Neutron-reflectance measurements under controlled temperature and humidities on new hydrocarbon-type fuel-cell membranes formed on Si, SiO_2, Pt, and C substrates

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1. Introduction

Perfluorosulfonic acid ionomers, such as Nafion, have been practically used for the proton exchange membranes and the binders in polymer electrolyte fuel cells, because of their high proton conductivity and chemical/mechanical stability. Although the characteristic 3-dimensional network-structures of the hydrated water molecules in polymer electrolyte are known to be important for obtaining high ion-conductivity inside membranes and binders for fuel cells, the structures of the networks are little understood. Neutron reflectivity is reflected by the nanometer-scale structures of thin films.[1)] Analyzing the previous data obtained by the neutron-reflectivity experiments performed under the proposals 2016A0246 and 2016B0036, we modeled the 1-dimensional distributions of water absorbed in Nafion thin films at different relative humidities on Si(100).[2)] At the film/substrate interface, a water-rich layer was found, which changed at different humidities. In order to reduce cost and increase environmental friendliness, hydrocarbon-type membranes with no fluorine are actively synthesized and studied. Under this proposal, the reflectivity was measured at different temperatures and humidities using H_2O and D_2O on newly-synthesized hydrocarbon-type membranes with an extremely high chemical stability.[3)]

2. Experimental

Figure 1 shows the chemical formula of an SPP electrolyte.[3)] SPP thin films 100 nm in thickness were formed on flat Si(100), Pt/Si(100), C/Si(100), and SiO_2 substrates. The environment-controlled sample chamber was made of aluminum. Neutron reflectivity measurements were carried out at 80 ˚C under N_2 gas at 30% and 80% RH humidified with H_2O or D_2O. The neutron irradiation area was 40 mm x 30 mm. Incident angle was 0.3-3.5 degree.

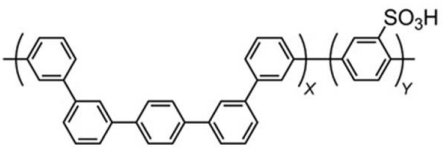

Fig. 1 Chemical structure of SPP.

3. Results

Neutron reflectivity curves are shown in Fig. 2, vertically offset for clarity. The oscillations from the reference substrates are in black, whereas those from the SPP-coated substrates at 30% and 80% RH in red and blue, respectively. For an SPP thin film on a Si substrate, the oscillations were hardly observed because of the similar densities of SPP and Si. On Pt/Si and C/Si substrates, clear oscillations from the interference between the thin layer of Pt or C and Si substrate were observed. Oscillations smaller in amplitude were considered to be originated from the thin SPP film on the substrate. When H_2O was used instead of H_2O for the humidification, those smaller oscillations became more distinct reflecting the absorbed water. However, in the high Q region for SPP/C/Si at 80% RH with H_2O (Fig. 3(e)), the oscillations were not clear, probably due to the influence of an extremely large amount of water absorbed in the membrane.

Detailed analyses of the data are now in progress to understand the differences between Nafion and SPP.

