

XAFS Analysis of Pt and Pt-Ru Catalysts for PEFCs by *In-Situ* Measurements under Operating Conditions in the Fluorescence Mode

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Abstract. *In-situ* X-ray absorption fine structure (XAFS) is one of powerful spectroscopic techniques to analyze valence state and chemical bonding in Pt and Pt-Ru electrocatalysts under fuel cell operating conditions. We measured Pt L_3 and Ru K-XAFS of Pt and Pt-Ru electrocatalysts in fluorescence mode under different operation voltages using pure H_2 or 97 ppm CO containing H_2 as fuel gases that were fed to the anode. The radial structure functions that derived from the obtained XAFS spectra showed that the local structure around Pt and Ru atoms in the electrocatalysts changes depending on the operation voltage and shows difference with the existence of CO in the fuel gas.

Keywords: *in-situ* XAFS, fluorescence mode, PEFC, Pt-Ru and Pt electrocatalysts, local structure.

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INTRODUCTION

The deterioration of Pt and Pt-Ru electrocatalysts is one of probable causes for performance fading of Polymer Electrolyte Fuel Cells (PEFCs). Among the spectroscopic techniques, *in-situ* X-ray absorption fine structure (XAFS) is one of powerful spectroscopic techniques for analyze valence state and chemical bonding in Pt and Pt-Ru electrocatalysts under fuel cell operating conditions [1-5]. In this study we measured Pt L_3 and Ru K-XAFS of Pt and Pt-Ru electrocatalysts after *ca.* 1000 h steady fuel cell operation under different operating conditions by the fluorescence XAFS measurement with a Lytle-type ionization chamber. This study will be the second step to investigate the long-term deterioration mechanism of actually used Pt and Pt-Ru electrocatalysts following to our previous work on the electrocatalysts at the initial state [6].

EXPERIMENTAL

Figure 1 shows the actual arrangement of *in-situ* XAFS measurements. The membrane electrode assembly (MEA), which was composed of a cathode electrocatalyst (Johnson Matthey 40% Pt/C), a Nafion[®] electrolyte membrane and anode electrocatalyst (Johnson Matthey 45% PtRu/C (Pt:Ru

= 50:50)), was installed between the graphite cell covers with thin X-ray windows of less than 3 mm thickness and stainless steel cell walls with incident X-ray and excited fluorescence X-ray passage holes.

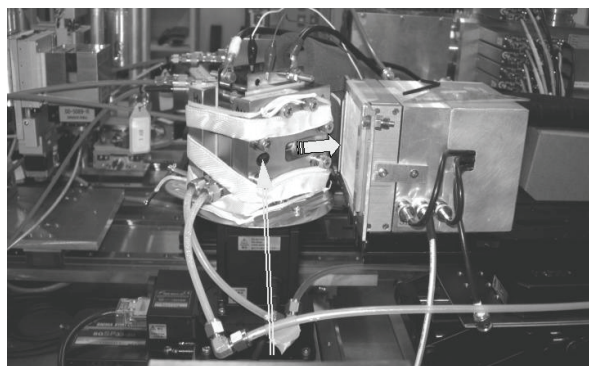


FIGURE 1. The actual arrangement of *in-situ* fluorescence XAFS measurement of electrocatalysts of a PEFC operated using a portable operation apparatus. The *in-situ* cell is set on the optical stage of which rotation, vertical and horizontal axes were remote-controlled. Long thin and short fat arrows denote the incident X-ray from the storage ring and the excited fluorescence X-ray from the Pt-Ru and the Pt electrocatalysts of the MEA, respectively.

The fuel cell has been operated in steady state for 1227 h before the XAFS measurement. During *in-situ*

XAFS measurement, the cell was set on optical stage and operated using a portable fuel cell operation apparatus (Microequipment, Tokyo). Typically 82 ml min⁻¹ H₂ or 97 ppm CO containing H₂ saturated with water at 70 °C were fed into the anode while 341 ml min⁻¹ of air saturated with water at 70 °C were fed into the cathode.

