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Author(s)	Nagao, Yuki
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Proton Transport Property of Nafion Thin Films on MgO(100) with Anisotropic Molecular Structure*

Yuki Nagao†
Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa Oiwake-cho, Kyoto 606-8502, Japan
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To investigate the proton transport properties of the Nafion thin films on MgO(100) substrates, impedance measurements of the 60 and 400 nm thick thin films were carried out. The proton conductivity of two thin films were quite lower values compared to that of the commercial Nafion membrane, and the thickness dependence of the proton conductivity was also observed. To investigate in-plane and out-of-plane molecular vibrations in an identical 400 nm thick film of Nafion on the MgO(100) substrate, an infrared p-polarized multiple-angle incidence resolution spectrometry (p-MAIRS) technique was carried out. The in-plane spectrum showed well-known spectrum, however, the out-of-plane spectrum was quite different compared to the in-plane spectrum. The largely different shapes of the spectra clearly indicate that the 400 nm thick film of Nafion has an anisotropic molecular structure.
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Keywords: Nafion; Thin film; Proton conductivity; MAIRS; Anisotropic molecular structure

I. INTRODUCTION

The polymer electrolyte membrane fuel cells are one of the ideal power sources for portable electronic devices with high power-to-weight ratios and fast start-up performance. Nafion is an ionomer produced by Du Pont Co., and it is the most widely studied polymer electrolyte membrane because it exhibits high conductivity, good mechanical stability, and is commercially available. The chemical structure of Nafion consists of a perfluorocarbon backbone and side chains terminated with sulfonic acid groups.

Nafion is also used as a solution state with various solvents for preparing membrane-electrode assembly. Catalytic reactions mainly occur at triple phase boundary, which consist of the catalyst, proton conducting electrolyte, and gaseous reactant. Proton-conductive ionomers such as Nafion solution are used to fabricate suitable triple phase boundary. A liquid electrolyte can be one of the useful ionomers not only to fabricate the membrane but also to work as binder to form triple phase boundary because of their excellent properties of proton conductivity and penetration to the catalytic layer in the electrode.

Ma *et al.* reported the heavy conductivity anisotropy of the ratio of the proton conductivity between the in plane and thickness direction to the Nafion membrane by hot-pressing at a temperature of 150°C with different pressures [1]. They found that ion domains flattened along the in-plane direction and ordered along the thickness direction from the results of small angle X-ray scattering measurements. Recently, anomalous proton conductivity through the synthesis of thin films of proton-conductive oligomeric amides and polypeptide has been reported [2–5]. These proton conductivities are dependent on the thickness of the thin film, and the maximum proton conductivity of the thin film exhibits a value 10 times higher than that of the pelletized sample. Siroma *et al.* reported that the conductivity decreased with a decrease in the thickness of recast Nafion film on flat substrate [6, 7]. In this paper, impedance measurements and an infrared p-polarized multiple-angle incidence resolution spectrometry (p-MAIRS) technique were carried out to investigate the proton transport properties of the Nafion thin films on MgO(100) substrates. Infrared p-MAIRS can provide the in-plane (IP) and out-of-plane (OP) molecular vibration data simultaneously from an identical infrared transparent substrate. Conventional ATR methods need the substrates with the high refractive index, however, p-MAIRS technique does not need them. The same substrate can be used to measure the proton transport property and IR spectra. These results can be applied to the further developing much more powerful polymer electrolyte membrane fuel cells.

II. EXPERIMENTAL

The thin films of Nafion were prepared by using an Active ACT-200 Spincoater on MgO(100) substrates. To improve the hydrophilicity on the surface of the substrate before the spincoat, a plasma treatment was performed by using a FEMTO SCIENCE CUTE-MP vacuum plasma system. Nafion solution was obtained from Wako Pure Chemical Industries. The obtained thin films on the MgO substrates were dried in desiccator over 12 hours, then those thicknesses were measured by using a Dektak 8 Surface Profiler. The thicknesses of two thin films were 60 (5%Nafion solution) and 400 nm (5% Nafion solution: ethanol: water = 2: 3: 3), respectively.

