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In-situ X-ray nano-CT System for Polymer Electrolyte Fuel Cells under Operating Conditions

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Abstract. We developed two types of in-situ three-dimensional imaging systems on the basis of full-field transmission X-ray computed tomography (XCT) methods for polymer electrolyte fuel cells (PEFCs) under operating conditions at beamline BL36XU at SPring-8. One was for a wide field of view (more than 500 μm) to obtain the whole membrane electrode assembly (MEA) images, and the other was for nano spatial resolution (less than 100 nm) using a Fresnel zone plate as objective optics. We succeeded in in-situ three-dimensional visualization of an MEA in PEFC using both XCT measurement systems and show preliminary results.

1. Introduction
A crucial issue for developing next generation polymer electrolyte fuel cells (PEFCs) is spatiotemporal information on the active factor and reaction mechanism, especially the degradation factor and mechanism in PEFC cathode catalysts. A PEFC has a multi-layered structure consisting of a membrane electrode assembly (MEA), gas diffusion layer (GDL), bipolar plate, and separator. An MEA consists of an anode catalyst layer, polymer electrolyte membrane (PEM), and cathode catalyst layer. The electrochemical reactions occur spatially inhomogeneously under potential operating conditions. To visualize the degradation mechanisms for the electrocatalysis, the internal structures of MEA in PEFC require in-situ non-destructive three-dimensional (3D) imaging under operating conditions.

We succeeded in 3D imaging of the chemical state distribution of electrode catalysts in an MEA by using an X-ray computed laminography (XCL) XAFS technique [1-3]. XCL is a 3D imaging technique suitable for laterally extended planar objects, such as MEAs. The geometric restriction of XCL measurement, however, imposed a specific design on the PEFC, which made it difficult to maintain the operating conditions of the PEFC due to heat dissipation from a large X-ray window. Also, X-ray scattering from support of PEFC disturbed transmission X-ray images of PEFCs. To improve this situation, we developed two types of in-situ 3D full-field transmission X-ray computed tomography (XCT) systems consisting of a newly designed PEFC at BL36XU at SPring-8 [3, 4]
2. Methods and results

3D reconstruction ideally requires two-dimensional (2D) projection images measured at a projection angle from 0 to 180 deg. In the case of measurements of real PEFCs, 2D projection images are difficult to measure at all angles. To measure images at the widest possible angle, we designed a new PEFC single cell to cover a measurement angle from -80 to 80 deg for the XCT measurement. The newly designed PEFC single cell was based on the Japan Automobile Research Institute (JARI) standard cell [5], which made it possible to conduct XCT measurements under experimental conditions almost the same as usual laboratory conditions. The MEA consisted of an anode catalyst layer (10–15 µm thick), a Nafion membrane (50 µm thick) and a cathode catalyst layer (10–15 µm thick). The MEA was sandwiched with GDL (190 µm thick) in the PEFC cell [6]. The MEA was larger than an X-ray beam, so X-ray absorption of the area outside of the reconstruction produced artifacts on reconstructed images. We used a simple correction method to reduce the artifacts by approximating absorption of the area outside of the reconstruction by using the average value of the reconstruction area. Figure 1 shows the simulation results with and without the correction. The original image used was a cross-sectional image of PEFC measured by XCL. The number of projection was 1600 images (-80 to 80 deg) and reconstructed by OS-EM method [7]. The original image was well reconstructed using the approximate correction.

We developed the following two types of in-situ full-field XCT measurement system having different fields of view (FOVs) and spatial resolutions to conduct the nondestructive microscopic imaging of an MEA in a PEFC under operating conditions. One is a wide full-field transmission XCT system for obtaining microscopic images of the overall MEA between the cathode and anode GDLs, and the other is a full-field high-spatial resolution imaging nano-XCT system using a Fresnel zone plate (FZP) as objective optics to achieve a detailed imaging of the cathode catalyst layer and PEM.

