Operando three-dimensional XAFS imaging of the degradation of a polymer electrolyte fuel cell Pt/C cathode electrocatalyst

The 3D visualization of heterogeneous catalysts is one of the most challenging subjects in catalytic chemistry and would be helpful for solving serious problems faced in the practical use of heterogeneous catalysts. X-ray absorption fine structure (XAFS) using hard X-rays is a powerful technique for analyzing the chemical state and local coordination of heterogeneous catalysts, and the high transmission of hard X-rays enables *operando* XAFS measurements under catalyst working conditions. We have developed 3D XAFS imaging combining computed tomography (CT) and XAFS spectroscopy (CT-XAFS) [1] and used it to visualize the degradation process of Pt cathode electrocatalysts in a polymer electrolyte fuel cell (PEFC) under PEFC operating conditions.

PEFCs are promising next-generation energy devices that can realize high energy conversion, on-site power generation, a sustainable clean power source, and so forth. For the practical application and commercialization of PEFCs, the durability of the cathode electrocatalyst must be improved. It is well known that the dissolution and degradation of the cathode electrocatalyst, such as Pt nanoparticles, proceeds under the practical operation conditions of fuel-cell vehicles, consisting of repeated cell voltage operations. We performed *operando* CT-XAFS at the Pt L_{III}-edge for a Pt/C cathode electrocatalyst in a practical membrane electrode assembly (MEA) under PEFC operating conditions, and the distribution and oxidation states of the Pt catalyst before and after an accelerated degradation test (ADT) were successfully visualized [2].

The *operando* CT-XAFS measurements were performed at SPring-8 **BL36XU** [3]. X-rays were monochromatized by Si(111) channel-cut crystals through a paper rotation diffuser, and X-ray transmission images of the sample (I_1) and I_0 images were recorded by a high-resolution X-ray imaging unit (Fig. 1). A PEFC cell designed for the CT-XAFS measurements was rotated between angles of −80° and +80° perpendicular to the optical path and 1,600 X-ray projection images were recorded at 184 X-ray energies around the Pt L_{III}-edge. The total measurement time was less than 2.5 h. We used a commercial MEA (EIWA Co., Ltd.; 3×3 cm^2) with a Pt/C cathode catalyst and a Pd/C anode catalyst (0.5 mg·cm$^{2}_{\text{-Pt/Pd}}$). The MEA was conditioned and aged in the PEFC cell by supplying H_2 (150 mL·min^{-1}) at the anode and N_2 (600 mL·min^{-1}) at the cathode. *Operando* CT-XAFS measurements were performed for the MEA before and after the 20,000 cycles of the ADT (rectangular voltage cycling between 0.6 and 1.0 V for 3 s) at 1.0 V.

We reconstructed 3D images of three structural parameters from the series of CT-XAFS data: morphology images, Pt distribution images, and Pt

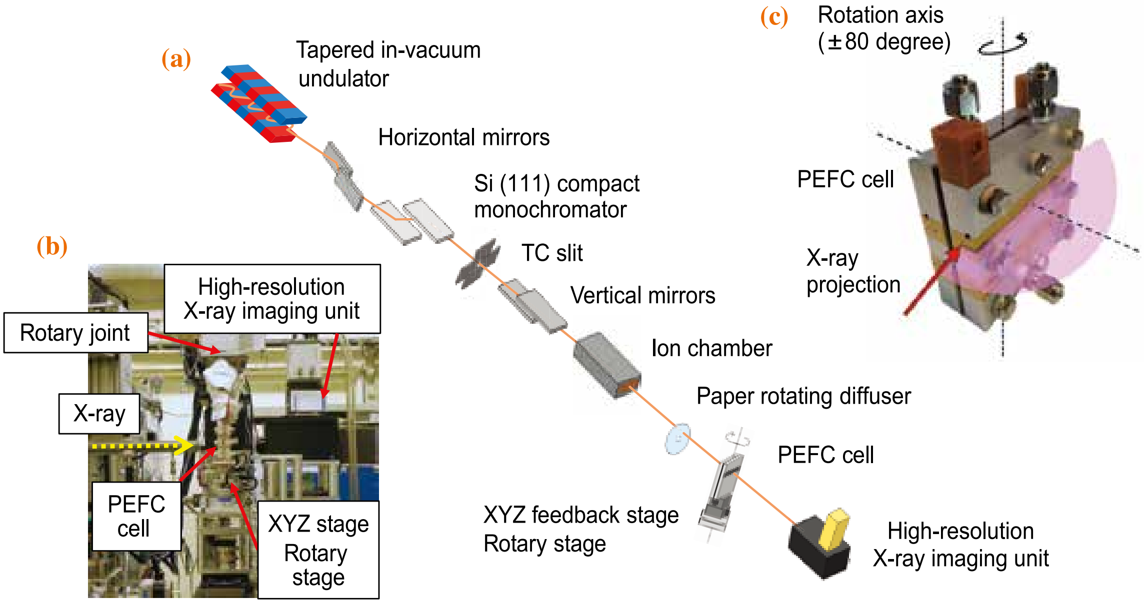

Fig. 1. **(a,b)** Schematic and image of CT-XAFS experimental setup at beamline BL36XU. **(c)** Image of the PEFC cell designed for the CT-XAFS measurements. [2]

