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# Humidity-Dependent Structure of Surface Water on Perfluorosulfonated Ionomer Thin Film Studied by Sum Frequency Generation Spectroscopy

Hidenori Noguchi,<sup>†,§</sup> Kento Taneda,<sup>†</sup> Hiroshi Minowa,<sup>†</sup> Hideo Naohara,<sup>‡</sup> and Kohei Uosaki<sup>\*,†,§</sup>

Physical Chemistry Laboratory, Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan, Fuel Cell System Development Division, Toyota Motor Corporation, Susono, Shizuoka 410-1193, Japan, and International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan

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Humidity-dependent water structure on the Nafion thin film surface was determined at room temperature by using sum frequency generation spectroscopy (SFG). When the Nafion thin film was exposed to a low relative humidity (RH) environment, a peak at 3720 cm<sup>-1</sup> due to the “dangling OH” or “free OH” of water molecules and a peak centered around 3600 cm<sup>-1</sup>, which was assigned to be due to water molecules interacting with sulfonate groups of the Nafion surface, were observed. The intensities of these peaks increased as RH was increased. A broad peak centered around 3200–3300 cm<sup>-1</sup> due to water adsorbed on hydrophobic, i.e., fluorocarbon, sites of Nafion was observed when the Nafion thin film was exposed to a high RH environment (RH > 60%). The behavior of surface water is compared with that of water in bulk Nafion.

## 1. Introduction

A proton exchange membrane fuel cell (PEMFC), which electrochemically converts the chemical energy of a fuel, e.g., hydrogen, directly into electrical energy is one of the most promising energy conversion systems due to its high conversion efficiency, high power density, and benign environmental impact.<sup>1,2</sup> Considerable research efforts have been focused on the improvements of efficiency and stability of the PEMFC,<sup>1,2</sup> which require highly efficient and durable electrocatalyst/membrane/carbon support assembly. The most commonly used PEM is Nafion, a perfluorosulfonated ionomer, which contains a fluorocarbon backbone with a pendant side chain terminated with a sulfonate group.<sup>5,6</sup> The hydrophilic domain of Nafion, which is formed as a result of the presence of the sulfonate group, facilitates the uptake and transport of water and proton.<sup>7–9</sup> Water management is one of the most critical issues in the PEMFC operation,<sup>3,4</sup> since the performance of a PEMFC is strongly dependent on the proton conductivity of the membrane, which is in turn strongly dependent not only on temperature<sup>10</sup> but also on the water content within the membrane.<sup>8,9</sup> Thus, understanding the hydration behavior of a Nafion membrane is a subject not only of chemical interest but also of great importance for the development of PEMFC.

Although many studies on water structure in the Nafion membrane have been carried out by using a wide variety of techniques such as IR,<sup>11–15</sup> NMR,<sup>16–18</sup> neutron scattering,<sup>19,20</sup> thermogravimetric analysis (TGA),<sup>15,21</sup> and impedance measurements,<sup>10</sup> all these experiments deal with the structure of water only “within” the Nafion membranes. Since electrochemical reactions of PEMFC take place at gas/Nafion/electrode interfaces, a molecular level understanding of water structure at the Nafion membrane surface is essential to clarify the electrode reaction mechanism of PEMFC.

Sum frequency generation (SFG), in which two photons of frequencies  $\omega_1$  and  $\omega_2$  generate one photon of sum frequency ( $\omega_3 = \omega_1 + \omega_2$ ), is one of second order nonlinear optical processes and does not take place in media with inversion symmetry under the electric dipole approximation but only at the interface between these media where the inversion symmetry is necessarily broken. By using visible light of fixed wavelength and tunable IR light, SFG spectroscopy can be surface sensitive vibrational spectroscopy and, therefore, is one of the most powerful techniques to investigate the structure of water molecules at interfaces.<sup>22,23</sup> Actually, SFG has successfully been applied to investigate the structure of water at gas/liquid,<sup>22,24–26</sup> liquid/liquid,<sup>23,27</sup> and solid/liquid interfaces.<sup>28–32</sup>

Here, the structure of water at the Nafion thin film surface under various relative humidity (RH) values was examined by using SFG spectroscopy. When the Nafion thin film was exposed to low RH (<60%) environment, peaks at 3720 and 3600 cm<sup>-1</sup> were dominant in the SFG spectra. In high RH environment, a broad peak centered around 3200–3300 cm<sup>-1</sup> was observed. The origins of these peaks are discussed and the behavior of surface water is compared with that of water in bulk Nafion.

