetics of both structural changes of the metal catalysts and electrochemical reactions on the electrode surfaces in PEFCs. Tada *et al.* in collaboration with Toyota Motor Corporation and Toyota Central R&D Labs. Inc. reported a major breakthrough in fuel cell research with their development of a novel time-gating quick XAFS technique with a high time resolution. They found evidence of dynamic surface events and a significant time lag among those events at the Pt/C cathode in a PEFC under *operando* fuel-cell conditions for the first time. We

also collaborated with Honda Motor Co., Ltd. in 2008–2010 to study the potential-dependent chemical bonding and electronic states at the surfaces of different types of core-shell cathode by *operando* time-resolved XAFS and found potential-dependent restructuring and hysteresis due to the adsorbed oxygen in PEFCs [2]. Such novel molecular-level information, which is difficult to obtain by other analysis techniques, may have contributed to the realization of the world's first commercialization of FCVs from Japan; MIRAI from Toyota and CLARITY FUEL CELL from Honda. *In situ* and *operando* XAFS techniques are very powerful for the *in situ/operando* and element-selective investigation of electronic states and local coordination structures as well as the fluctuations of cathode electrocatalysts in PEFCs, which are regarded to be relevant to the oxygen reduction reaction (ORR) performance and durability of PEFC electrocatalysts [3].

Following these achievements in the *in situ* and *operando* characterization of operating PEFCs by synchrotron XAFS,

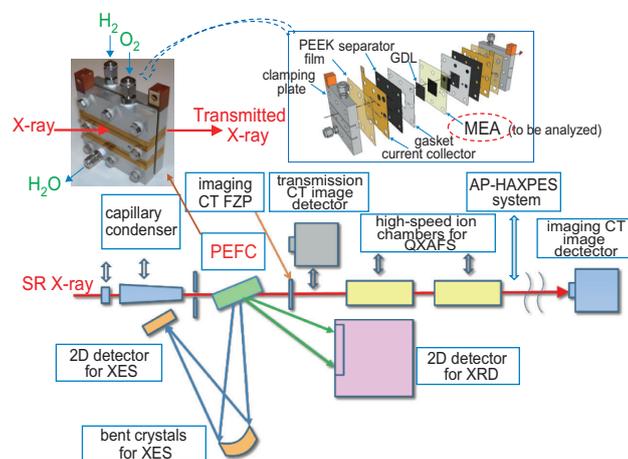


Fig. 1. Schematic of simultaneous and sequential *in situ/operando* multi-analytical measurement system for PEFC [6].

NEDO initiated a PEFC program (2010–2014 FY) to construct the world’s only and highest performance beamline BL36XU for *in situ* and *operando* PEFC characterization by XAFS and related X-ray analysis techniques for understanding the dynamic electrocatalysis and severe degradation of the membrane-electrode assembly (MEA), which is a power generation part inside a PEFC, and to enable the rational and efficient development of next-generation PEFCs. In the subsequent NEDO program (2015–2019 FY) at BL36XU, we constructed several *in situ* and *operando* simultaneous and time-series multi-analysis systems by combining two to three X-ray techniques, for example, XAFS, HERFD-XANES, RIXS, 3D CT-XAFS imaging, nano-focused XAFS, and XRD. HAXPES at BL36XU is applicable to measuring time-resolved XPS and AP-XPS spectra of MEA electrocatalysts [4]. A new PEFC analysis platform project under NEDO has been ongoing since July 2020.

A schematic layout of the main components of BL36XU is illustrated in Fig. 1 [5,6]. In general, each beamline in synchrotron facilities has been optimized for each particular analysis technique separately, and different techniques at different beamlines have often given rise to contradictory results and conclusions regarding complex heterogeneous catalytic systems such as PEFC systems. An effective way of overcoming such a problem of contradiction may be to conduct simultaneous or sequential multi-analysis experiments under working conditions at the same beamline and beamtime on the same sample.

