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Author(s)	Nagao, Yuki
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Description	

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Highly Oriented Sulfonic Acid Groups in a Nafion Thin Film on Si Substrate

*Yuki Nagao**

School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292 Japan

Keywords: Proton conductivity, Multiple-angle incidence resolution spectrometry, Interface, Molecular oriented structure, Substrate

Abstract

Solid state ionics is a research field attracting much current attentions because of the ideal power sources for use with portable electronic devices having high power-to-weight ratios. One of the most urgent subjects in this field is to understand proton transport properties at the interface between inorganic materials and polymer electrolyte from the viewpoint of developing much more powerful energy. In this study, a 150-nm-thick Nafion thin film was prepared by spincoating on a silicon (Si) substrate to investigate the proton transport property at the interface. The infrared (IR) p-polarized multiple-angle incidence resolution spectrometry (p-MAIRS) technique was applied to investigate the in-plane (IP) and out-of-plane (OP) spectra to the surface. The IP spectrum showed a well-known spectrum, but the OP spectrum was quite different from the IP spectrum. An anomalous IR peak was observed in the OP spectrum at 1260

cm^{-1}. From density functional theory (DFT) calculations, this peak was attributed to the $–SO_3H$ vibration modes between two sulfonic acid groups with hydrogen bonds. These results demonstrate that the Nafion thin film on Si substrate had a highly oriented structure with the sulfonic acid groups at the side chain. Impedance measurements of Nafion thin film were conducted to investigate the proton transport property of the Nafion thin film on SiO_2 substrate. The proton conductivity of the thin film exhibited a lower value than that of the commercial Nafion membrane. The low proton conductivity of the Nafion thin film was related with these highly oriented structures.

1. Introduction

Polymer electrolyte membrane fuel cells such as direct methanol fuel cells (DMFCs) are ideal power sources for portable electronic devices having high power-to-weight ratios. The energy density of DMFC increases along with the methanol concentration. An issue hindering development of these fuel cells is methanol crossover through an electrolyte membrane, which decreases cell voltage. This crossover phenomenon mainly occurs by the expansion of electrolyte membrane because of water or methanol absorption.[1] To solve this crossover problem, Munakata and Kanamura *et al.* sought to use the concept of three-dimensionally ordered macroporous (3DOM) silica composite membrane including polymer electrolytes.[2-6] The methanol permeability of their composite membranes was reduced and the proton conductivity was improved.

To obtain effective and high-power energy sources of the fuel cell, understanding the interface between a proton conductive material and another material is necessary. Many results have been reported from studies using the interface between inorganic materials and proton conductive

polymers.[7-9] Some reports described that the proton transport properties were improved by adding fillers, which presents advantages for the suppression of swelling and shrinking of the proton conductive membrane surrounded by water and methanol. The origin was inferred as related to their structural modification. Using the interface between the polymer thin films and inorganic substrates, anomalous proton transport properties were also reported.[10,11] However, the mechanism and structural information at the interface are insufficiently revealed.

Nafion, a commercially available ionomer produced by Du Pont, is the most widely studied polymer electrolyte membrane because it exhibits high conductivity and good mechanical stability.[12-14] The Nafion chemical structure consists of a perfluorocarbon backbone and side chains terminated with sulfonic acid groups as shown in Figure 1. Nafion is also used as a solution state with various solvents for preparing membrane-electrode assembly. Catalytic reactions occur mainly at the triple phase boundary, which consists of the catalyst, proton conducting electrolyte, and gaseous reactant. Proton-conductive ionomers such as Nafion solution are used to fabricate suitable triple phase boundaries. A liquid electrolyte can be a useful ionomer not only to fabricate the membrane but also to function as binder to form a triple phase boundary because of their excellent properties of proton conductivity and penetration to the catalytic layer in the electrode.

In an earlier report, the proton conductivity of the Nafion thin film on the MgO(100) substrate was described as quite lower than that of the commercial Nafion membrane.[15] The infrared (IR) p-polarized multiple-angle incidence resolution spectrometry (p-MAIRS) technique developed by Hasegawa[16-19] revealed that the Nafion thin film had a highly oriented molecular structure. However, the attribution was not fully analyzed at that time. As described herein, an IR p-MAIRS technique and impedance measurements were conducted to investigate the proton

transport property of the Nafion thin film on a Silicon (Si) substrate. Infrared p-MAIRS is increasingly regarded as a powerful spectroscopic tool for revealing molecular orientation in thin films. The p-MAIRS analysis showed that in-plane (IP) and out-of-plane (OP) transition dipoles are distinguishable in an identical infrared transparent substrate. These results are applicable to further development of much more powerful polymer electrolyte membrane fuel cells.