## 2. Experimental Section

**2.1. Sample Preparation.** The Nafion thin film was formed on the flat face of an IR grade hemicylindrical-shaped quartz prism (Daico MFG Co., Ltd.) for the SFG measurements after the quartz prism was thoroughly cleaned by “piranha” solution (3:1 concentrated H<sub>2</sub>SO<sub>4</sub> and 30% H<sub>2</sub>O<sub>2</sub>) for 30 min, then rinsed thoroughly with Milli-Q water. The Nafion solution (Dupont, DE1020) was sprayed on the prism, which was being rotated at 2000 rpm, and then the sample was placed into a vacuum desiccator at room temperature overnight. The thickness of the Nafion film was determined by ellipsometry (SOPRA, GESP-5) to be ca. 500 nm.

**2.2. SFG Measurements.** A detailed description of the SFG system used in the present study has been given elsewhere.<sup>28</sup> A picosecond Nd:YAG laser (EKSPLA, PL2143B) was employed

\* To whom correspondence should be addressed. Phone: +81-11-706-3812. Fax: +81-11-706-3440. E-mail: uosaki@sci.hokudai.ac.jp.

<sup>†</sup> Hokkaido University.

<sup>‡</sup> Toyota Motor Corporation.

<sup>§</sup> National Institute for Materials Science.

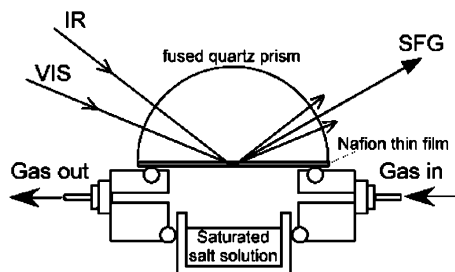


Figure 1. The experimental arrangement for SFG measurements.

TABLE 1: Saturated Salt Solutions Used in the Present Experiment and the Actual RH Measured by the Present Hygrometer

hygrostat at 22 °C	RH (%)
dry Ar gas	0
LiCl	17
MgCl <sub>2</sub>	40
NaBr	61
H <sub>2</sub> O	100

to pump an optical parametric generation/optical parametric amplification/difference frequency generation (OPG/OPA/DFG) system (EKSPLA PG401 VIR/DFG), which generates a tunable IR beam from 2.3 to 8.5  $\mu\text{m}$ . The second harmonic output (532 nm) from the Nd:YAG laser was used as the visible light. The intensity of the SFG signal was normalized to those of IR and visible beams.

The experimental arrangement for SFG measurements is shown in Figure 1. The Nafion thin film was in contact with the Ar gas flow or nonflowing water vapor with various RH, which was obtained by positioning a saturated salt solution in a holder located under a quartz prism. The different saturated salt solutions used in the present experiment are listed in Table 1.<sup>12,13</sup> The IR (15  $\mu\text{J}/\text{pulse}$  at 3000  $\text{cm}^{-1}$ ) and 532 nm (0.6 mJ/pulse) beams were incident from the quartz prism side and were overlap at the Nafion surface. The incident angle of the visible

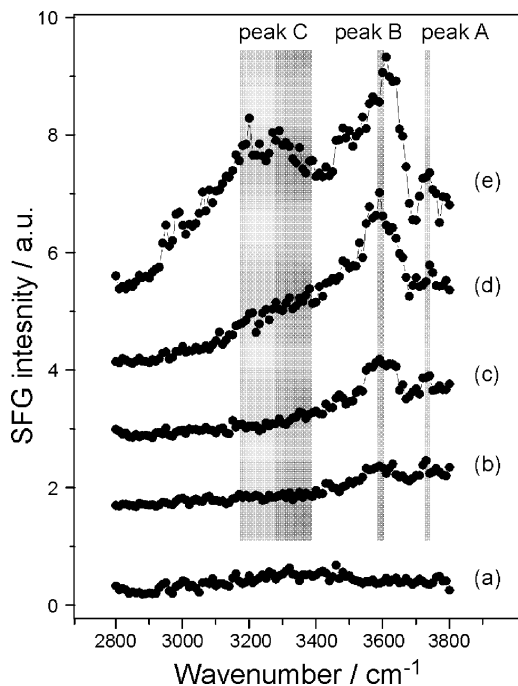


Figure 2. (A) SFG spectra in the OH stretching region of at the Nafion thin film/water vapor interface under various RH conditions: (a) 0%, (b) 17%, (c) 40%, (d) 61%, and (e) 100%.

