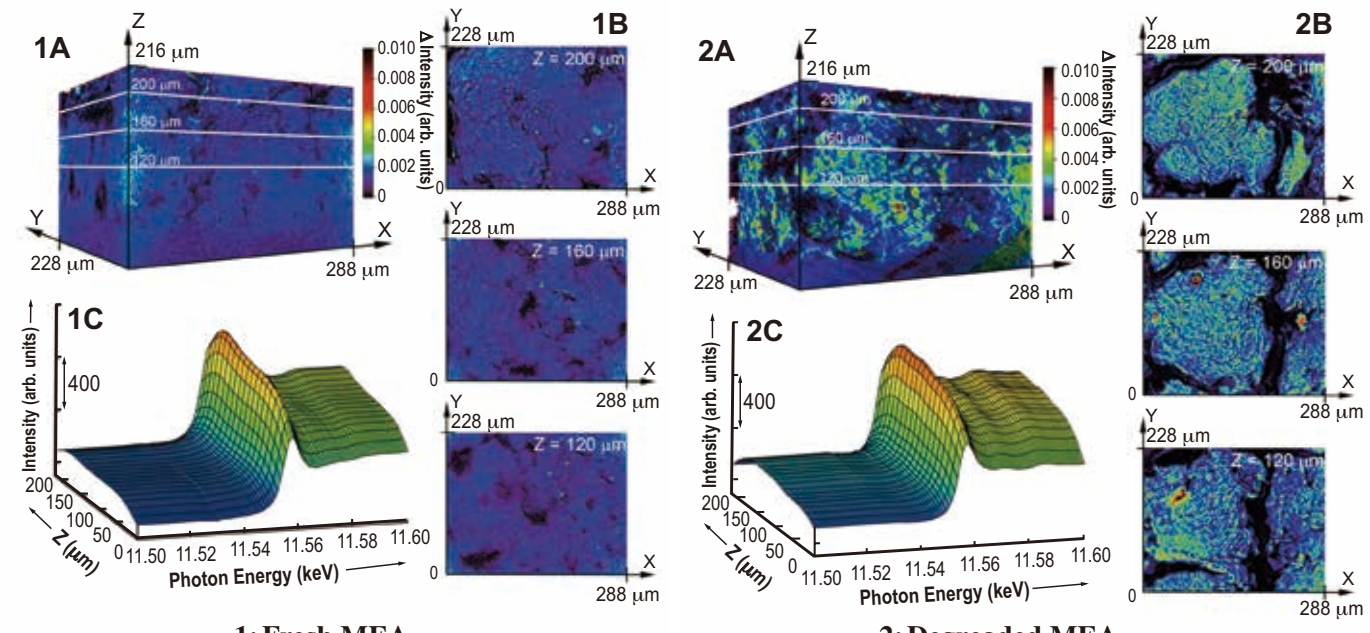
Visualization of Pt/C cathode catalyst layers in polymer electrolyte assemblies by X-ray computed laminography XANES

A polymer electrolyte fuel cell (PEFC) is one of the promising power sources, and many trials are being carried out to apply them to clean power generation with highly efficient energy systems. The prevention of degradation of cathode catalyst layers by fluctuations in cathode potential under variable loads and during startup and shutdown is crucial for the practical use of PEFCs. There are many investigations on the degradation processes of Pt cathode catalysts in PEFCs, but the three-dimensional (3D) structural information of the Pt cathode catalyst degradation has not yet been fully investigated because of a lack of nondestructive characterization methods for directly observing the spatial distribution chemical states of cathode catalyst layers inside membrane electrode assemblies (MEAs). We have developed X-ray computed laminography–X-ray absorption near-edge structure (XCL–XANES) analysis as a powerful tool to visualize the 3D structural information of Pt cathode catalysts in MEAs [1].

X-ray computed tomography (XCT) is a typical method for obtaining 3D images of a sample, in which the sample is rotated about an axis perpendicular to the incident X-ray beam. XCT can be applied to a sample smaller than the observation field area in all projected directions of XCT, but it cannot analyze a flat sample. On the other hand, XCL is applicable to partial 3D imaging of such a flat shaped sample. In XCL, the rotation axis of a sample is not fixed at 90° with respect to the incident X-ray beam, and the sample is inclined. We applied the XCL technique to XAFS spectroscopy, which provides not only morphological/structural information but also the 3D distribution of Pt catalysts and their chemical states in cathode catalyst layers in MEAs.