XAFS measurements were made with the X-ray monochromatized with Si (111) double crystals at the beam line BL01B1 in the SPring-8 of the Japan Synchrotron Radiation Research Institute (Hyogo, Japan, Proposal No. 2006A1042-NX-p). We measured typically three scans of Pt L₃-XAFS (11.546 keV) and Ru K-XAFS (22.117 keV) of the Pt-Ru and the Pt electrocatalysts with energy range of 350 eV below and 1100 eV above the absorption edge in the fluorescence mode with a Lytle-type ionization chamber. The XAFS measurements were done both irradiating X-ray to the anode side and the cathode side of the *in-situ* cell under N₂ atmosphere saturated with 70 °C water and two different operation voltages. Also the Pt L₃-XAFS and Ru K-XAFS of the reference samples were measured in the transmission mode. Data were analyzed by the standard procedure using TECHXAS-SW Version 3.0 (Technos Co., Ltd.). Some reference EXAFS functions were calculated by FEFF6. The radial structure functions (RSFs) were obtained by the Fourier transform of the *k*³-weighted EXAFS functions typically in the *k* range between 1.8 and 13.5 Å⁻¹.

RESULTS AND DISCUSSION

Figure 2 shows the comparison of the radial structure function (pseudo radial distribution function) around the Ru atoms of the anode electrocatalyst under different operating conditions with those of reference samples. The remarkable change of the scattering atom peak distribution is observed for the catalysts under fuel cell operation as compared with the catalysts in N₂ atmosphere saturated with 70 °C water, especially in the *R* region below 2.0 Å. Figure 3 shows the comparison of the RSF around the Pt atoms of the anode electrocatalyst under different operating conditions with those of reference samples. Also the significant variation of the scattering atom peak distribution is observed for the catalysts under fuel cell operation as compared with the catalysts in N₂ atmosphere saturated with 70 °C water. An especially significant peak distribution change is observed for the catalysts under open circuit voltage, OCV (0.99 V). In contrast to the anode side, the comparison of the RSF around the Pt atoms of the cathode electrocatalyst under different operating conditions with those of reference samples indicated that the difference of the scattering atom peak distribution is not so prominent

as compared with the catalysts in N₂ atmosphere saturated with 70 °C water.

Figure 4 and 5 shows the comparison of the RSF around the Ru atoms and the Pt atoms of the anode catalyst under different operating conditions using 97 ppm CO containing H₂ with those of reference samples, respectively. Also “difference” RSFs were showed in the figures; the “difference” RSF was obtained by Fourier transforms of direct “difference” EXAFS functions between experimentally obtained *k*³-weighted EXAFS functions of the catalyst under fuel cell operation using 97 ppm CO containing H₂ and the catalyst under fuel cell operation using pure H₂.

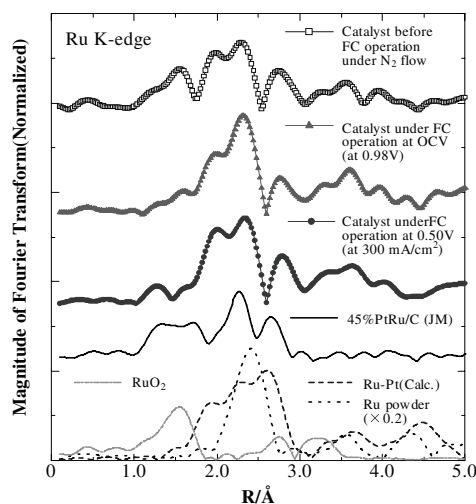


FIGURE 2. The radial structure functions of *k*³-weighted Ru K-EXAFS for the anode electrocatalyst under different operation voltages using pure H₂ as a fuel gas.

