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%
with a thickness less than 10 nm composed of alternating water-rich and Nafion-rich layers was proposed at the interface between the SiO₂ surface and the Nafion film. Kalisvaart et al. described the water uptake and swelling in a very thin (≈15 nm) Nafion film on SiO₂ at nearly water-saturated conditions at different temperatures from 25 to 60°C. They observed large swelling strain and water content in a Nafion film at 60°C. DeCaluwe et al. reported the effect of film thickness on water uptake using Nafion films ranging from 5 to 153 nm on SiO₂ on Si. At thicknesses of 103 and 120 nm, an additional layer between the gas/Nafion interface was proposed. We have carried out NR measurements on a 130-nm thick Nafion film prepared on native SiO₂ on Si(100) using an environment-controlled chamber at 80°C and 30, 50, 65, and 80% RH, simulating the conditions for power generation, and the in-plane water distributions in the 4 sublayers of a Nafion film were determined. At the Nafion/SiO₂ interface, a water-rich layer approximately 1.3 nm in thickness existed, regardless of the humidity. On the water-rich layer, an intermediate layer with the thickness of 2 to 3 nm was found. The thickness of the bulk layer increased monotonically from 120 to 140 nm as the humidity increased from 30 to 80% RH. The gas/Nafion interface was proposed to have a hydrophobic conformation, the thickness of which did not change by increasing the humidity. Our structural and distributional data on Nafion/SiO₂ are summarized in Fig. S1 in Supporting Information.

On Pt substrates, the structure of Nafion films has also been investigated to understand the interfaces between Nafion binders and Pt catalysts in PEFCs. Murthi et al. studied the nanometer scale compositions of Nafion and water inside spin-coated Nafion films on a Pt thin film on an Si substrate at RT and humidities up to 97% RH. A thin, partially hydrated single interfacial layer was reported, and the thickness decreased to a few tenths of a nm as the humidity approached zero. Wood et al. used Pt-on-glassy carbon substrates. A hydrophobic Nafion region was reported adjacent to the Pt film, in contrast to the earlier report by Murthi et al. When Nafion was in contact with a Pt oxide surface, the Nafion film at the Pt oxide interface became hydrophilic. A long-range restructuring of the perfluorosulfonic acid polymer chains of Nafion in the film was induced by the Pt oxide layer. Recently, Harada et al. reported the compositions of Nafion and water inside a Nafion film designed to be 20 nm thick on a Pt thin film on an Si substrate using H₂O and D₂O (deuterium oxide) at RT. Even at 80% RH, a condensed layer of Nafion molecules existed with a small amount of water on the Pt substrate. The thickness of the segregated Nafion layer was approximately 3 nm, which was consistent with the diameter of the rod-like micelles of Nafion molecules in solution.

NR investigations of Nafion thin films on Pt surfaces have been mainly conducted at RT. However, PEFCs used for residential and automotive power sources are generally operated at temperatures above 70°C and at various RHs. In this study, Nafion with a thickness of approximately 150 nm on a vapor-deposited Pt layer on Si(100) was used as a model film for the NR measurements. The temperature and humidities were 80°C and 30–80% RH, respectively. A large influence of the Pt substrate was observed, not only on the interface but also on the entire Nafion film. A larger amount of water was incorporated at the Nafion/Pt interface at 80°C than at RT, most likely because of the oxidation of the Pt surface.

2. Experimental and Analytical Methods

On an Si(100) substrate (2 inch diameter, 1 mm thick) with a native SiO₂ layer, Pt was deposited with a thickness of approximately 20 nm (FUJIFILM Wako Pure Chemical Corp.). An alcohol dispersion of 5 wt% Nafion (D-521, Du Pont) was spin-coated onto the Pt/SiO₂/Si(100) substrate and annealed at 80°C 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/SiO₂/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° 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 PtO₂ 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 2³-weighted χ² data ranging from 0.3 to 2.0 nm were Fourier-transformed into R-space spectra for fitting in Artemis. The NR measurements were carried out with an environment-controlled chamber made of Al for controlling the temperature and humidity of ultrapure N₂ (99.999%) humidified with ultrapure water (H₂O, 18.3 MΩ) continuously supplied into the chamber (Fig. S2 in Supporting Information). NR measurements were performed at the BL16 beamline of the Materials and Life Science Facility (MLF), Japan Proton Accelerator Research Complex (J-PARC). The NR experiments were performed at 80°C and 30, 50 and 80% RH in that order. The Nafion thin film on Pt/SiO₂/Si(100) was maintained at each condition for 1 hour prior to each NR measurement. An area of 30 mm × 40 mm was illuminated with pulsed neutrons with wavelengths of 0.20–0.88 nm at a repetition rate of 25 Hz. The neutrons were introduced with varying incident angles of 0.3, 0.6, 1.2, and 2.4°. The exposure time of the neutron beam was approximately 40 minutes to complete each NR measurement. The reflection intensity at each angle was normalized by that of the direct beam, and the reflectivity profile depending on the momentum transfer normal to the substrate, Qₓ, was obtained.