The NEDO and FC communities were in need of such a high-performance beamline as BL36XU because there were no public beamlines capable of enabling XAFS measurements with the high time and spatial resolutions required for dynamic PEFC analysis under operating conditions. BL36XU was designed and built on a definite concept and with high-performance specifications by The University of Electro-Communications (T. Uruga and Y. Iwasawa) in close collaboration with

Nagoya University (M. Tada; moved from Institute for Molecular Science in 2013) and Institute for Molecular Science (Y. Takagi and T. Yokoyama) with the invaluable assistance of JASRI and RIKEN in 2010–2012. From 2013, it was operated by the three-university team. In 2015–2016, BL36XU was advanced and upgraded to conduct the *in situ* and *operando* simultaneous and sequential multi-analysis of an identical area of the same PEFC sample by the X-ray techniques described above; it became the world’s only and highest performance multi-analysis beamline for FC research (Fig. 1) [5,6]. From 2016, it was operated by the three-university team and was also opened to six other university groups involved in the NEDO PEFC program. After the NEDO program, BL36XU was transferred to RIKEN in March 2020, where it is now positioned as a key beamline for a new NEDO PEFC program.

In 2010–2012 after the start of the NEDO program but before the start of BL36XU operation, 23 articles on PEFCs and solid oxide fuel cells (SOFCs) were published at SPring-8. From 2013 to Feb. 2021, 103 articles were reported at SPring-8, and among them 53 articles on PEFCs were reported by the three-university team using beamline BL36XU. After the construction of BL36XU, the number of users and that of publications concerning the PEFC research area

at SPring-8 increased as a result of increased attention from people who had previously never used SR X-ray-based techniques. SPring-8 is now a central base for the SR research of fuel cells not only in Japan but also in the world.

## 2. Operando simultaneous XAFS–XRD at high time resolution

Sekizawa *et al.* [7] investigated the mechanism behind the electrochemical processes involved in rapid voltage control processes of Pt/C in PEFC at BL36XU. The simultaneous observation of time-resolved quick XAFS (20 ms acquisition) and XRD (20 ms acquisition) at a time resolution of 60 ms in the transient response process against the voltage jumps 0.4 → 1.4 V and 1.4 → 0.4 V (vs RHE) was conducted to directly monitor the chemical bonding and electronic states and the lattice parameters and crystalline phase transformation, respectively, in the Pt nanoparticles. The reaction mechanism and structural kinetics for Pt surface events and crystalline core events of the Pt/C electrocatalyst in the MEA under the transient voltage cyclic process were revealed by the simultaneous *operando* XAFS–XRD technique, as shown in Fig. 2. Under the voltage operation 0.4 → 1.4 V, the first fast surface Pt–O bond formation event (rate constant  $k_1$ ) was followed by the second slow events of Pt–O formation, Pt charging, Pt–Pt dissociation, and Pt size decrease

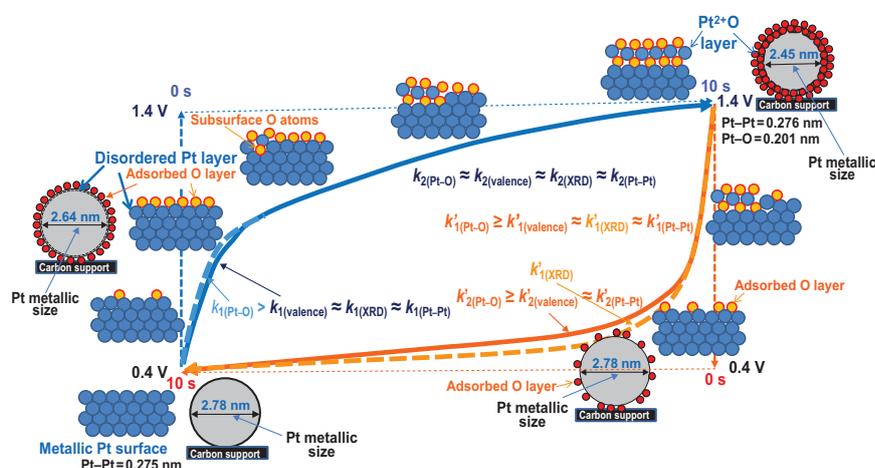


Fig. 2. Operando time-resolved Pt  $L_{III}$ -edge XANES, EXAFS, and XRD profiles of an MEA Pt/C cathode electrocatalyst and reaction mechanism for Pt nanoparticles under transient voltage cyclic operations [7].