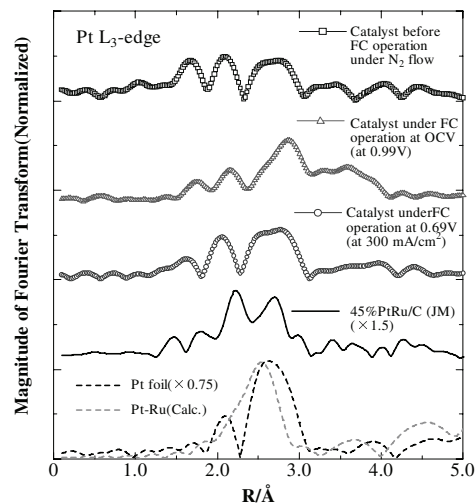


FIGURE 3. The radial structure functions of *k*³-weighted Pt L₃-EXAFS for the anode electrocatalyst under different operation voltages using pure H₂ as a fuel gas.

A major difference peak is observed in the Ru-metal (Ru or Pt) peak region for the RSF around the Ru atoms in the anode catalyst under OCV (*ca.* 1 V) in Figure 4.

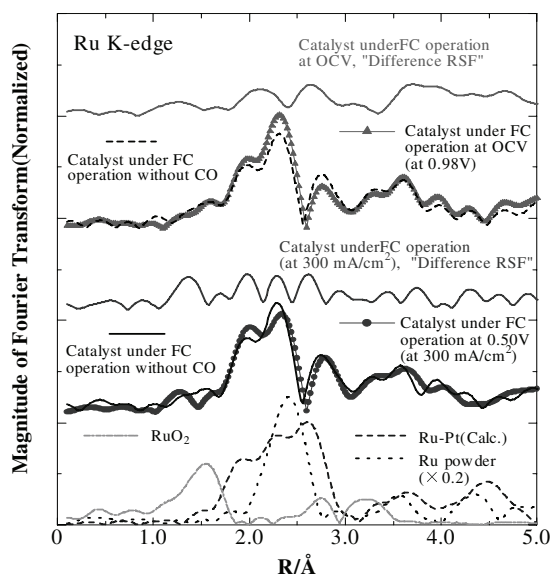


FIGURE 4. The radial structure functions of k^3 -weighted Ru K-EXAFS for the anode electrocatalyst under different operation voltages using 97 ppm CO containing H_2 and their “difference” ones as to “without CO”.

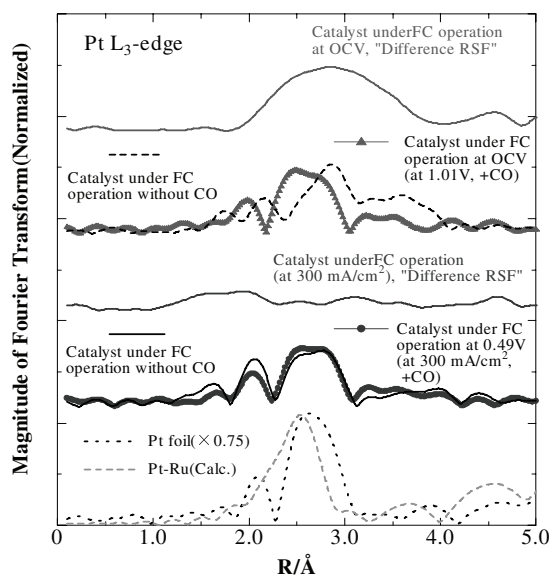


FIGURE 5. The radial structure functions of k^3 -weighted Pt L_3 -EXAFS for the anode electrocatalyst under different operation using 97 ppm CO containing H_2 and their “difference” ones as to “without CO”.

However, a prominent difference peak is also found in the Ru-light atom (O or C) region for the RSF around the Ru atoms in the catalyst under fuel cell operation at 300 mAcm^{-2} . A large broad difference peak is observed in the Pt-metal (Pt or Ru) region for the RSF around the Pt atoms in the anode catalyst under OCV (*ca.* 1V) in Figure 5. In contrast, only a broad difference peak is slightly found in Pt-light atom (O or C) regions for the RSF around the Pt atoms in the catalyst under fuel cell operation at 300 mAcm^{-2} .

The results suggest that local structure of PtRu clusters may rearrange in CO containing H_2 , especially around the Pt atom under OCV. Although the cluster structure would be reconstructed under fuel cell operation at 300 mAcm^{-2} , additional ‘absorbates’ might be on the Ru atoms.

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