valence state images in the MEA. The morphology images were obtained by the reconstruction of CT data measured at 11.497 keV, which was lower than the energy of the Pt L_{III}-edge (Figs. 2(A1, B1)). We found the clear contrasts derived from the structures of the components in the MEA, and a heterogeneous structure with random cracks was clearly imaged in the cathode catalyst layer.

Then, we reconstructed the Pt L_{III}-edge jump, which corresponds to the amount of Pt. Figures 2(A2, B2) show 3D reconstructed images of the Pt L_{III}-edge jump, where the distribution of the Pt catalyst in the MEA was clearly visualized before and after the ADT. Before the ADT, the distribution of the Pt catalyst was observed as tiny spots in the whole of the cathode catalyst layer, suggesting that the Pt catalyst was originally dispersed in the cathode catalyst layer. The 3D images of the distribution of the Pt catalyst markedly changed after the 20,000 ADT cycles. The observed tiny structures almost disappeared and the dissolution of the Pt catalyst from the cathode catalyst layer to the Nafion membrane was also observed. Severe aggregation was observed in some parts, whereas the Pt catalyst was lost in parts around the crack structures. The 3D images of the Pt distribution before and after the ADT showed the migration and degradation of the Pt cathode catalyst caused by the ADT cycles.

Figures 2(A3, B3) show 3D images of the Pt valence at 1.0 V obtained by the reconstruction of the white-line height of the Pt L_{III}-edge. After the ADT cycles, it was clear that the 3D image had changed from yellow to blue, showing decreases in the Pt valence caused by the ADT. This was observed in the entire cathode catalyst layer, indicating that Pt aggregation proceeded in the cathode catalyst layer with reduction in the active surface area of the Pt catalyst.

Briefly, we have succeeded in measuring *operando* CT-XAFS data of an MEA of a PEFC with a Pt/C cathode catalyst and reconstructing the Pt distribution and valence state in the MEA under PEFC operating conditions for the first time. The *operando* 3D-CT-XAFS images before and after the ADT showed that the dissolution, migration, and aggregation of the Pt cathode catalyst occurred in the entire cathode layer and spread to the Nafion membrane in the MEA during the ADT. The 3D visualization by CT-XAFS is a promising method for visualizing heterogeneous catalyst migration and the degradation of electrocatalysts in PEFCs to obtain a deeper understanding of catalyst degradation in PEFCs and for developing new catalysts and PEFC systems for practical use.

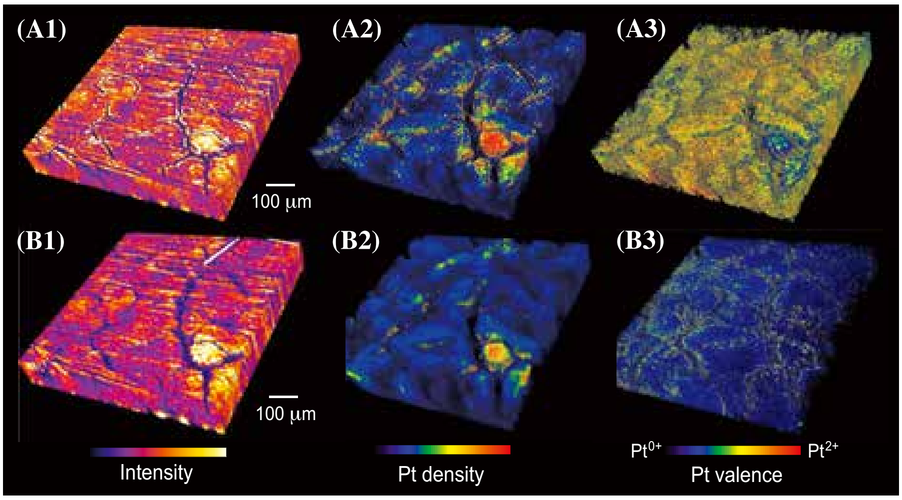

Fig. 2. Set of 3D images of (1) morphologies, (2) Pt densities, and (3) Pt valence states for the MEA **(A)** before and **(B)** after the 20,000 cycles of the ADT. [2]

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