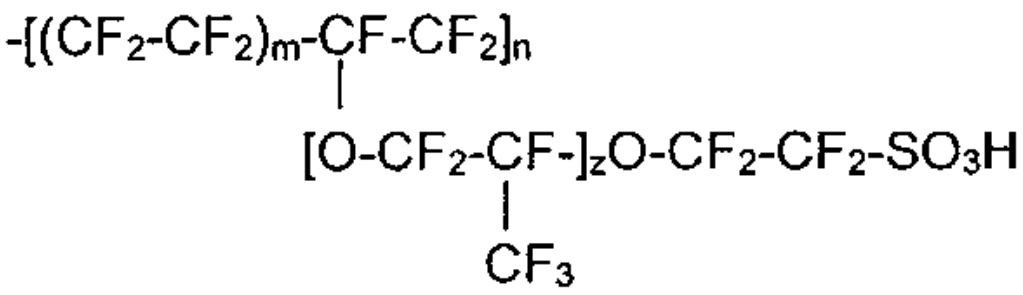

Fig. 1 Nafion structure.

2. Experimental

The Nafion thin film was prepared using an Active ACT-200 Spincoater on a high-resistivity and mirror-polished Si substrate. To improve the hydrophilicity on the surface of the substrate before spincoat, plasma treatment was performed using a vacuum plasma system (Cute-MP; Femto Science, Korea). Nafion solution was obtained from Wako Pure Chemical Industries Ltd. The obtained thin film on the Si substrate was dried in a desiccator for 12 hr. Then its thickness was measured using a surface profiler (Dektak 8; Veeco Instruments). The thin film thickness was ca. 150 nm.

To investigate IP and OP molecular vibrations in an identical 150-nm-thick film of Nafion on the Si substrate, the infrared p-polarized multiple-angle incidence resolution spectrometry (p-MAIRS) technique was performed. The p-MAIRS measurements were taken using an FT-IR spectrometer (Nicolet 6700; Thermo-Fisher Scientific Inc.) equipped with a mercury-cadmium-

telluride (MCT) detector. Single-beam spectra were collected from 38° through 8° by 6° steps between the angle of incidence. The optical configuration is shown in Figure 2. 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 p-MAIRS analysis of the collected spectra was conducted automatically using p-MAIRS analyzer software (Thermo Fisher Scientific Inc.).

Density functional theory (DFT) calculations were performed using the DMol3 package in Materials Studio v6.0.0 (Accelrys Software Inc.). The Perdew–Burke–Ernzerhof (PBE) function was chosen. The convergence threshold for the maximum force and maximum displacement for normal geometry optimization were set respectively to 0.004 Ha $Å^{-1}$ and 0.005 Å.

To investigate the proton transport properties of the thin film on SiO_2 substrate, impedance measurements of the thin films were conducted in the relative humidity (RH) range of 40‑90% with an Impedance/gain-phase analyzer (Solartron 1260; Solartron Analytical) and a dielectric interface system (1296; Solartron Analytical). The RH and temperature were controlled with a humidity-controlled and temperature-controlled chamber (SH-221; Espec Corp). 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 using Au paste is located at the edge of the thin film. The electrode configuration is parallel. The distance between electrodes is ca. 3 mm. The porous Au electrode is also covered at the side of the thin film. The conductivity of the SiO_2 substrate is negligible because its resistance is much higher than that of the thin film.

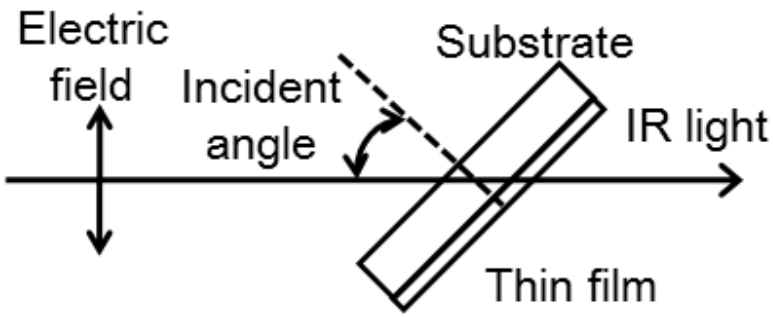

Fig. 2. Configuration of the polarized incident beam path and incident angle.