MEAs were commercially prepared using 50 wt% Pt/C (TKK) as a cathode catalyst. A fresh MEA was subjected to 4 cycles of current steps held for 30 s each. A degraded MEA was subjected to 150 cycles of aging and 200 cycles of accelerated degradation testing. Each MEA has a layered structure of a cathode catalyst layer with the Pt/C catalyst, polymer



1: Fresh MEA **2: Degreaded MEA**

Figs. **1A** and **2A**: 3D spatial distribution of the Pt catalysts in the cathode catalyst layers of a fresh MEA (**1A**) and degraded MEA (**2A**) observed by XCL-XANES spectroscopy. Figs. **1B** and **2B**: Cross sectional images of Figs. **1A** and **2A** in the X-Y plane at Z = 120, 160, and 200 μm. Figs. **1C** and **2C**: Series of depth-resolved Pt L_{III}-edge XCL-XANES spectra along the Z-axis for the cathode catalyst layers, **1C** for a fresh MEA and **2C** for a degraded MEA. The XANES spectra are presented every 12 μm depth.

electrolyte, and anode catalyst layer with a Pd/C catalyst. The average particle sizes of Pt cathode catalysts in the fresh and degraded MEAs were 3.5±0.9 nm and 5.4±2.1 nm, respectively, observed by TEM. The treated MEAs were cut into 10×10 mm^2 pieces for XCL measurements and clipped a 300-nm-thick SiC membranes. 3D XCL-XANES spectra were recorded at **BL47XU**, and the rotational axis of the MEA was inclined 30° from the normal toward the downstream direction. The incident X-ray beam to a high spatial resolution X-ray image detector, which consisted of a visible light conversion unit and a CCD camera, was converted to visible light by an LSO crystalline scintillator, and a visible light image was focused onto the CCD camera using a microscope objective. Transmission images of MEAs were acquired from 360° rotation, and the number of transmission images was 1800 per energy scan. Sectional images were reconstructed using a filtered back-projection method considering the inclination of the rotational axis. 83 XCL images were obtained for Pt L_{III}-edge in the X-ray energy range of 11.394–11.609 keV. The field of view of a sectional image (X-Y section) obtained from laminography reconstruction became 400×400 μm^2.

XCL images obtained at 11.496 keV before the Pt L_{III}-edge provided 3D morphology images of cathode catalyst layers in the MEAs. For the fresh MEA without the accelerated degradation testing, many cracks in a random pattern were observed in both SEM and XCL images. On the other hand, cracks in the degraded MEA, whose cathode catalyst layer was about 115–210 μm in thickness, were much more conspicuous. SEM and XCL provided similar images of the MEAs.

We obtained a series of XCL images of incident X-rays at the Pt L_{III}-edge, and the reconstruction of the series of XCL images at different energies provided the XCL-XANES spectra for the first time. XCL-XANES provided both 3D images of the spatial distribution of Pt catalysts and their chemical states at the cathode catalyst layers in the two MEAs. The spatial distribution of Pt catalysts was visualized by mapping the Pt L_{III}-edge intensity, which corresponds to the difference in the intensity of X-ray absorption at 11.572 keV (isosbestic point of Pt and PtO_2) from that at 11.496 keV (before Pt L_{III}-edge) (Fig. 1A). Bright areas indicate high-Pt-concentration areas and the contrast in the images was clear. In the fresh MEA, Pt catalysts were almost fully loaded throughout the cathode catalyst layer (Fig. 1A), whereas the Pt distribution was heterogeneous throughout the entire cathode catalyst layer in the degraded MEA (Fig. 1B), which suggests that Pt migration, aggregation, and cracking spread throughout the cathode catalyst layer in the degraded MEA. Cross sectional images (Figs. 1B and 2B) of the MEAs clearly show the differences in the Pt spatial distribution in the cathode catalyst layers.

Pt L_{III}-edge XCL-XANES spectra were obtained for every piece of the cathode catalysts layers, whose depth-resolved XANES spectra are presented in Fig. 1C. A difference in the edge intensity of the Pt L_{III}-edge XANES spectra indicates a difference in the Pt quantity in the MEAs along the Z depth. In the fresh MEA, the Pt quantity gradually increased with depth and reached a maximum at about 170 μm in depth (Fig. 1C). In contrast, a series of depth-resolved laminography-XANES spectra of the degraded MEA were wavy in the Z depth, probably reflecting the degradation of the MEA (Fig. 2C). The XCL-XANES spectra at different positions were different in the degraded MEA, suggesting that the chemical states of Pt catalysts depend on the area/position in the cathode catalyst layer in the MEA. The XCL-XANES spectra indicated the heterogeneous chemical states of the Pt nanoparticle catalysts in the cathode catalyst layer in the degraded MEA, which cannot be monitored by conventional XAFS. They also indicated that the Pt catalysts in the degraded MEA were in the form of larger Pt nanoparticles with a lower Pt L_{III}-edge white-line intensity. We observed large aggregated areas of μm sizes in the XCL images of the degraded MEA. *In situ* XCL-XANES would potentially reveal the degradation process of Pt catalysts at each part of a cathode catalyst layer in an MEA under PEFC operating conditions.

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References

[1] *T. Saida, O. Sekizawa, N. Ishiguro, K. Uesugi, M. Hoshina, T. Uruga, S. Ohkoshi, T. Yokoyama and M. Tada: Angew. Chem. Int. Ed.* ***51*** *(2012) 10311.*