

First direct observation on the degradation of both Pt catalyst and carbon in MEA Pt/C cathode by the same-view nano-XAFS/STEM-EDS imaging technique

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Abstract: The same-view nano XAFS/STEM-EDS imaging of Pt/C cathode in polymer electrolyte fuel cell after triangular ADT(accelerated durability test) cycles elucidated a Pt/C degradation process, in which carbon corrosion to a critical size induced the Pt catalyst degradation. The triangular ADT cycles caused a carbon corrosion of the Pt/C cathode layer to reduce the carbon nanoparticle size in the boundary region with the electrolyte and crack. From these deteriorated carbon Pt nanoparticles detached. After the carbon nanoparticles decreased to less than 8 nm, Pt nanoparticles transformed to four-coordinated oxidized species, Pt²⁺-O₄.

Keywords: Polymer electrolyte fuel cell, Pt/C cathode catalyst degradation, same-view nano XAFS /STEM-EDS.

1. Introduction

Fuel cell is one of clean and efficient power generation systems. For widespread commercialization of polymer electrolyte fuel cell (PEFC) vehicles, cost reduction, performance increase, and durability improvement are still challenges, and it is mandatory to understand activation and degradation factors and mechanisms on a molecular level. The degradation of Pt/C cathode occurs with both carbon and Pt nanoparticles. Pt aggregation, detachment, and dissolution occur during the PEFC degradation. It has been suggested electrochemically that the carbon corrosion occurs at first, and secondly the Pt degradation proceeds. Carbon oxidation catalyzed by Pt nanoparticles is also considered. However, there are no direct evidences on the order and mechanism of these deteriorations. Herein, we report direct observations of the degradation of Pt/C cathode catalyst in PEFC by the same-view nano XAFS STEM-EDS imaging technique.

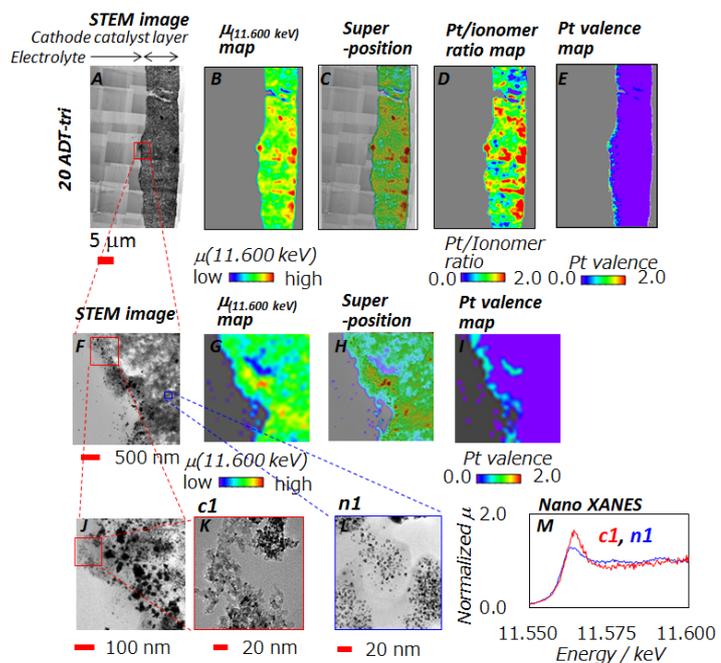


Figure 1. The same-view nano XAFS/STEM-EDS imaging of the degraded MEA cathode catalyst layer after 20 ADT cycles (A-L). M: Nano XANES for the regions c1 (red) and n1 (blue).

2. Experimental

In this study special MEAs with flat cathode/anode layer planes and few cracks were employed. Anode and cathode catalysts were 50 wt% Pt/C (TKK, TEC10E50E) and their Pt loadings were 0.3 mg-Pt/cm². The Pt/ionomer ratio was 1/1. We applied 150 aging cycles for catalyst activation, and then measured cyclic voltammogram (CV) at 2 mV s⁻¹, 20 mV s⁻¹ and 50 mV s⁻¹ under anode/cathode H₂/N₂. The degraded MEA Pt/C samples were prepared by accelerated durability test (ADT) treatments by triangle wave 1.0 - 1.5 V_{RHE} voltage cycles (10, 20, and 50 cycles). After CV and I-V curve measurements to obtain the electrochemical properties, the MEA was left under the anode/cathode gases H₂/N₂ until the cell voltage reached to open circuit voltage (OCV). Then we removed the MEA from the fuel cell under humid N₂. We prepared a small piece of the MEA for the same-view nano XAFS-STEM-EDS imaging by the same method as that described in our previous report.¹ The nano XAF/STEM-EDS measurements were carried out by the similar procedure to our previous report.²

3. Results and discussion

We measured same-view nano XANES maps and STEM images in the wide range (40 μm x 24 μm, Figure 1 A-E) for the MEAs before and after the 1.0-1.5 V_{RHE} ADT- cycles, using a beam size of 142 nm x 159 nm. The nano XANES maps clearly display the heterogeneous degradation of the cathode catalyst layer in the boundary region with the electrolyte membrane and cracks after the ADT cycles. In order to clarify the reason of such location-selective degradation, we analyzed the same-view nano XANES and STEM images in the smaller regions (3 μm x 3 μm, Figure 1 F-I) of the cathode catalyst layer around the boundary with the electrolyte membrane. Also, we measured nano XAFS for the 142 nm x 159 nm spots, where Pt particles simply detached from the carbon support to the electrolyte, which were compared with the images of the reference sample which consists of the pristine Pt/C. The obtained data and analysis revealed that the detached Pt species were Pt⁰ metallic nanoparticles. We also found that the degraded carbon particles smaller than 8 nm were present around the boundary region of the cathode catalyst layer with the electrolyte and cracks (Figure 1 F, J, and K). The nano XANES (Figure 1 M) and EXAFS studies indicated that the oxidation of Pt to a four-coordinated oxidized species, Pt²⁺-O₄ occurred in those degraded carbon region.

4. Conclusions

We have achieved the direct observation of the degradation process in the MEA Pt/C cathode after the 1.0-1.5 V_{RHE} ADT cycles, and observed the deterioration of carbon support and oxidation of Pt nanoparticles in the boundary of the cathode catalyst layer with the electrolyte membrane and cracks. By increasing ADT cycles, carbon corrosion occurred and the size of carbon decreased in these boundary regions, where the detachment of Pt⁰ nanoparticles was also observed. In the region of carbon sizes smaller than 8 nm, Pt nanoparticles were oxidized to a four-coordinated Pt²⁺-O₄ species.

References

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