To investigate the proton transport properties of the thin films on MgO substrates, impedance measurements

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†Corresponding author: ynagao@jaist.ac.jp; Present address: School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

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of the thin films were carried out in the relative humidity (RH) range of 40-90% with a Solartron 1260 Impedance/Gain-Phase analyzer and a 1296 Dielectric Interface system. The RH and temperature were controlled with an Espec Corp. SH-221 humidity- and temperature-controlled chamber. In the impedance measurements of the thin films, the electrode configuration was selected to obtain measurements of the current flow in the plane parallel to the substrate surface. The electrode by using Au paste is located at the edge of the thin film, and electrode configuration is parallel. The distance between electrodes is ∼3 mm. The porous Au electrode is also covered at the side of the thin film. The conductivity of the MgO(100) substrate is negligible because its resistance is quite higher than that of the thin film. The Nafion 117 was used as a reference for the bulk proton conductivity.

To investigate in-plane and out-of-plane molecular vibrations in an identical 400 nm thick film of Nafion on the MgO(100) substrate, an infrared p-polarized multiple-angle incidence resolution spectrometry (p-MAIRS) technique, which had been developed by Hasegawa [8–11], was carried out. Infrared MAIRS and p-MAIRS are being recognized as powerful spectroscopic tools for revealing molecular orientation in thin films. The p-MAIRS measurements were performed on a Thermo-Fisher Scientific Nicolet 6700 FT-IR spectrometer equipped with a mercury-cadmium-telluride (MCT) detector. Single-beam spectra were collected from 38° through 8° by 6° steps in the range of the angle of incidence. The aperture was fully opened (size of 150), a metal plate with small pores was placed in the light path of the incidental beam to prevent saturation. The MgO(100) substrate was purchased from Neotron (Tokyo, Japan), and the size of the substrate was 15 × 15 × 0.5 mm. The p-MAIRS analysis of the collected spectra was automatically performed by p-MAIRS analyzer software (Thermo Fisher Scientific).

III. RESULTS AND DISCUSSION

Figure 1 shows the RH dependence of the proton conductivity of two thin films and bulk membrane of Nafion. Each thin film and bulk membrane of the proton conductivity depended on the RH, but the proton conductivity of two thin films were quite lower values compared to that of the commercial bulk Nafion membrane. And the thickness dependence of the proton conductivity was observed. The proton conductivity of the 60 nm thick film was lower than that of 400 nm thick film. This tendency of the decrease of the proton conductivity with decreasing the thickness had been reported by other research groups [6, 7, 12–14]. Siroma *et al.* reported that the proton conductivity of recast Nafion thin films on quartz plates decreased with a decrease in the thickness of the film. Kongkanand investigated the water content in Nafion thin films by supporting them on a quartz-crystal microbalance (QCM) [15]. The results of his work suggested that the depression in proton conductivity observed in thin ionomer layers in earlier studies is not predominantly a result of reduced water content. The origin was still unknown, but it was supposed that this phenomenon was due to an intrinsic change of the structure.

Figure 2 shows the incident angle dependence of the transmission IR spectra. The CF_2 stretching vibration bands ($\nu_{as}(CF_2)$ at 1155, 1210, and 1235 cm^{-1}) and C-C stretching vibration band (ν(C-C) at 1300 cm^1) were observed. The absorbance around 1260 cm^1 increased with the angle of incidence.