The analyses of the NR profiles were carried out using the MOTOFIT program. For the values of the scattering length density (SLD) of Nafion, Si, SiO₂, and Pt at 80°C, the values at RT were employed in the calculations without correcting for thermal expansion: 4.16 × 10⁻⁴, 2.07 × 10⁻⁴, 3.47 × 10⁻⁴, and 6.35 × 10⁻⁴ nm⁻², respectively. For the SLD of water at 80°C, −0.54 × 10⁻⁴ nm⁻² was used. To calculate the Nafion and water densities at each sublayer, the combined SLD value at each Nafion layer containing water was treated as a linear combination of the SLDs of dry Nafion and water. For the density of solid Nafion at 80°C, the density at RT or 1.98 cm⁻³ was employed without correcting for thermal expansion. For the density of liquid water at 80°C, 0.97 g cm⁻³ was used.

3. Results and Discussion

Figure 1(a) shows the PL₃-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 PtO₂ 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/SiO₂/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 PtO₂ powder (green line) was assigned as Pt-O. In the spectrum of Pt in Nafion/Pt/SiO₂/Si(100) (red line), no peak was seen for Pt-O. Therefore, the Pt of the pristine Nafion/Pt/SiO₂/Si(100) was metallic.

Figure 2 shows the NR profiles of substrate and Nafion. The symbols show the NR data, whereas the solid lines show the best-fit curves. Prior to the NR measurements on Nafion, we investigated the structures of a native SiO₂ layer and a Pt layer on Si(100) at RT.
under dry N₂ (Fig. 2(I)). The thickness and roughness (explained in Supporting Information) of the SiO₂ layer were obtained as 2.3 and 0.5 nm, respectively, and those of the Pt layer were obtained as 21.7 and 0.7 nm, respectively. These values were used to analyze all of the subsequent data of the Nafilm on Pt/SiO₂/Si(100). In the NR profiles in Fig. 2(II–IV) at 80°C under N₂ humidified by H₂O, larger oscillations are seen to be overlapped with very small oscillations. The larger oscillations were easily explained by the existence of a Pt layer (Fig. 2(I)), whereas the small oscillations contained the information from Nafilm and water. For the Nafilm, a 3-sublayered structural model was applied, based on a hypothesized Nafilm/substrate interface, Nafilm bulk layer, and Nafilm/gas interface. With more layers, the U² values did not decrease very much, showing that the Nafilm can essentially be described with 3 sublayers. Table 1 provides the fitting-curve parameters from the NR data at different RHs: layer thickness, SLD, and surface/interface roughness defined at the neutron-irradiation side of each sublayer (see Supporting Information). The deviations

| Humidity | Layer          | Thickness /nm | Error /nm | SLD /10⁻⁴nm⁻² | Error /10⁻⁴nm⁻² | Roughness /nm | Error /nm |
|----------|----------------|---------------|-----------|---------------|-----------------|---------------|-----------|
| SiO₂     | Topmost layer  | 4.5           | 0.1       | 4.13          | 0.05            | 0.5           | 0.1       |
|          | Bulk layer     | 147           | 0.3       | 3.71          | 0.03            | 0.1           | 0.2       |
|          | Pt-attached layer | 0.5         | 0.3       | 1.43          | 0.23            | 0.0           | 0.5       |
| 30% RH   | Topmost layer  | 4.5           | 0.2       | 4.21          | 0.07            | 0.8           | 0.5       |
|          | Bulk layer     | 150           | 0.4       | 3.53          | 0.05            | 0.5           | 0.4       |
|          | Pt-attached layer | 1.0         | 0.1       | 1.80          | 0.11             | 0.2           | 0.2       |
| 50% RH   | Topmost layer  | 5.3           | 7.4       | 3.10          | 0.10             | 0.9           | 0.1       |
|          | Bulk layer     | 158           | 7.5       | 3.40          | 0.07             | 4.6           | 2.5       |
|          | Pt-attached layer | 0.8         | 0.0       | 1.22          | 0.15             | 0.1           | 0.1       |
| 80% RH   | Topmost layer  | 5.3           | 7.4       | 3.10          | 0.10             | 0.9           | 0.1       |
|          | Bulk layer     | 158           | 7.5       | 3.40          | 0.07             | 4.6           | 2.5       |
|          | Pt-attached layer | 0.8         | 0.0       | 1.22          | 0.15             | 0.1           | 0.1       |
The water density was approximately 0.55 g cm\(^{-3}\) at 80°C, therefore, Pt in Nafton/Pt/SiO\(_2\)/Si(100) is expected to be slightly oxidized and hydrophilic, in contrast to the Pt of the samples investigated at RT.\(^{37,46}\) The standard electrode potential of the PtO/Pt couple, +0.980 V vs. the standard hydrogen electrode at pH 0, explains the oxidation of the Pt surface at 80°C under humidified conditions. Further XAS measurements at high temperature and different humidities are needed. In the case of Nafton/SiO\(_2\)/Si(100) (Fig. S1), the water density at the “water-rich layer” on the hydrophilic SiO\(_2\) layer increased from 0.72 g cm\(^{-3}\) at 30% RH to 0.97 g cm\(^{-3}\) at 80% RH, evidence for the large hydrophilicity of the sublayer.\(^{47}\)