3. Results

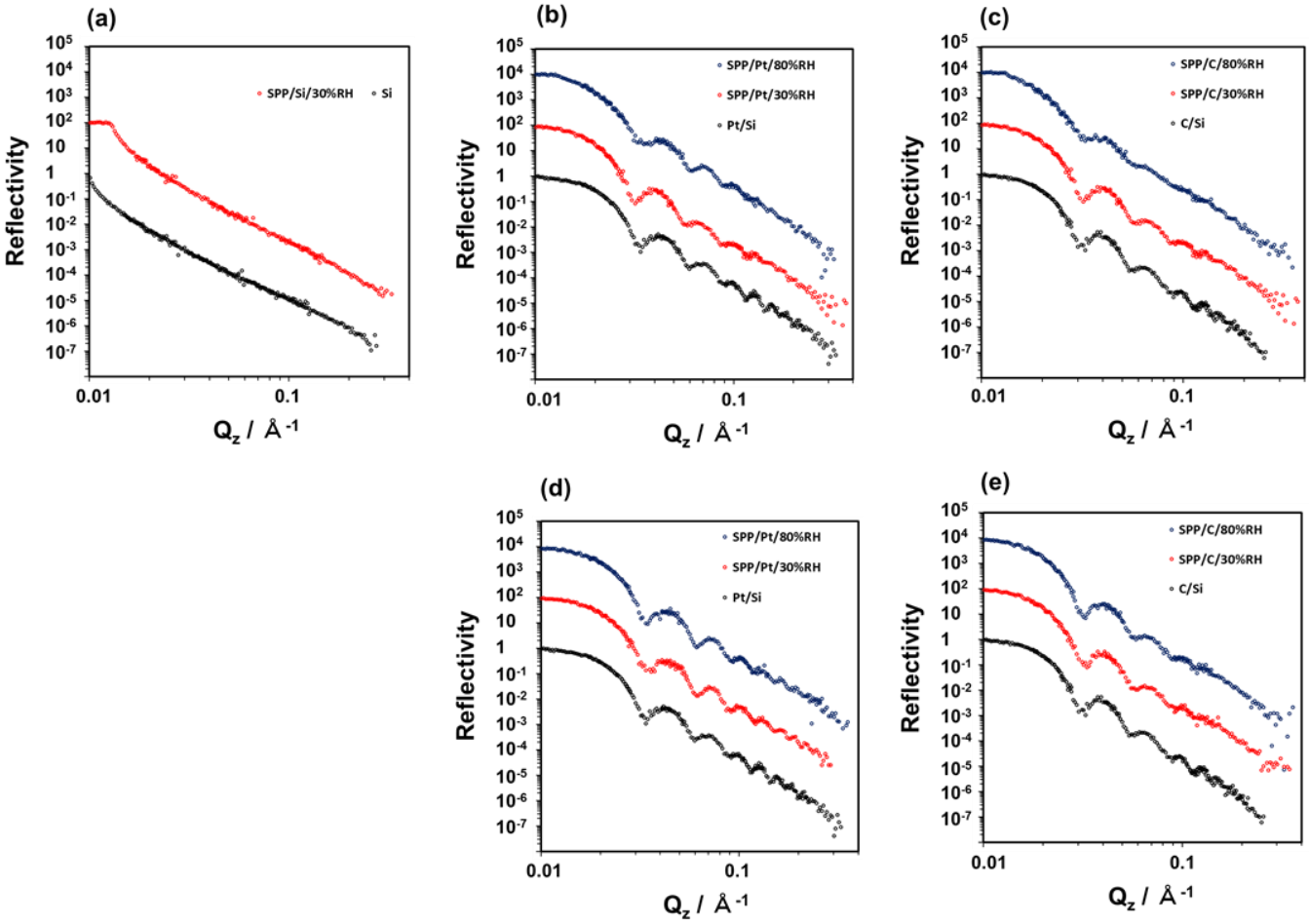

Fig. 2 Neutron reflectivity on SPP under N_2+D_2O on Si (a), Pt/Si (b) and C/Si, and under N_2+H_2O on Pt/Si (d) and C/Si (e). All reflectivity curves on the reference substrates of Si, Pt/Si, and C/Si are shown in black. The reflectivity curves with SPP thin films at 30 and 80% RH are shown in red and blue, respectively.

4. Conclusion

Neutron reflectivity on SPP films with a thickness of 100 nm at different substrates at different relative humidities was successfully measured under nitrogen humidified with either H_2O or D_2O. The neutron reflectivity data are being analyzed by curve fitting to understand the 1-dimensional densities of SPP and water at different humidities.

Reference

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2) T. Kawamoto, M. Aoki, T. Kimura, T. Mizusawa, N. L. Yamada, J. Inukai, Poster ID s2-010, 22nd Topical Meeting of the International Society of Electrochemistry, Tokyo, Japan, April 15-18.
3) J. Miyake, R. Taki, T. Mochizuki, R. Shimizu, R. Akiyama, M. Uchida, K. Miyatake, Science Advances, 3(10), DOI: 10.1126/sciadv.aao0476.