To discuss the details of the molecular orientation, p-MAIR spectra after the collection of single-beam spectra measured from 38° through 8° by 6° steps were shown in Fig. 3. Nafion membrane consists of a perfluorocarbon backbone and side chains terminated with sulfonic acid groups. The in-plane spectrum showed well-known spectrum of Nafion membrane [16], however, the out-of-plane spectrum was quite different compared to the in-plane spectrum. The characteristic absorption band at 1260 cm^{-1} was observed in the out-of-plane spectrum. This absorption has not been assigned yet. The largely

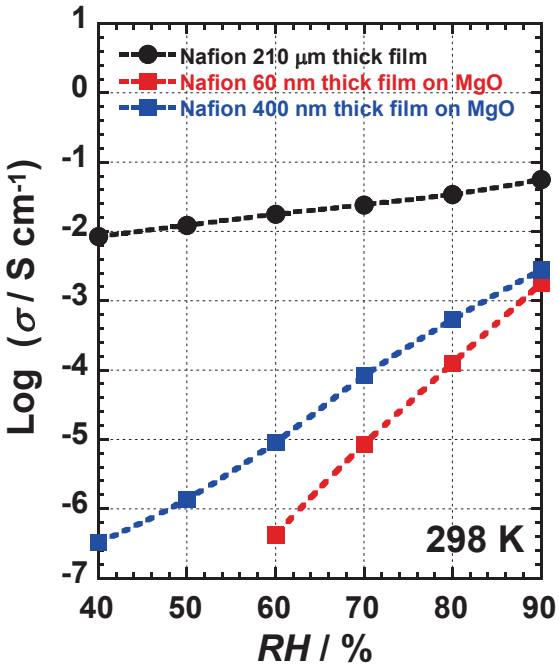

FIG. 1: Relative humidity (RH) dependence of the proton conductivity for 60 and 400 nm thick films on MgO(100) substrates and bulk membrane of Nafion.

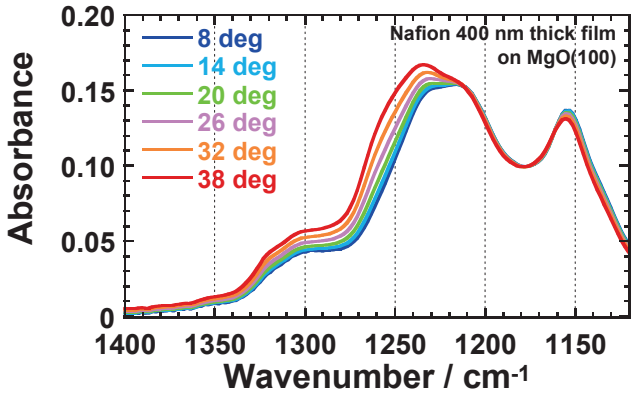

FIG. 2: Incident angle dependence of the transmission IR spectra.

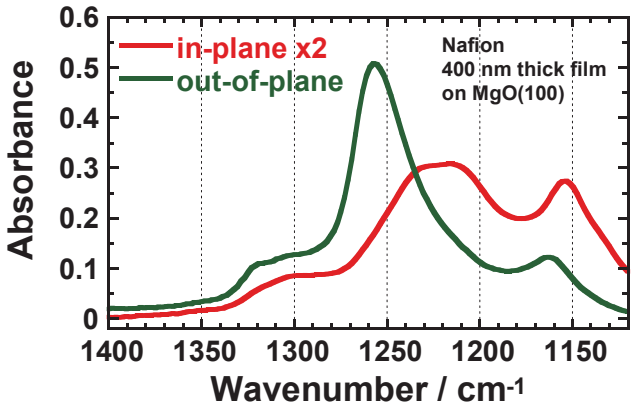

FIG. 3: Infrared p-MAIR spectra after the collection of single-beam spectra measured from 38° through 8° by 6° steps.