3. Results and discussions

Figure 3 shows the incident angle dependence of the transmission IR spectra. The shape of the spectra depends strongly on the incident angle. The absorbance around 1260 cm^{-1} increased with the angle of incidence. This result suggests that the thin film had a highly oriented structure. For a low incident angle, the peak was not observed around 1260 cm^{-1}. Therefore no IP transition dipole moment exists around that wavenumber. However, the peak gradually appeared with the incident angle, meaning that OP transition dipole moments were excited by polarized light.

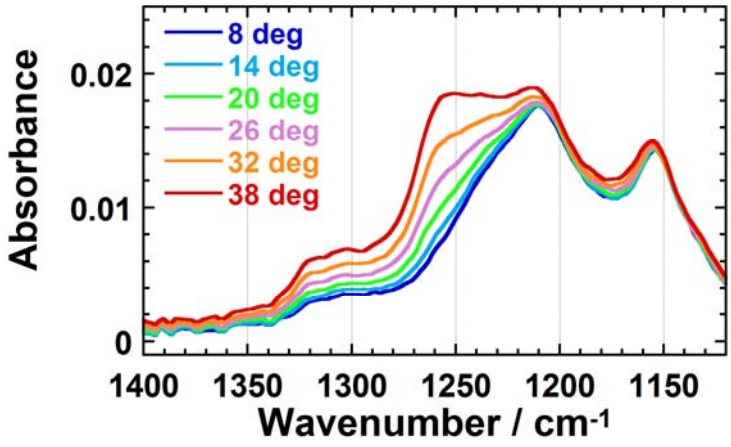

Fig. 3. Incident angle dependence of the transmission IR spectra.

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 are shown in Figure 4. A Nafion membrane consists of a perfluorocarbon backbone and side chains terminated with sulfonic acid groups. The IP spectrum shows the well-known spectrum of Nafion membrane.[20] However, the OP spectrum was quite different from the IP spectrum. The greatly differing shapes of the spectra indicate clearly that the 150-nm-thick film of Nafion has an anisotropic molecular arrangement. The nanostructure of commercial Nafion membranes at different states of hydration by IR and Raman spectroscopy was investigated by Gruger *et al.*[20] The CF_2 stretching vibration bands ($\nu(CF_2)$ at 1155, 1210, and 1235 cm^{-1}) and C–C stretching vibration band (ν(C–C) at 1300 cm^{-1}) were observed in the IP spectrum. The CF_2 stretching vibration bands ($\nu(CF_2)$ at 1210 cm^{-1}) were overlapped on the SO_3^- stretching vibration band. The characteristic absorption band at 1260 cm^{-1} was observed in the OP spectrum. Many investigations of IR spectra were conducted using commercial Nafion films with several hundred or ten micrometer order thickness. However, no absorption band at 1260 cm^{-1} has been reported.[20-25] Since this band is also recognized in Figure 3, the band at 1260 cm^{-1} is not an artifact. A similar result, obtained using p-MAIRS method, was described in an earlier report of a study using a MgO(100) substrate.[15] The peak at 1260 cm^{-1} had not been attributed at that time. A possible reason was inferred: the MgO surface was modified by the reaction with Nafion because of the strong acidity and sulfonic acid magnesium salt was created in the interface. Then Mg^{2+} ion may migrate to the film. However, that presumption is contradicted by the present result obtained using Si substrate because Si substrate does not include any metal ions.

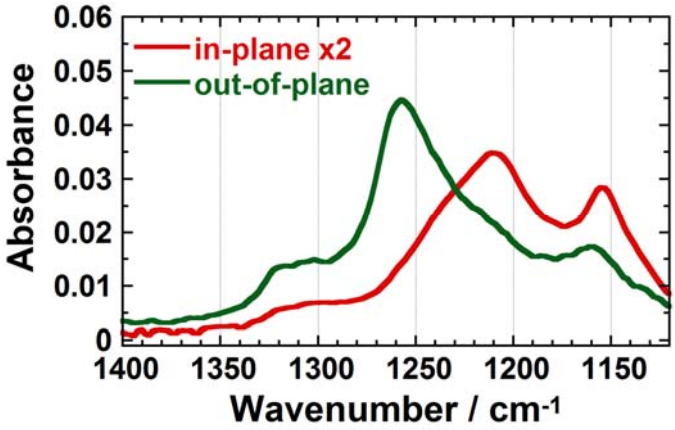

Fig. 4. Infrared p-MAIR spectra after the collection of single-beam spectra measured from 38° through 8° by 6° steps.

