Operando three-dimensional imaging of distribution and degradation process of Pt-Co cathode catalyst in polymer electrolyte fuel cell

The membrane electrode assembly (MEA) of a polymer electrolyte fuel cell (PEFC) is a heterogeneous device for clean energy production, and the visualization of the heterogeneous structure of an MEA is crucial to the understanding of chemical events proceeding in a practical PEFC device. In particular, the migration and degradation of electrocatalysts in an MEA are key issues of PEFC performance, and we have performed the *operando* imaging of the three-dimensional distribution and degradation event of a Pt-Co cathode catalyst in an MEA under PEFC operating conditions [1].

Computed-tomography XAFS (CT-XAFS) combining CT imaging and XAFS spectroscopy at the Pt L_{III}-edge and Co *K*-edge was performed at SPring-8 **BL36XU** beamline. Monochromatized hard X-rays (Pt L_{III}-edge: E = 11.386–11.697 keV, Co *K*-edge: E = 7.517–7.849 keV) were irradiated to the MEA with the Pt-Co cathode catalyst enclosed in an *in situ* PEFC cell designed for CT-XAFS measurements. The cell was operated at 353 K with N_2 flow of 600 mL·min^{-1} at the cathode and H_2 flow of 150 mL·min^{-1} at the anode, and electrochemical performances were investigated during a series of *operando* measurements. The recorded X-ray transmission images of the sample (I) and X-ray intensity images (I_0) were converted to absorption coefficient images (μt), and a fitting analysis of the obtained XANES spectra was conducted on 2D images. Finally, the three-dimensional matrices of extracted XANES fitting parameters were reconstructed into the three-dimensional images of morphology, Pt density, Co density, and Pt valence state in real space (Fig. 1). The *operando* CT-XAFS measurements were performed before and after a PEFC accelerated degradation test (ADT) (voltage cycling between 0.6 V and 1.0 V for each 3 s).

The *operando* CT-XAFS measurements provided the distribution and degradation images of the cathode catalyst in the MEA, as shown in Fig. 1. The visualized morphology images of the MEA clearly suggested the structures of domains and cracks in the cathode catalyst layer, and similar patterns in the morphology images before and after the ADT process showed that the *operando* measurements successfully visualized the same parts in the MEA before and after the ADT process. The distributions of Pt and Co in the cathode catalyst layer were obtained by analyzing Pt L_{III}-edge and Co *K*-edge XANES spectra, respectively, and suggested different degradation manners of the Pt and Co species in the Pt-Co bimetallic catalyst in the MEA. The aggregation of Pt was observed in the observation area, but the migration to the depth direction of the MEA was negligible. This was considerably different from the behavior of an MEA with a Pt cathode catalyst. In contrast, a significant amount of Co was dissolved and migrated in the depth direction of the MEA, changing the Pt valence state of the Pt-Co catalyst (Fig. 1).

The CT-XAFS analysis provides huge experimental data sets of the structural parameters, and data

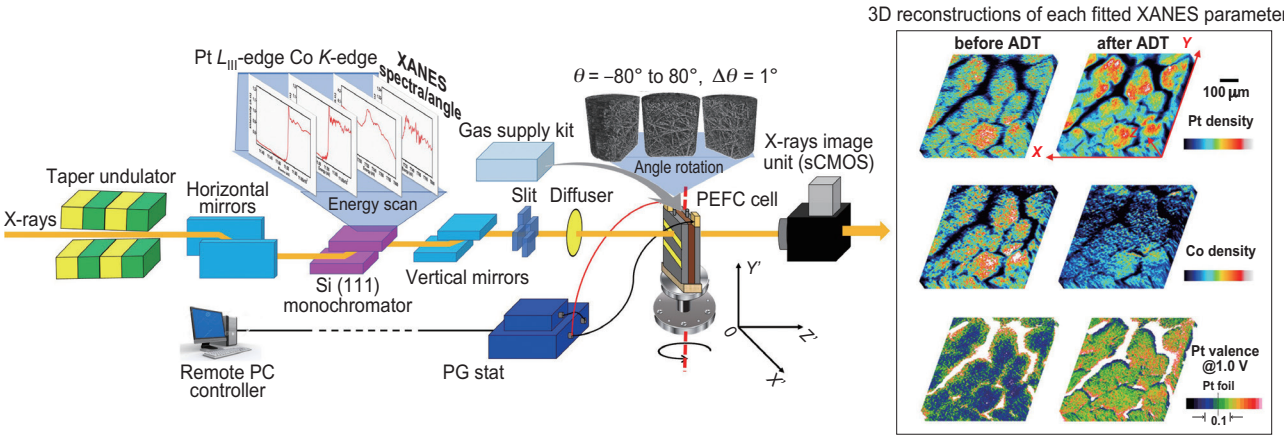

Fig. 1. Schematics of *operando* CT-XAFS measurements of PEFC MEA under operating conditions and the reconstructed 3D images of Pt density, Co density, and Pt valence state of the cathode catalyst layer at 1.0 V before and after 34,000 cycles of ADT. [1]

