Ionomer Films for Fuel Cells Cast on Different Substrates Analyzed by In-Situ Neutron Reflectometry under Controlled Temperature and Humidity

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Three-dimensional structures of polymer electrolyte membranes and binders, as well as the concentrations of water in the electrolytes, under controlled temperature and humidity are important for designing ionomers for fuel cells. Neutron reflectometry (NR) is known as a powerful technique to investigate layered structures. The distributions of water inside thin Nafion films cast on SiO_2, Pt, and C substrates, models for glass plate, Pt catalyst, and C support, respectively, were studied by NR under controlled temperature and humidity [1,2]. Nafion films were prepared by spin-coating an alcohol dispersion of Nafion on native-SiO_2/Si(100), Pt/SiO_2/Si(100), and C/SiO_2/Si(100) with a thickness of approximately 100 nm. The sample was placed in a home-made environment-controlled chamber (Fig. 1) [1], continuously purged with an N_2 gas set at 80 °C humidified with H_2O at a relative humidity (RH) between 30% and 80%. NR measurements were carried out at the beamline BL16 of J-PARC, Japan. Clear modulations were obtained on Nafion films on all substrates.

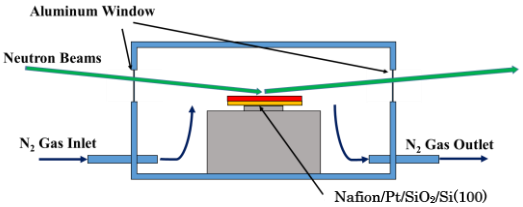

Figure 1. Illustration of environment-controlled chamber.

Figure 2 shows 4-sublayered structural models of Nafion on SiO_2 at 30%, 50%, 65%, and 80% RH, representing the thicknesses and the Nafion/water densities of each sublayer [1]. The topmost layer had a hydrophobic conformation at the interface between Nafion and humidified N_2 and its thickness did not change by increasing the humidity. The thickness of bulk layer monotonically increased from 120 to 140 nm as the humidity increased from 30 to 80% RH. At the intermediate layer, the film thickness slightly increased from 2.3 to 3.0 nm. The water density in the intermediate layer was two times higher than that in the bulk layer. The thickness of Water-rich layer was ca. 1.3 nm regardless of the humidity, while the water density greatly increased up to 0.97 g cm^{-3} at 80% RH. The sublayered structures of Nafion differed on three different substrates of SiO_2, Pt, and C; a large influence of substrates was observed not only on the substrate/Nafion interfaces but on the entire structures of Nafion films. The ionomer structures in fuel cells are modeled and discussed based on the NR data.

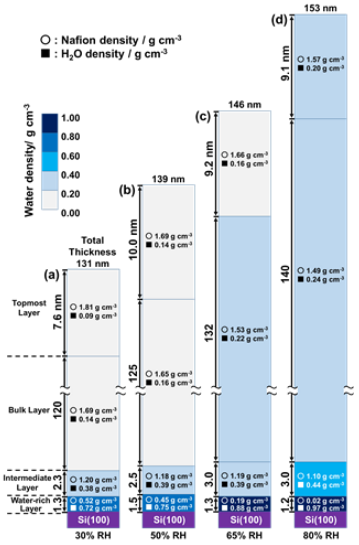

Figure 2. Thicknesses and water densities of 4 sublayers of Nafion on SiO_2/Si(100) at 30% (a), 50% (b), 65% (c), and 80% RH (d).

References

[1] T. Kawamoto, M. Aoki, T. Kimura, T. Mizusawa, N. L. Yamada, J. Miyake, K. Miyatake, and J. Inukai, *Jpn. J. Appl. Phys.*, **58**, (2019), doi: 10.7567/1347-4065/ab0c7c..

[2] T. Kawamoto, M. Aoki, T. Kimura, P. Chinapang, T. Mizusawa, N. L. Yamana, F. Nemoto, T. Watanabe, H. Tanida, M. Matsumoto, H. Imai, J. Miyake, K. Miyatake, and J. Inukai, *Electrochemistry*, accepted.