Another explanation for the anomalous peak at 1260 cm^{-1} is the coupling vibrational modes via hydrogen bonds between two or more sulfonic acid groups. To analyze the vibration modes around 1260 cm^{-1}, a DFT calculation was conducted. Three molecular structures were produced as Nafion-like models, as shown in Figure 5. The geometry of their molecular structure was optimized and vibrational analysis was applied. The result shows that the structures of Figures 5(a) and 5(b) did not exhibit any vibration mode around 1260 cm^{-1}. However, the dimer structure of Figure 5(c) exhibited some vibration modes around 1260 cm^{-1}. Every mode of 1238, 1249, 1271, and 1276 cm^{-1} resulted from the OH vibrational mode of the sulfonic acid groups interacted with another sulfonic acid groups via hydrogen bonds. These modes did not appear in the monomer structure shown in Figures 5(a) and 5(b). Since MAIRS spectra reveals both IP and OP spectra from an identical sample, all the transition moments with any directions appear in the spectra. Therefore these results suggest that the sulfonic acid groups are strongly coupled rather than separated. Considering the result of p-MAIR spectra in this study, the 150-nm-thick thin

film of Nafion had a highly oriented structure, which was built by hydrogen bonds of sulfonic acid groups at the side chain.

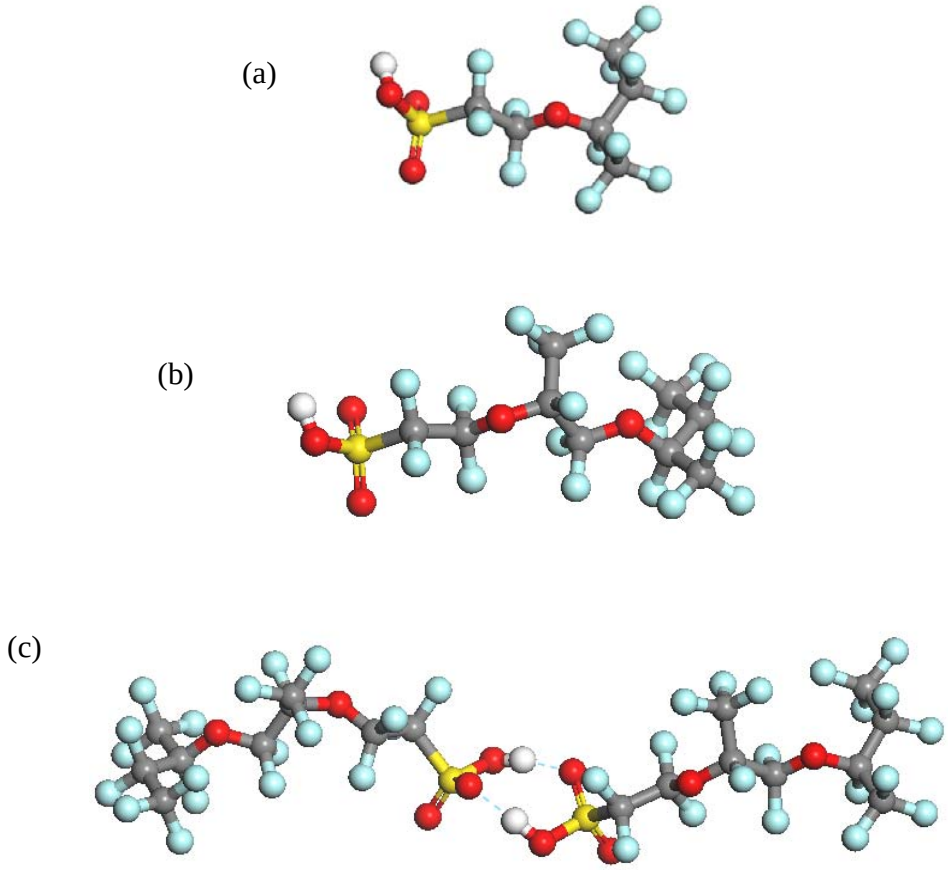

Fig. 5. Nafion-like models for DFT calculation: C, gray; F, light blue; H, white; O, red; S, yellow. Light-blue dotted lines show hydrogen bonds.

