# Neutron-reflectance measurements under controlled temperatures and humidities on filmes of ionomer used for fuel cells formed on Si, platinum, and carbon substrates

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## 1. Introduction

Perfluorosulfonic acid ionomers, such as Nafion, are used as proton exchange membranes for polymer electrolyte fuel cells, because of their high proton conductivity and chemical/mechanical stability. The structures of polymer electrolyte membranes and binders, as well as the concentration of water molecules in the electrolyte, are important for designing ion-conductive membranes and binders. Under the proposal #2016A0246, we investigated the distributions of water in 100-nm thick Nafion thin films formed on Si(100) at different relative humidities by neutron reflectivity.[1)] Under this proposal (#2016B0034), we investigated a newly synthesized ionomer, SPK,[2)] as well as Nafion, on Si(100), C/Si(100), and Pt/Si(100) substrates. The carbon and platinum substrates are used for models of fuel cell catalysts. Not only $H_2O$ but also $D_2O$ was used for the elucidation of the effects of water absorbed in the electrolyte films. The data on a humidified Nafion film on Si(100) were analyzed as explained in Results.

## 2. Experimental

Figure 1 shows the chemical formula of an SPK ionomer.[2)] Nafion and SPK thin films 100 nm in thickness were formed on atomically-flat Si(100), Pt/Si(100), C/Si(100) substrates. The environment-controlled chamber was made of aluminum. Neutron reflectivity measurements were carried out at 80 ˚C under $N_2$ gas humidified with $H_2O$ or $D_2O$ at 30%, 50%, 65%, and 80% RH. The neutron irradiation area was 40 mm x 30 mm. The incident angle was 0.3-3.5 ˚.

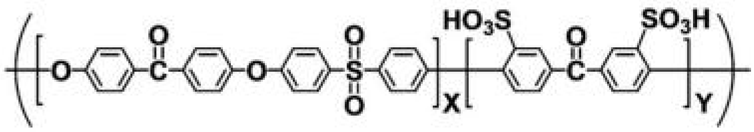


Fig. 1 Chemical structure of SPK.

## 3. Results

Neutron reflectivity curves of Nafion and SPK on different substrates are shown in Fig. 2, vertically offset for clarity. The oscillations from the reference substrates are shown in black, whereas those from the electrolyte-coated substrates at 30% and 80% RH in red and blue, respectively. On Pt/Si(100) and C/Si(100) substrates, clear oscillations were observed, originated from the interference between the 10-nm layers of Pt or C and Si(100). Oscillations smaller in amplitude were considered to be originated from the thin electrolyte films on the substrates. The characteristic bumps observed in Fig. 2(c) at 80% RH on Nafion/Pt/Si can be explained by the existence of a layer with a different scattering length density from that of Nafion. In a high Q region in Fig. 2(d) on Nafion/C/Si, the oscillations were not clearly observed, probably due to the influence of a large amount of water absorbed in the membrane. The reflectivity data of SPK films were also successfully obtained on Si, Pt/Si, and C/Si substrates (Fig. 2). The SPK data are now in the process of analysis

The reflectivity data on Nafion films were fit based on the four-layer model on Pt/Si(100). The thickness of each layer and the water uptake was analyzed for the first time (Fig. 3). The analysis of the other reflectivity data including those on SPK is now in progress.