different shapes of the spectra clearly indicate that the 400 nm thick film of Nafion has an anisotropic molecular structure. The nanostructure of commercial Nafion membranes at different states of hydration by IR and Raman spectroscopy has been investigated by Gruger *et al* [16]. They observed the absorption bands due to the SO_3^- stretching vibration bands ($\nu_s(SO_3^-)$ at 1058 and $\nu_{as}(SO_3^-)$ at 1130 and 1204 cm^{-1}). The CF_2 stretching vibration bands ($\nu_{as}(CF_2)$ at 1204 cm^{-1}) were overlapped on the SO_3^- stretching vibration band. This absorption band was observed in the in-plane spectrum of this work. In the out-of-plane spectrum, the absorption band at 1260 cm^{-1} might be due to the vibration of the SO_3^- groups at the end of the side chains. Many investigation of IR spectra were carried out in the commercial Nafion films with several hundred or ten micrometer order thickness, however, the absorption bands at 1260 cm^{-1} has not been reported. These results suggested that the 400 nm thick Nafion film on MgO substrate had quite different structure compared to the commercial Nafion membranes. The crystal structure of Nafion thin film was known as amorphous [17]. The p-MAIRS is powerful technique to investigate the information of the structure, even if the sample was amorphous. Moore and Martin discovered that the morphologies, physical properties, and chemical characteristics of the solution-cast Nafion films were not identical characteristics of those of the as-received membranes [17]. Considering the result of p-MAIR spectra, the 400 nm thick thin film of Nafion has the anisotropic molecular structure. It is supposed that the origin for the lower proton conductivity in the 60 and 400 nm thick Nafion films is due to the anisotropic molecular structure.

IV. CONCLUSIONS

The proton conductivity of the 60 and 400 nm thick thin films of Nafion on MgO(100) substrates were quite lower values compared to that of the commercial Nafion membrane. Thickness dependence of the proton conductivity was also observed. The author tried to use an infrared p-polarized multiple-angle incidence resolution spectrometry (p-MAIRS) technique to the thin film, and found that the 400 nm thick film of Nafion on MgO(100) has an anisotropic molecular structure. It is supposed that the origin for the lower proton conductivity in the 60 and 400 nm thick Nafion films is due to the anisotropic molecular structure.

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[1] S. Ma, Z. Siroma, and H. Tanaka, J. Electrochem. Soc. **153**, A2274 (2006).
[2] Y. Nagao, M. Ando, H. Maekawa, C. H. Chang, F. Iguchi, and N. Sata, ECS Transactions **16**, 401 (2008).
[3] Y. Nagao, N. Naito, F. Iguchi, N. Sata, and H. Yugami, e-J. Surf. Sci. Nanotech. **7**, 530 (2009).
[4] Y. Nagao, N. Naito, F. Iguchi, N. Sata, and H. Yugami, Solid State Ionics **180**, 589 (2009).
[5] Y. Nagao, F. Iguchi, N. Sata, and H. Yugami, Solid State Ionics **181**, 206 (2010).
[6] Z. Siroma, T. Ioroi, N. Fujiwara, and K. Yasuda, Electrochem. Commun. **4**, 143 (2002).
[7] Z. Siroma, R. Kakitsubo, N. Fujiwara, T. Ioroi, S. Yamazaki, and K. Yasuda, J. Power Sources **189**, 994 (2009).
[8] T. Hasegawa, J. Phys. Chem. B **106**, 4112 (2002).
[9] T. Hasegawa, L. Matsumoto, S. Kitamura, S. Amino, S. Katada, and J. Nishijo, Anal. Chem. **74**, 6049 (2002).
[10] T. Hasegawa, Anal. Chem. **79**, 4385 (2007).
[11] T. Hasegawa, Y. Itoh, and A. Kasuya, Anal. Sci. **24**, 105 (2008).
[12] F. N. Büchi and G. G. Scherer, J. Electrochem. Soc. **148**, A183 (2001).
[13] S. Slade, S. A. Campbell, T. R. Ralph, and F. C. Walsh, J. Electrochem. Soc. **149**, A1556 (2002).
[14] M. N. Tsampas, A. Pikos, S. Brosda, A. Katsaounis, and C. G. Vayenas, Electrochim. Acta **51**, 2743 (2006).
[15] A. Kongkanand, J. Phys. Chem. C **115**, 11318 (2011).
[16] A. Gruger, A. Régis, T. Schmatko, and P. Colomban, Vib. Spectrosc. **26**, 215 (2001).
[17] K. A. Mauritz and R. B. Moore, Chem. Rev. **104**, 4535 (2004).