(rate constant  $k_2$ ). The surface Pt–O formation induces the partial disordering of the outermost Pt layer, resulting in a decrease in metallic phase size from 0.278 to 0.264 nm. The slow events occur concertedly to ultimately produce the tetragonal Pt<sup>2+</sup>–O layer (Pt–O = 0.201 nm) at the Pt surface. At the transient voltage operation 1.4→0.4 V, the first fast steps of Pt–O dissociation, Pt valence decrease, Pt–Pt reformation, and Pt size increase proceed concertedly at rates similar to the rate constants  $k'_1$ . The second slow steps of Pt–O dissociation, Pt valence decrease, and Pt–Pt reformation also occur concertedly (rate constants  $k'_2$ ). The change in metallic phase size is completed at the fast step, and the changes in Pt valence, Pt–O dissociation, and Pt–Pt reformation at the surface proceed further at the lower rates (Fig. 2). It was found that the rate constants for the 15 elementary steps are related to the PEFC performance and durability [8,9].

### 3. Operando XAFS–CT imaging and unsupervised machine learning

Current PEFC systems suffer from critical problems, particularly the low ORR activity and poor durability of Pt/C cathode electrocatalysts during practical PEFC operation [3,10]. A Pt<sub>3</sub>Co/C cathode catalyst shows higher activity and durability than standard Pt/C catalysts, but still degrades to an unacceptable degree under PEFC operating conditions. Although the dissolution and aggregation of Pt nanoparticles in Pt<sub>3</sub>Co/C are more suppressed than in Pt/C, Co gradually dissolves from the bimetallic catalyst, and hence the alloy benefit gradually disappears [11]. Tada and colleagues, for the first time, successfully visualized 3D images of the morphology, Pt and Co distributions, Co/Pt atomic ratio, and Pt valence of a Pt<sub>3</sub>Co/C cathode electrocatalyst in an MEA before and after an accelerated durability test (ADT) by combining the *operando* XAFS–CT and unsupervised machine learning of the 3D images, revealing a catalyst degradation mechanism for Pt and Co

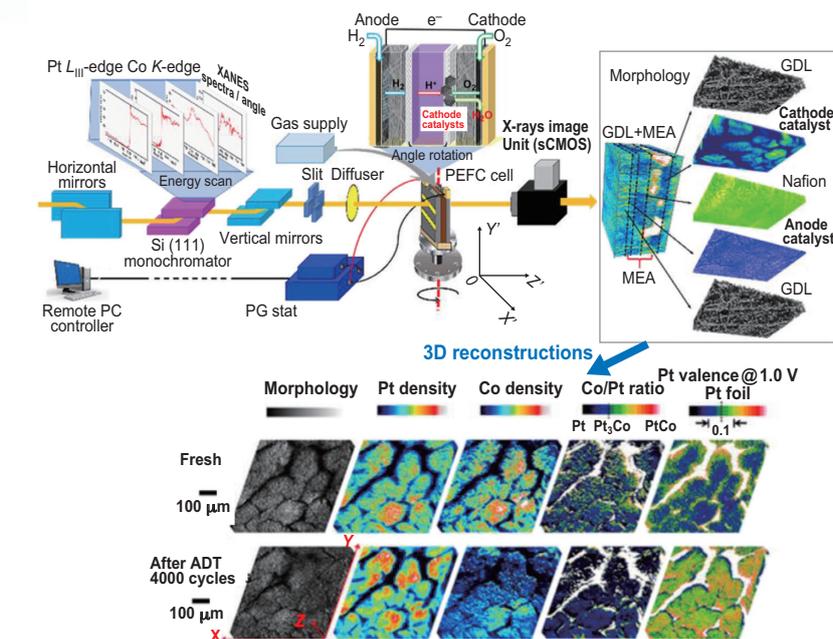


Fig. 3. Schematic of *operando* XAFS–CT imaging for MEA Pt<sub>3</sub>Co/C under PEFC operating conditions and reconstructed 3D images of the cathode catalyst layer in an MEA [11].

with different degradation and migration behaviors in the 3D catalyst layer depending on the structure of the carbon support [11].

