

Mapping Pt Chemical Species in Polymer Electrolyte Fuel Cell Catalysts by Nano-XAFS at the Unique Beamline with the Best Performance in the World for Fuel Cell Analysis

-Spatial distribution of platinum species in fuel cell catalyst layers observed using nano-XAFS technique: contributing to control of fuel cell catalyst degradation-

Key points

- We succeeded in mapping the degradation of fuel cell catalysts at the unique beamline BL36XU at SPring-8 with the best performance in the world for fuel cell catalyst analysis, which was constructed by the University of Electro-Communications under a New Energy and Industrial Technology Development Organization (NEDO) program.
- We succeeded in the two-dimensional mapping of platinum (Pt) species in electrode catalyst membranes and in the identification of dissolved species and preferential sites using the nano-X-ray absorption fine structure (XAFS) technique with the highest spatial resolution in the world.
- These achievements will promote the development of electrode catalysts for next-generation fuel cells, enabling the widespread use of fuel-cell-powered cars, and provide new scientific guidelines for the development and design of electrode catalysts.

1. Determination of the cause and mechanism of fuel cell degradation is desired because significantly improving the durability of electrode catalysts in polymer electrolyte fuel cells (PEFCs) is one of the key

requirements for realizing the widespread use of fuel-cell-powered cars. However, direct observation of the catalysts has been very difficult. The research group has developed a technique to directly observe catalysts that are spatially distributed.

2. We have been the first to succeed in the two-dimensional mapping of Pt species in the membrane electrode assembly (MEA), the active site in practical PEFCs. The two-dimensional mapping of Pt species in PEFCs has been difficult but was enabled by nano-XAFS measurements (beam size, $570 \times 540 \text{ nm}^2$ or $228 \times 225 \text{ nm}^2$) performed at the unique beamline BL36XU at Spring-8, for XAFS measurements on fuel cells with the best performance in the world. This beamline was constructed by the University of Electro-Communications under a NEDO program.

3. The spatially heterogeneous processes of oxidation and dissolution of Pt nanoparticles on carbon carriers, namely, fuel cell electrode catalysts, in the MEA were directly observed in the XAFS measurements. Also, the selective oxidation and dissolution of the Pt nanoparticles as the four-coordinate $\text{Pt}^{2+}\text{-O}_4$ in the 2–3 μm region around the boundary between the cathode catalyst layer and the electrolyte membrane and around the micro-crack boundary were for the first time visualized as images.

4. The specific site where the dissolution and degradation of fuel cell catalysts begin and the underlying mechanism were partially but definitely clarified by the spatially resolved nano-XAFS technique.

5. The mapping information on the Pt species such as the amount of Pt and the oxidation state in MEA, the active site in fuel cells, is expected to provide scientific guidelines for the development of highly durable electrode catalysts for next-generation fuel cells required to promote the widespread use of fuel-cell-powered cars.

(Figures and captions)

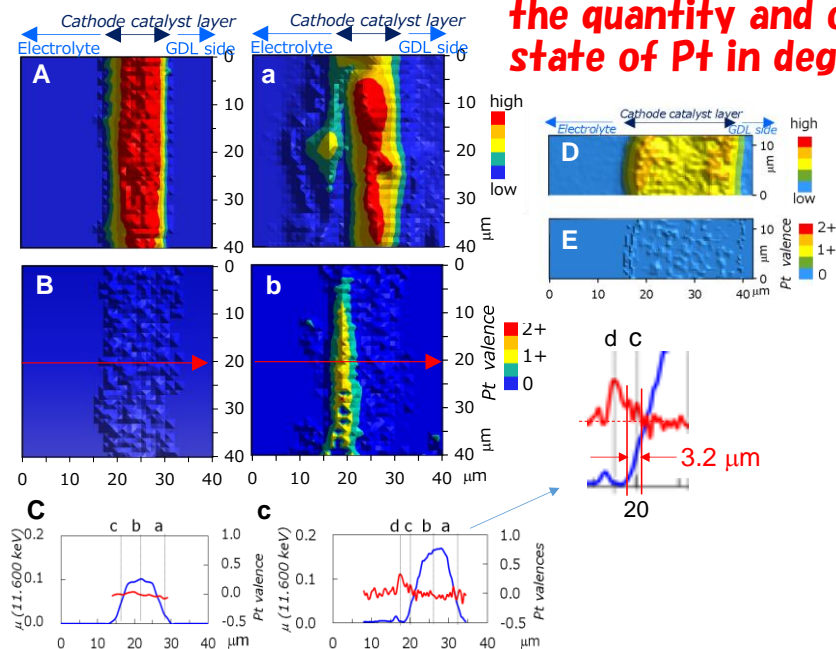
Achievement 1 Mapping of Pt distribution and oxidation state in fuel cell cathode catalyst layers