A large portion of the Nafton film was occupied by the “bulk layer” (Fig. 3). The thickness of the bulk layer increased monotonically from 147 to 150 and 158 nm as the humidity increased from 30 to 50 and 80% RH, respectively. The water density slightly increased from 0.09 g cm\(^{-3}\) at 30% RH to 0.16 g cm\(^{-3}\) at 80% RH. In the case of the bulk layer on SiO\(_2\) (Fig. S1), the water density increased from 0.14 to 0.24 g cm\(^{-3}\) as the humidity increased from 30 to 80% RH.\(^{47}\) Therefore, the water swelling at the bulk layer was larger on SiO\(_2\) than on Pt by 50%; the difference in substrate had an influence not only on the interfacial layer between the substrate and Nafton but also on the bulk.

At the “topmost layer” under humidified N\(_2\), the water density was essentially 0 g cm\(^{-3}\) at 30 and 50% RH but jumped to 0.22 g cm\(^{-3}\) at 80% RH, while the layer thickness was approximately 5 nm. In the case of the topmost layer on SiO\(_2\) (Fig. S1), the water density gradually increased from 0.09, 0.14, 0.16 to 0.20 g cm\(^{-3}\) as the humidity increased from 30, 50, 65 to 80% RH.\(^{47}\) Therefore, the hydrophobicity of the topmost layer was very large in the case of Nafton on Pt at lower RH (30% and 50% RH). At 50% RH, the roughnesses of the topmost layer, bulk layer, and Pt-attached layer were 0.8, 0.5, 0.2 nm, respectively, whereas, at 80% RH, they became 0.9, 4.6, and 0.1 nm, respectively. The sudden increase of the roughness occurred only at the bulk layer. A large conformational change of Nafton molecules at the interface does not seem probable, because the hydrophobic framework is stable, with a glass-transition temperature of 130°C. Therefore, the large roughness (4.6 nm) might originate mainly from the inclined, continuously-changing water density at the interface of the topmost layer/bulk layer; the water distribution might still exist in a transition state. This large roughness at the interface was not observed on Nafton/SiO\(_2\)/Si(100), where the water swelling should be reasonably fast.\(^{47}\) At 80% RH, the hydrophobic topmost layer (at lower RH, as shown in Fig. 3) started to accept water vapor more easily, and the water density at the topmost layer on Pt (0.22 g cm\(^{-3}\)) became nearly the same as that on SiO\(_2\) (0.20 g cm\(^{-3}\)). This change of water density at 80% RH might be related to changes in the structure and properties at the gas/surface interfaces of electrolyte membranes, which have been investigated by use of current-sensing atomic force microscopy.\(^{39}\)

The water uptake, calculated from the thicknesses and densities of the sublayers of the Nafton films (Figs. 3 and S1) obtained by NR, on Pt (open circles) and on SiO\(_2\) (open triangles) are shown in Fig. 4 as a function of RH. The total thicknesses of the Nafton films on Pt (filled circles, 152 nm at 30% RH) and SiO\(_2\) (filled triangles, 131 nm at 30% RH) are also shown. The water uptake and film thickness increased rather linearly with respect to the increase in RH at these thin films. The increasing ratio of water uptake was 0.10 and 0.17 (%water uptake/%RH) for Nafton films on Pt and SiO\(_2\), respectively, whereas those of total thickness were 0.25 and 0.44 (nm/%RH) on Pt and SiO\(_2\), respectively. This increase in thickness can be directly explained by the water swelling. The 3-dimensional as errors are also listed. The errors were very small, with the only exceptions being those of the topmost layer and bulk layer at 80% RH (discussed later), showing the validity of our 3-sublayered models. Models of the Nafton thin films based on the data in Table I are illustrated in Fig. 3.