Impedance measurements were conducted to check the proton transport property of the thin film on Si substrate. The Si substrate is conductive compared to the Nafion thin film. Therefore, the electrical conductivities between the Si substrate and Nafion thin film were not separated. Normally, the surface of the Si substrate was oxidized and became SiO_2. Therefore, the proton conductivity was measured using the SiO_2 substrate. Figure 6 shows the RH dependence of the proton conductivity of the Nafion thin film. The thin film of the proton conductivity depended on

the RH. The proton conductivity of the thin film on SiO_2 substrate was 10^{-2} S cm^{-1} under RH of 90% and 298K. However, its proton conductivity was a lower value than that of the commercial bulk Nafion membrane. Presumably, the origin for the lower proton conductivity in the Nafion film results from the highly oriented structure with sulfonic acid groups.

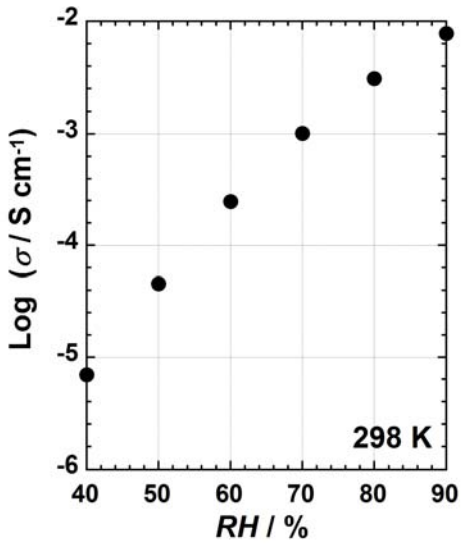

Fig. 6. Relative humidity dependence of proton conductivity for the Nafion thin film on SiO_2 substrate.

Proton transport properties at the interface between inorganic materials and polymer electrolyte have been investigated widely. Some reports described that the proton transport properties were improved by the filler-impregnated composite membranes,[6] and the origin was interpreted regarding their structural modification. The surface structure modified by the interface can contribute to these improvements of the proton transport properties. Tamura and Kawakami found that the composite bulk membrane containing uniaxially aligned sulfonated polyimide nanofibers exhibited a high proton conductivity.[26] This result shows a possibility for improving the proton transport property using the molecular orientation. For this Nafion thin film on the MgO substrate, it is presumed that the change of proton transport property is derived from

this highly oriented structure at the interface. The highly oriented sulfonic acid groups used in this study can contribute to a discussion about proton transport property at the interface.

4. Conclusions

A highly oriented structure in the Nafion thin film on Si substrate was revealed using the IR p-MAIRS technique. Based on DFT calculations, an anomalous IR peak at 1260 cm^{-1} was attributed to $–SO_3H$ vibration modes between two sulfonic acid groups with hydrogen bonds. The low proton conductivity of the Nafion thin film on SiO_2 substrate was related with highly oriented sulfonic acid groups. The results are expected to be useful for investigations of Nafion thin film at the interface.

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ASSOCIATED CONTENT

Supporting Information

The measurement of p-MAIRS. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*ynagao@jaist.ac.jp Phone: +81(Japan)-761-51-1541.

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REFERENCES

(1) Ren, X.; Springer, T. E.; Gottesfeld, S. *J.* Water and methanol uptakes in Nafion membranes and membrane effects on direct methanol cell performance. *Electrochem. Soc.* **2000**, *147*, 92-98.

(2) Munakata, H.; Ochiai, S.; Kanamura, K. Pore Size Effect on Improvement of Surface Proton Conductivity for Three-Dimensionally Ordered Macroporous Silica Composite Membrane. *J. Electrochem. Soc.* **2007**, *154*, B871-B875.

(3) Munakata, H.; Yamamoto, D.; Kanamura, K. Three-dimensionally ordered macroporous polyimide composite membrane with controlled pore size for direct methanol fuel cells. *J. Power Sources* **2008**, *178*, 596-602.

(4) Sasajima, K.; Munakata, H.; Kanamura, K. Properties of Composite Membrane Consisting of 3DOM Silica Matrix Filled with Sulfonated Poly(1,4-phenylene ether ether sulfone) at Various Ratios. *J. Electrochem. Soc.* **2008**, *155*, B143-B147.

(5) Yamamoto, D.; Munakata, H.; Kanamura, K. Synthesis and characterization of composite membrane with three-dimensionally ordered macroporous polyimide matrix for DMFC. *J. Electrochem. Soc.* **2008**, *155*, B303-B308.

(6) Munakata, H.; Sasajima, K.; Kanamura, K. 3DOM silica composite membrane including binary PAMPS-SPEES polymer electrolyte for DMFC. *Fuel Cells* **2009**, *9*, 226-230.