Figure 3 shows a schematic of *operando* XAFS–CT imaging under PEFC operating conditions at BL36XU and reconstructed 3D images of the cathode catalyst layer in an MEA [11]. The effective viewing area of the image was 666×666 μm<sup>2</sup> with a pixel resolution of 325 nm. However, the actual spatial resolution was around 1 μm because of blurring on the scintillator crystal. The PEFC cell was mounted on a rotation stage and rotated perpendicularly with respect to the incident X-ray beam. At each particular angle, the Pt *L*<sub>III</sub>-edge (11.386–11.697 keV, merged to 375 points) or Co *K*-edge XAFS (7.517–7.849 keV, merged to 374 points) spectrum was recorded by quick scanning using an X-ray image unit for 25 or 18 s, respectively. Then, the rotation angle  $\theta$  was changed in steps of 1° and the quick XAFS scanning was repeated over a range of  $\theta$  from –80° to 80° to obtain 161 data sets of quick XAFS spectra. The imaging data were reconstructed into a 3D (x, y, z) matrix

in real space using the angle-limited CT calculation of the ordered-subset expectation maximization (OS-EM) method [10,11].

The 3D XAFS–CT imaging indicated the occurrence of intrinsic heterogeneous degradation of the Pt<sub>3</sub>Co/C electrocatalyst in the MEA. Each reconstructed 3D image contained 18, 620, 250 structural parameter data points. Hence, unsupervised machine learning was conducted to find correlations between the structural parameters in the observed 3D imaging data [11]. The data mining of the difference in Pt or Co density between the ADT states suggested that the regulation of the 3D morphology inside the cathode layer is one of the key parameters to consider in order to control the degradation of the MEA Pt<sub>3</sub>Co/C electrocatalyst. Here, further explanation of the results on *operando* XAFS–CT imaging and unsupervised learning is omitted owing to the page limitation of this review. Their infographic approach of combining the 3D chemical imaging and unsupervised learning may be a promising way to reveal intrinsic events of PEFCs as well as of practical materials and devices [11].

#### 4. Same-view nano-XAFS–STEM/EDS combined technique

A visualization analysis of Pt and Co species of Pt<sub>3</sub>Co/C in an MEA following aging and degradation processes has been performed by the same-view nano-XAFS–STEM/EDS technique using a membrane cell under humid N<sub>2</sub> atmosphere. Figure 4 shows the results of the same-view nano-XAFS/STEM-EDS visualization analysis for the Pt<sub>3</sub>Co/C cathode layer in the MEA after 5,000 cycles of 0.6–1.0 V rectangular ADT [12]. The same-view nano-XAFS/STEM-EDS measurements were carried out in areas of 3 μm × 3 μm at two typical locations with different degrees of degradation, e1 and m1 in Fig. 4(a). Results are shown in images labeled e1, E1<sub>1</sub>, E1<sub>2</sub>, v<sub>e</sub>, and V<sub>e</sub>, and in m1, M1<sub>1</sub>, M1<sub>2</sub>, v<sub>m</sub>, and V<sub>m</sub>, respectively. In the area of the cathode about ~400 nm from the electrolyte edge, the Co content decreased (E1<sub>2</sub>), where Co dissolved in electrolytes as Co<sup>2+</sup> ions (V<sub>e</sub>). Moreover, there was little change in Pt content (E1<sub>1</sub>), and the Pt valence remained at zero (v<sub>e</sub>), unlike the MEA Pt/C. In contrast, Co was oxidized and dissolved over a wide range of the cathode layer (~70% of the initial Co