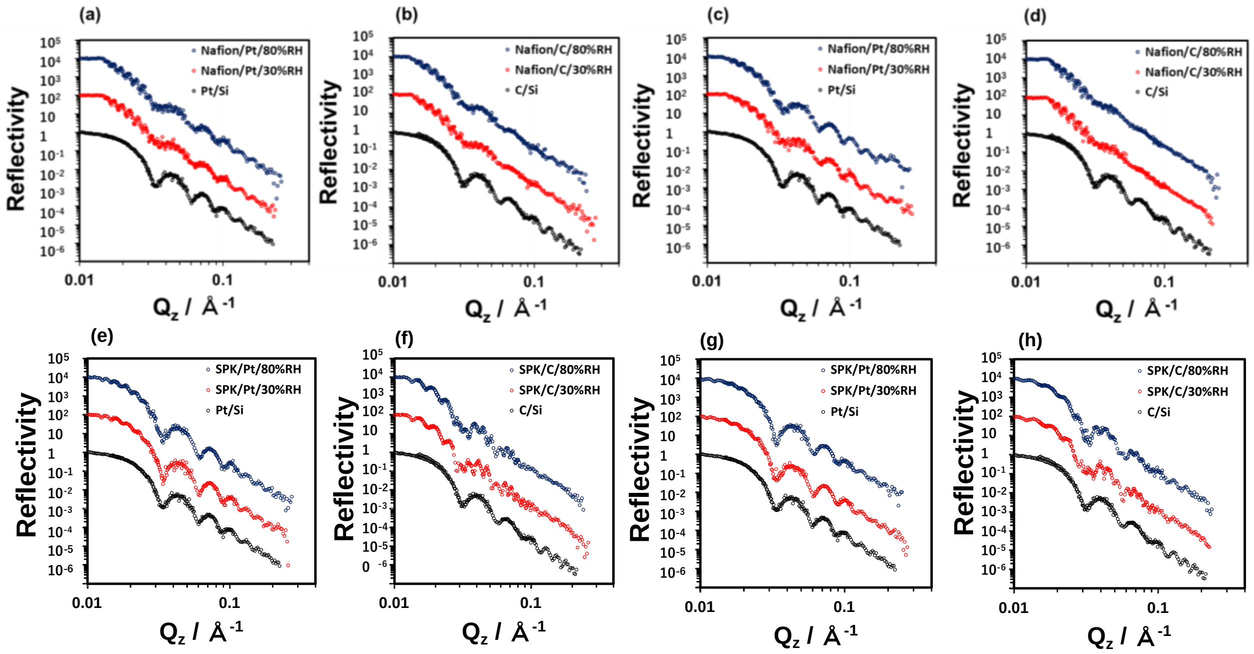


Fig. 2 Neutron reflectivity of Nafion under $N_2$+$D_2O$ on Pt/Si (a) and C/Si (b), and under $N_2$+$H_2O$ on Pt/Si (c) and C/Si (d), and that of SPK under $N_2$+$D_2O$ on Pt/Si (e) and C/Si (f), and under $N_2$+$H_2O$ on Pt/Si (g) and C/Si (h). Reflectivity curves on the reference substrates of Si,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

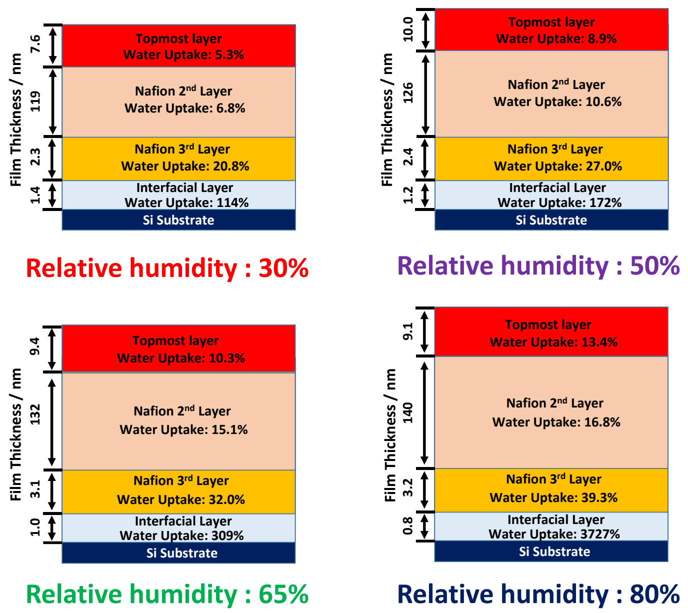


Fig. 3 Four-layer models of a Nafion film on Si(100) at 80 ˚C under $N_2$ gas humidified with $H_2O$ at 30%, 50%, 65%, and 80% RH. The thickness of each layer in nanometer and the water uptake in percentage are shown. At Nafion/Si interfaces, water layers were found.

## 4. Conclusion

Neutron reflectivity on Nafion and SPK thin films formed on Si, Pt/Si, C/Si at different relative humidities was successfully measured. The Nafion/Si(100) data were analyzed by using curve fitting method. The analysis of the other data is now in progress.

## References

1) Y. Ogata, D. Kawaguchi, N. L. Yamada, and K. Tanaka, *ACS Macro Lett.*, **2**, 856-859 (2013).

2) T. Miyahara, T.Hayano, S. Matsuno, M. Watanabe, K. Miyatake, *ACS Appl. Mater. Interfaces*, **4**, 2881 (2012).