(7) Dimitrova, P.; Friedrich, K. A.; Vogt, B.; Stimming, U. Transport properties of ionomer composite membranes for direct methanol fuel cells. *J. Electroanal. Chem.* **2002**, *532*, 75-83.

(8) Nunes, S. P.; Ruffmann, B.; Rikowski, E.; Vetter, S.; Richau, K. Inorganic modification of proton conductive polymer membranes for direct methanol fuel cells. *J. Membr. Sci.* **2002**, *203*, 215-225.

(9) Ruffmann, B.; Silva, H.; Schulte, B.; Nunes, S. P. Organic/inorganic composite membranes for application in DMFC. *Solid State Ionics* **2003**, *162*, 269-275.

(10) Nagao, Y.; Naito, N.; Iguchi, F.; Sata, N.; Yugami, H. Synthesis of oligomeric poly (1, 2-propanediamine)-alt-(oxalic acid) and anomalous proton conductivities of the thin films. *Solid State Ionics* **2009**, *180*, 589-591.

(11) Nagao, Y.; Iguchi, F.; Sata, N.; Yugami, H. Synthesis and proton transport property of poly(aspartic acid) thin film on SiO(2) substrate. *Solid State Ionics* **2010**, *181*, 206-209.

(12) Hsu, W. Y.; Gierke, T. D. Ion transport and clustering in nafion perfluorinated membranes. *J. Membr. Sci.* **1983**, *13*, 307-326.

(13) Kreuer, K. D. On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. *J. Membr. Sci.* **2001**, *185*, 29-39.

(14) Mauritz, K. A.; Moore, R. B. State of understanding of Nafion. *Chem. Rev.* **2004**, *104*, 4535-4585.

(15) Nagao, Y. Proton Transport Property of Nafion Thin Films on MgO(100) with Anisotropic Molecular Structure. *e-Journal Surf. Sci. Nanotechnol.* **2012**, *10*, 114-116.

(16) Hasegawa, T. A novel measurement technique of pure out-of-plane vibrational modes in thin films on a nonmetallic material with no polarizer. *J. Phys. Chem. B* **2002**, *106*, 4112-4115.

(17) Hasegawa, T.; Matsumoto, L.; Kitamura, S.; Amino, S.; Katada, S.; Nishijo, J. Optimum condition of Fourier transform infrared multiple-angle incidence resolution spectrometry for surface analysis. *Anal. Chem.* **2002**, *74*, 6049-6054.

(18) Hasegawa, T. Advanced multiple-angle incidence resolution spectrometry for thin-layer analysis on a low-refractive-index substrate. *Anal. Chem.* **2007**, *79*, 4385-4389.

(19) Hasegawa, T.; Itoh, Y.; Kasuya, A. A., Experimental optimization of p-polarized MAIR spectrometry performed on a fourier transform infrared spectrometer. *Analytical Sciences* **2008**, *24*, 105-109.

(20) Gruger, A.; Regis, A.; Schmatko, T.; Colomban, P. Nanostructure of Nafion membranes at different states of hydration An IR and Raman study. *Vib. Spectrosc.* **2001**, *26*, 215-225.

(21) Falk, M. An infrared study of water in perfluorosulfonate (Nafion) membranes. *Can. J. Chem.* **1980**, *58*, 1495-1501.

(22) Kanamura, K.; Morikawa, H.; Umegaki, T. Observation of Interface Between Pt Electrode and Nafion Membrane. *J. Electrochem. Soc.* **2003**, *150*, A193-A198.

(23) Korzeniewski, C.; Adams, E.; Liu, D. Responses of hydrophobic and hydrophilic groups in Nafion differentiated by least squares modeling of infrared spectra recorded during thin film hydration. *Appl. Spectrosc.* **2008**, *62*, 634-639.

(24) Korzeniewski, C.; Snow, D. E.; Basnayake, R. Transmission infrared spectroscopy as a probe of Nafion film structure: analysis of spectral regions fundamental to understanding hydration effects. *Appl. Spectrosc.* **2006**, *60*, 599-604.

(25) Perusich, S. A. FTIR equivalent weight determination of perfluorosulfonate polymers. *J. Appl. Polym. Sci.* **2011**, *120*, 165-183.

(26) Tamura, T.; Kawakami, H. Aligned Electrospun Nanofiber Composite Membranes for Fuel Cell Electrolytes. *Nano Lett.* **2010,** *10*, 1324-1328.