amount) (Figs. 4(c) and 4(f)). It was shown in Figs. 4(e) and 4(h) that Co dissolved in the electrolyte region had an octahedral Co<sup>2+</sup>–O<sub>6</sub> structure by 150 nm × 150 nm nano-XAFS analysis. It was also shown that the existence of Co suppressed the oxidation and dissolution of Pt. From CN<sub>Pt–Pt</sub> and CN<sub>Pt–Co</sub> and from CN<sub>Co–Co</sub> and CN<sub>Co–Pt</sub>, the number of Pt shell layers of the core-shell nanoparticles near the cathode edge and near the center of the cathode was estimated to be 7 and 4, respectively. The MEA Pt<sub>3</sub>Co/C after 10,000 ADT-rec cycles had many cracks and pores in the cathode electrocatalyst layer, and about 90% of Co was dissolved and removed from the cathode layer. We discovered square planar Pt<sup>2+</sup>–O<sub>4</sub> and octahedral Co<sup>2+</sup>–O<sub>6</sub> species in the area between the cathode edge and the Pt–Co band. Pt and Co chemical species in the Pt<sub>3</sub>Co/C cathode electrocatalyst in the MEA during the deterioration process and a fuel cell deterioration suppression process by Co were visualized for the first time at the nanoscale using the same-view nano-XAFS–STEM/EDS combination technique while maintaining the working environment of PEFCs.

#### 5. Conclusion and prospect

Humanity alone has created scientists throughout the long process of evolution of species. Scientists should have a definite mission and responsibility to make a happy, prosperous, and sustainable society for humans as well as all other species by discovering and developing modern science and technology. We have great expectations for fuel cell science and technology at the SR facility in a sustainable society and in our future life. However, we cannot simply apply the fruits of the current SR research to achieve this objective nor can we continue to develop the present technology in the present form to achieve this objective unless we have a new advanced-class SR facility.

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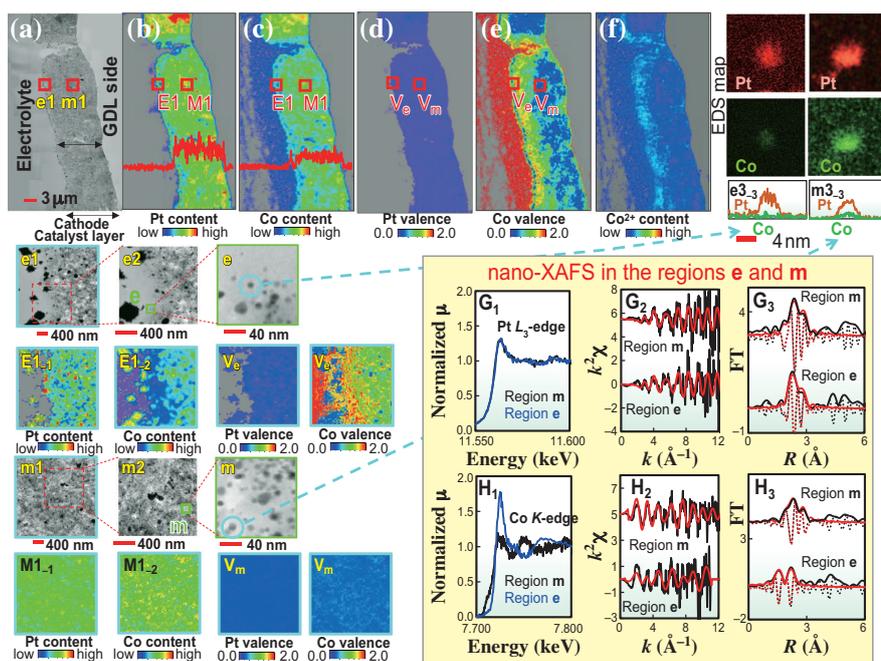


Fig. 4. Results of the same-view nano-XAFS and STEM/EDS measurements of the MEA Pt<sub>3</sub>Co/C cathode electrocatalyst layer after 5,000 ADT cycles. See the details of each nano-XAFS map, nano-XANES, and nano-EXAFS analysis in [12].

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