The total thicknesses of the Nafton film at 80°C were 152, 155 and 164 nm at 30, 50 and 80% RH, respectively (Fig. 3). A “Pt-attached layer” existed on the Pt film with a layer thickness less than 1 nm. The water density was approximately 0.55 g cm\(^{-3}\) regardless of the humidity at the Pt-attached layer, indicating the rigidity of this layer. Harada et al. reported structural data on a Nafton film with a thickness of approximately 20 nm on platinum at RT at 80% RH.\(^{46}\)

As in our case, 3 sublayers were reported to fit the NR curves satisfactorily. From the data of Harada et al.,\(^{46}\) the water density in a 3-nm sublayer on Pt was calculated as ca. 0.10 g cm\(^{-3}\), so that their sublayer on Pt was very hydrophobic, in contrast to ours (Fig. 3). In our case, at 80°C, therefore, Pt in Nafton/Pt/SiO\(_2\)/Si(100) is expected to be slightly oxidized and hydrophilic, in contrast to the Pt of the samples investigated at RT.\(^{37,46}\) The standard electrode potential of the PtO/Pt couple, +0.980 V vs. the standard hydrogen electrode at pH 0, explains the oxidation of the Pt surface at 80°C under humidified conditions. Further XAS measurements at high temperature and different humidities are needed. In the case of Nafton/SiO\(_2\)/Si(100) (Fig. S1), the water density at the “water-rich layer” on the hydrophilic SiO\(_2\) layer increased from 0.72 g cm\(^{-3}\) at 30% RH to 0.97 g cm\(^{-3}\) at 80% RH, evidence for the large hydrophilicity of the sublayer.\(^{47}\)

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Figure 3. Models for humidified Nafton thin films on Pt/SiO\(_2\)/Si(100). (a): 30% RH, (b): 50% RH, (c): 80% RH.
The thickness of the bulk layer increased monotonically from 147 to 158 nm as the humidity increased from 30 to 80% RH. At 30% and 50% RH, the topmost layer showed a large hydropobicity with almost no water content, but at 80% RH, the water content became as large as that obtained in a Naﬁon ﬁlm on SiO2. At 80% RH, the water density at the interface between the topmost layer and the bulk layer was suggested to be not discontinuous but inclined, owing to the transient distribution of water at the interface. The inﬂuence of the substrates was observed not only at the substrate/Naﬁon interfaces but also in the entire ﬁlms, because of the difference in polymer conformation formed during casting. XAS experiments are needed at elevated temperature and humidity. NR experiments are also needed for longer periods of time in order to further understand the transitional and stable states of Naﬁon.

Systematic XAS and NR analyses should help to elucidate the interactions between the ﬁlm and substrate, which could be useful for further synthesis of polymer electrolytes. NR measurements of synthesized membranes are now in progress.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.19-00042.

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4. Conclusions

XAS of Pt was carried out on pristine Naﬁon/Pt/SiO2/Si(100) at BL14B2 of SPring-8 in air at RT to show that the Pt was metallic. Subsequently, NR measurements on the same sample obtained by use of an environment-controlled chamber were conducted at 80°C and at 30, 50, and 80% RH at BL16 of MLF, J-PARC. The in-plane water distribution was determined inside a 150-nm thick Naﬁon ﬁlm prepared on Pt on SiO2/Si(100) based on a 3-sublayered model. At the Pt-attached layer, the thickness was less than 1 nm and was nearly constant, and the densities of Naﬁon and water did not change. Water existed at higher densities at 80°C than at RT, probably because of the partial oxidation of the Pt substrate at 80°C. The water distribution was determined inside a 150-nm thick Naﬁon and at 30, 50, and 80% RH, the topmost layer showed a large hydropobicity with almost no water content, but at 80% RH, the water content became as large as that obtained in a Naﬁon ﬁlm on SiO2. At 80% RH, the water density at the interface between the topmost layer and the bulk layer was suggested to be not discontinuous but inclined, owing to the transient distribution of water at the interface. The inﬂuence of the substrates was observed not only at the substrate/Naﬁon interfaces but also in the entire ﬁlms, because of the difference in polymer conformation formed during casting. XAS experiments are needed at elevated temperature and humidity. NR experiments are also needed for longer periods of time in order to further understand the transitional and stable states of Naﬁon.

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