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全反射蛍光 XAFS による白金モデル触媒表面上への高分子バインダー分子の吸着解析
Binder Polymers Adsorbed on Surface of Pt Model Catalyst Analyzed by Total Reflection Fluorescence XAFS

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The structure and the chemical state of a 100-nm Nafion thin film cast on a Pt substrate were examined by in-situ XAFS of Pt. The information of the interfacial properties were combined with the layered structures obtained by neutron reflectometry.

Key Word： polymer electrolyte fuel cell, binder, Pt model catalyst, total reflection fluorescence XAFS

１．Background and Aim of Research

The structures of polymer electrolyte membranes and catalyst layer binders and the distribution of water therein are important for designing new ion-conductive ionomers for polymer electrolyte fuel cells. To aid the understanding of the in-plane water distribution, we carried out neutron reflectometry (NR) in J-PARC on a Nafion® film with a thickness of 150 nm formed on a 20-nm Pt layer deposited on Si(100) with a native SiO_2 layer. In this study, ambient pressure X-ray absorption spectroscopy at room temperature in air was carried out.

２．Experimental

On an Si(100) substrate (2 inch diameter, 1 mm thick) with a native SiO_2 layer, Pt was deposited with a thickness of approximately 20 nm. An alcohol dispersion of 5 wt% Nafion was spin-coated onto the $Pt/SiO_2/Si(100)$ substrate and annealed at 80 ºC in air for 1 hour. The thickness of the Nafion film was approximately 150 nm. X-ray absorption spectroscopy (XAS) in the fluorescence mode was carried out on pristine Nafion/$Pt/SiO_2/Si(100)$ at the BL14B2 beamline of SPring-8 in air at RT. The glancing angle of the X-rays was set at 0.38 º to realize total reflection, and the fluorescence intensity from the sample was monitored at the front of the specimen in the perpendicular direction to the incident X-ray. The XAS information was obtained from the surface in the depth of approximately 2 nm. As reference samples, a Pt foil and PtO_2 powder were used for conducting XAS measurements in a transmission mode. The extended

X-ray absorption fine structure (EXAFS) data were analyzed by performing standard procedures using the Athena and Artemis programs in the IFEFFIT package. The k2-weighted χ(k) data ranging from 0.3 to 2.0 nm were Fourier-transformed into R-space spectra for fitting in Artemis.

３．Results

Figure 1(a) shows the Pt L3-near-edge regions (X-ray absorption near-edge structure, XANES) of pristine Nafion/Pt/SiO2/Si(100) (red line, fluorescence mode), Pt foil (black line, transmission mode), and PtO_2 powder (green line, transmission mode) obtained in air at RT. As has been reported, the heights of the white-lines of the XANES are directly connected with the oxidation state of Pt. From the XANES, the oxidation state of Pt in Nafion /Pt/SiO_2/Si(100) was found to be very similar to that of a Pt foil. Figure 1(b) shows the Fourier-transformed EXAFS spectra without a phase correction. The peak at ca. 0.27 nm for the Pt foil (black line) was assigned as Pt-Pt, whereas that at 0.17 nm for the PtO_2 powder (green line) was assigned as Pt-O. In the spectrum of Pt in Nafion/Pt/SiO_2/Si(100) (red line), no peak was seen for Pt-O. Therefore, the Pt of the pristine Nafion/Pt/SiO_2/Si(100) was metallic. The results have been published elsewhere [1].

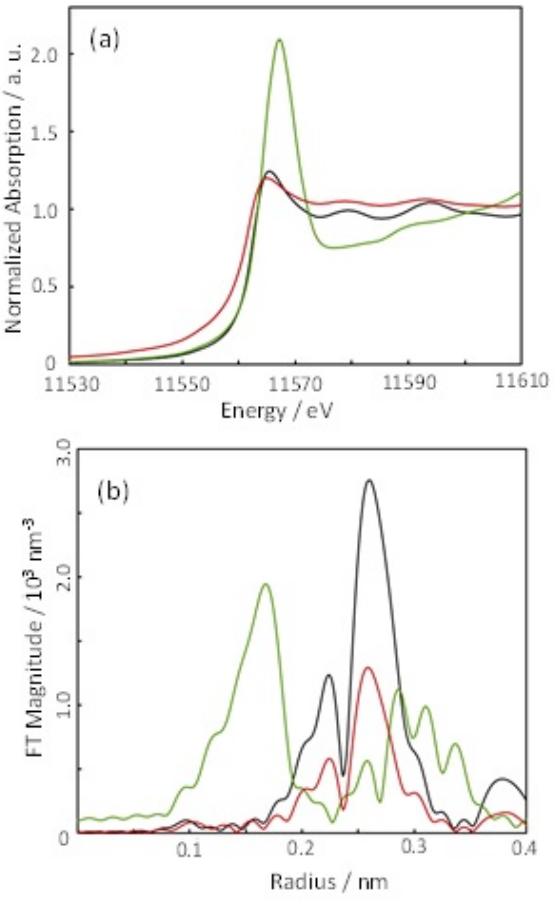

Fig. 1 Pt L3-edge XANES (a) and Fourier-transformed EXAFS (b) spectra for Pt foil (black line, transmission mode), PtO_2 powder (green line, transmission mode), and Nafion/Pt/SiO_2/Si(100) (red line, fluorescence mode) collected at room temperature in air.

４．Future Plans

In-situ measurements of total reflection fluorescence XAFS in solution under electrochemical conditions are now in progress.

Publication

[1] "Sublayered Structures of Hydrated Nafion® Thin Film Formed by Casting on Pt Substrate Analyzed by X-ray Absorption Spectroscopy under Ambient Conditions and Neutron Reflectometry at Temperature of 80°C and Relative Humidity of 30–80%", T. Kawamoto, M. Aoki, T. Kimura, P. Chinapang, T. Mizusawa, N. L. Yamada, F. Nemoto, T. Watanabe, H. Tanida, M. Matsumoto, H. Imai, J. Miyaka, K. Miyatake, J. Inukai, *Electrochemistry*, **87**, 270 (2019).