Mapping Pt species in MEA-A by scanning nano-XAFS

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A, B: 570 nm x 540 nm nano-X-ray beam
D, E: 228 nm x 225 nm nano-X-ray beam

First success in mapping the quantity and oxidation state of Pt in degraded MEA



A & D: Pt mapping before degradation

B & E: Pt valence mapping before degradation (metal Pt found throughout the layer)

C: Line profile along arrow in B [Pt amount (blue) and Pt valence (red)]

a: Pt mapping after degradation (heterogeneous)

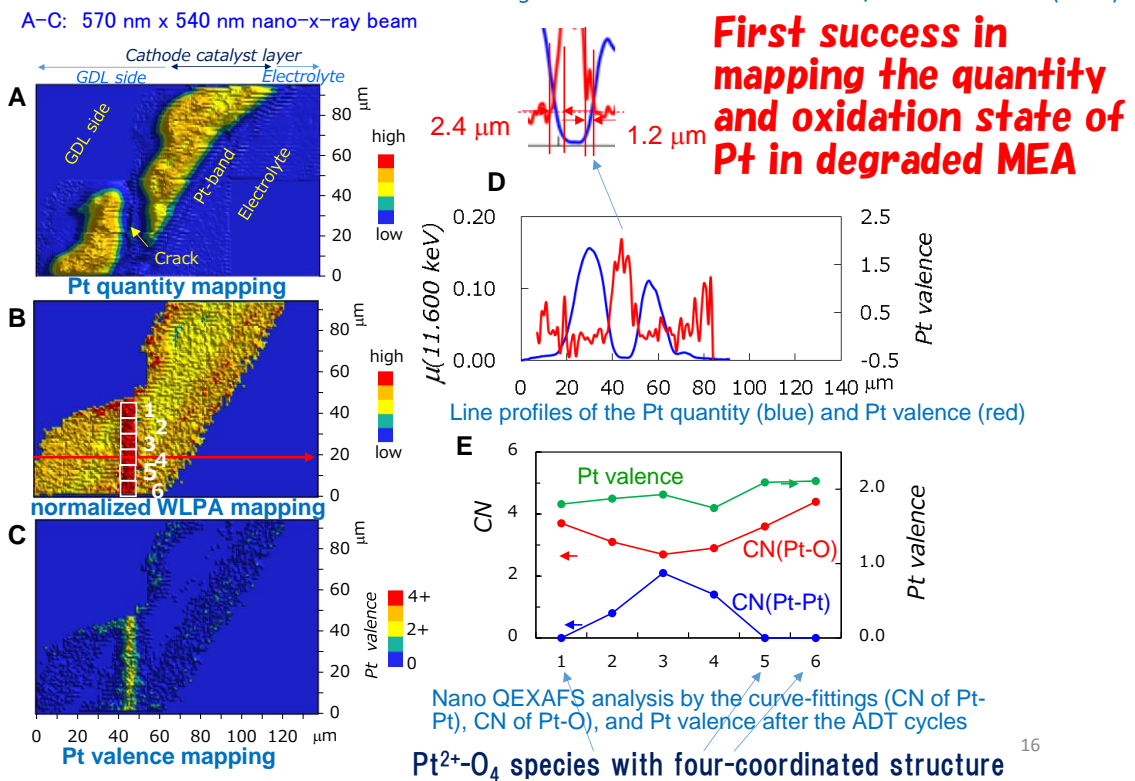
b: Pt valence mapping after degradation (Pt ions localized in yellow region)

c: Line profile along arrow in b [Pt amount (blue) and Pt valence (red)]

Achievement 2 Mapping of Pt distribution and its oxidation state in the micro-crack region in fuel cell cathode catalyst layers

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- A: Pt mapping after degradation
- B: Mapping of white line peak intensity of X-ray absorption near-edge structure (XANES) spectrum after degradation
- C: Pt valence mapping (Pt^{2+} ions dissolved in yellow region)
- D: Line profile along arrow in B [Pt amount (blue) and Pt valence (red)]
- E: Pt valence (green) and coordination numbers of Pt-O (red) and Pt-Pt (blue) obtained by XAFS measurements at numbered sites in the micro-crack region in B
- Line profile along red arrow in B