2.1. In-situ wide full-field transmission XCT measurement system

Figure 2 shows the layout of a wide full-field transmission XCT measurement system. Gas tubes and heater cables were connected to PEFCs through a rotary joint and slip ring to rotate the PEFCs smoothly and freely during full-field imaging measurement. The transmission X-ray images of PEFCs were measured by an indirect high-resolution X-ray imaging system, which is an imaging unit (Hamamatsu Photonics K.K., AA50) combined with a low noise sCMOS camera (Hamamatsu photonics K.K., ORCA-Flash 4.0). The transmitted X-ray

Figure 1. Simulation of reconstruction calculation with and without approximate correction during iterative reconstruction cycles. Original image (a), reconstructed image after 50 cycles without correction (b), after 10 cycles with correction (c), after 50 cycles with correction (d).

Figure 2. Layout of wide full-field transmission XCT system.
image was converted into a visible light image by a single crystal scintillator (Ce:Gd₃Al₂Ga₃O₁₂) and magnified by 20 on the camera by an objective lens in the imaging unit. The FOV and spatial resolution of the system were ca. 500×500 μm² and 1 μm, respectively.

Figure 3(a) shows preliminary results of 3D image reconstruction of an MEA in a PEFC under the operation conditions. The bright area shows high absorption area, such as metal catalyst-rich area. The whole the MEA in the PEFC was clearly visualized from anode to cathode GDL. Strong X-ray absorption of the area outside of the reconstruction, especially that of the GDLs, at high incident angles produced the artifact on the reconstructed images. Our simple approximate correction in this study could not fully reduce the artifact, which lowered the image resolution slightly. Figures 3(b-1) and (b-2) show reconstructed cross-sectional images at the cathode and anode catalyst layer during accelerated durability tests (ADTs). The anode catalyst layer had relatively uniform distribution of the catalyst particles before the ADTs and no significant change occurred during the ADTs. In contrast, in the cathode catalyst layer, the catalyst particles were unevenly distributed before the ADTs, and some catalyst particle-rich areas disappeared during the ADTs. The location-dependent degradation process of the MEA was successfully observed under operation conditions.

2.2. In-situ full-field high-resolution imaging nano-XCT measurement system

The wide full-field transmission XCT system mentioned in chapter 2.1 had FOV to observe the overall MEA, but its spatial resolution (ca. 1 μm) was insufficient to achieve detailed imaging of inside of the Pt catalyst layer (10~15 μm thick). To achieve high-resolution imaging, we developed an in-situ full-field nano-XCT measurement system using a FZP as objective optics. Figure 4 shows the layout of the system. The optics of the system was based on that
designed by Suzuki et al. at beamline BL47XU at SPring-8 [8]. An optical system for illuminating objects was a beam condenser consisting of a single-bounce conical-shape mono-capillary made of Pyrex glass. The objective FZP was a commercially available one (NTT-AT Corp., FZP-155/50). The zone material is 0.5-μm-thick tantalum. The outermost zone width of FZP is 50 nm, and the diameter is 155 μm. The focal length of the FZP is 75 mm at 12 keV. A detector was placed 2400 mm from FZP, and the magnification by FZP was ca. 30 at 12 keV. The magnification of the X-ray imaging detector was set to 5, so the total magnification of the imaging system was 150. By 2D imaging measurement of X-ray chart pattern (NTT-AT Corp., XRESO-50HC, Ta: 500 nmt), the minimum pattern (50 nm) was clearly distinguished. The sample cell and its connected equipment, such as a rotary joint and slip ring, were the same as those used for the wide full-field transmission XCT measurement system.

Figure 5 shows a preliminary result of a reconstructed cross-sectional image of an MEA measured using the nano-XCT measurement system. The FOV of the system was 60×60 μm². The fine image of the inside of the cathode catalyst layer, such as 100 nm width cracks, and its boundary with the PEM was clearly obtained, which indicates the spatial resolution of nano-XCT system was less than 100 nm.

3. Conclusion
We developed two types of in-situ full-field XCT measurement systems for PEFCs: a wide full-field transmission XCT system (FOV: 500 μm, spatial resolution: 1 μm) and a high-resolution imaging nano-XCT system (FOV: 60 μm, spatial resolution: < 100 nm). We successfully observed 3D structural changes in MEA under operating conditions during ADT. We plan to develop an automatic switching system for both XCT measurement systems to achieve sequential observations with wide FOV and with high spatial resolution on the same area in a PEFC.

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