mining is essential to extract key parameters in the imaging data. We conducted unsupervised learning of the obtained structural parameters, e.g., morphology, Pt density, Co density, Pt valence state, geometrical distance from the surface of cracks in the MEA, loss of Pt (ΔPt), and loss of Co (ΔCo), and investigated correlations between parameters. Figure 2 shows the Pearson plots of ΔPt or ΔCo (changes in the Pt or Co density by the ADT process) and the geometrical distance from the surface of cracks formed in the cathode catalyst layer, calculated using the morphology images. The Gaussian mixture model of the Pearson plots suggested the existence of four groups (G_1–G_4) in Fig. 2: a group with an increase in the density (G_4), a group with negligible changes in the density (G_3), and two groups with decreasing density (G_2 and G_1). In the case of Co, all four groups were widely distributed from the surface to the domains, as shown in Figs. 2(c) and 2(d). On the other hand, the G_3 component of Pt was found to be localized at the surface near cracks in the cathode catalyst layer Figs. 2(a) and 2(b). These results suggest that the morphological factors of the cathode catalyst layer depend on catalyst degradation. The present infographic approach combining three-dimensional imaging and unsupervised learning is promising for extracting essential parameters related to material functions.

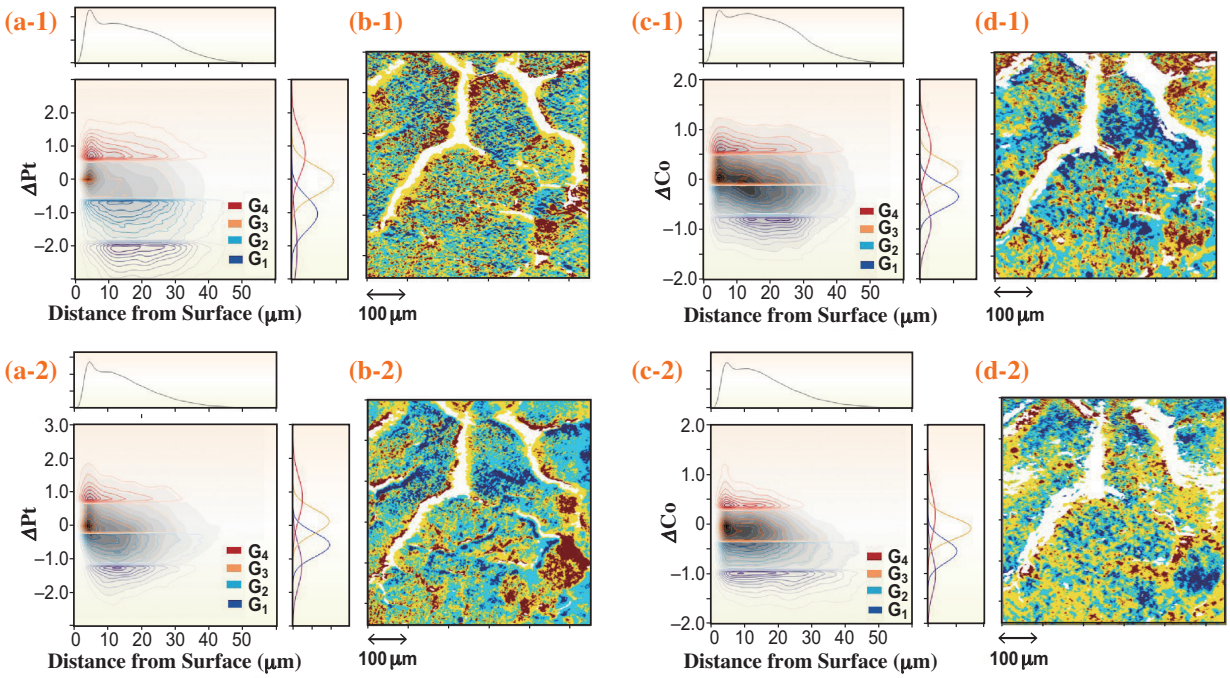

Fig. 2. Pearson plots of ΔPt **(a)** and ΔCo **(c)** and calculated geometrical distance from crack surface. **(1)** Differences in the densities after 21,000 cycles of ADT from those before ADT. **(2)** Differences in the densities after 34,000 cycles of ADT from those after 21,000 cycles of ADT. G_1–G_4: Groups classified by the Gaussian mixture model of the Pearson plots. **(b, d)** Spatial distribution maps of G_1–G_4 of each Pearson plot. [1]

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References

[1] *Y. Tan, H. Matsui, N. Ishiguro, T. Uruga, D.-N. Nguyen, O. Sekizawa, T. Sakata, N. Maejima, K. Higashi, H.C. Dam, M. Tada: J. Phys. Chem. C* ***123*** *(2019) 18844.*