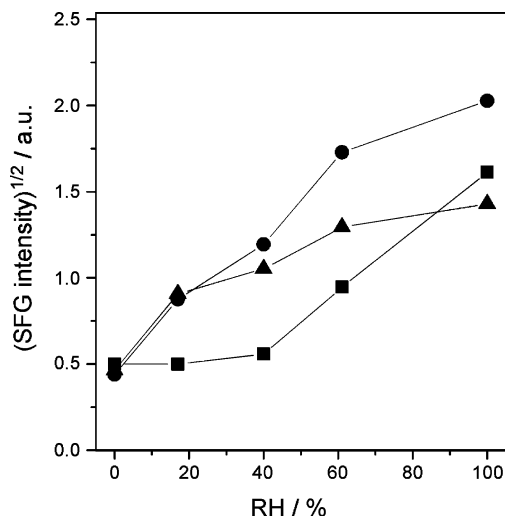


Figure 3. Square root of SFG peak intensities for 3200, (■), 3600, (●), and 3720  $\text{cm}^{-1}$  (▲) peaks observed in Figure 1 as a function of RH.

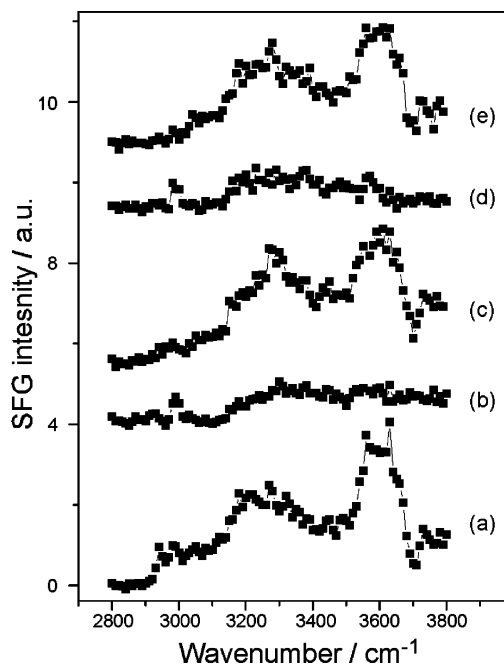
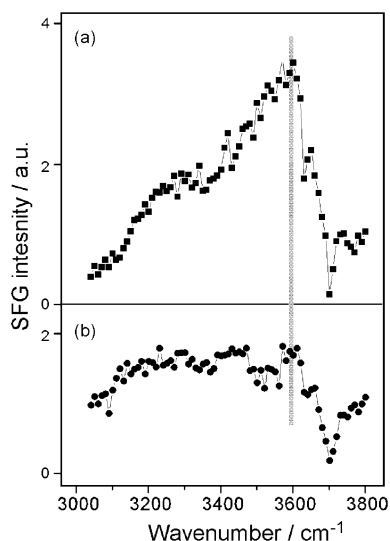


Figure 4. SFG spectra in the OH stretching region after RH change: (a) 100%, (b) 0% after spectrum a, (c) 100% after 2 cycles of RH change between 100% and 0%, (d) 0% after spectrum c, and (e) 100% after 4 cycles of RH change between 100% and 0%

and IR were was 70° and 50°, respectively. The polarization conditions in the present experiment were all s, s, and p for SFG, VIS, and IR laser beams. This polarization combination (ssp) is sensitive only to the vibrational mode normal to the surface of isotropic media. The SF light generated from the sample surface was detected by a monochromator (Oriel, M257) and PMT (Hamamatsu Photonics, R3896).

### 3. Results

**3.1. Humidity-Dependent SFG Spectra.** Figure 2 shows SFG spectra in the OH stretching region of the Nafion thin film surface measured at different RH values. Under dry Ar gas flow (RH = 0%), a very weak broad peak centered around 3300  $\text{cm}^{-1}$  was observed (Figure 2a). This peak should originate from water molecules on the Nafion surface physisorbed during the surface



**Figure 5.** SFG spectra in the OH stretching region of the Nafion thin film/water vapor (RH = 100%) interface (a) before and (b) after Nafion was immersed in 1 M LiCl solution for 1 h.

cleaning process. This broad peak disappeared when the Nafion surface was exposed to dry Ar gas for a long time.

SFG peaks centered around 3720 (peak A) and 3600  $\text{cm}^{-1}$  (peak B) appeared when Ar gas with low humidity was introduced into the cell (Figure 2b). Their intensities increased with the increase of RH (Figure 2c–e). When RH was increased to 61% (Figure 2d), another broad peak centered around 3300  $\text{cm}^{-1}$  (peak C) was observed. Its intensity increased and its position red-shifted as RH was increased. At RH = 100%, the position of this peak became ca. 3200  $\text{cm}^{-1}$  (Figure 2e).

The effect of RH on the square root of SFG peak intensity of the three main peaks observed in Figure 2 (peak A–C) is summarized in Figure 3.

**3.2. Effect of Dry/Wet Cycles on the Spectra.** The effect of RH change between 0% and 100% on the structure of water at the Nafion thin film surface was also investigated as shown in Figure 4. The measurements were carried out after dry Ar gas or Ar gas saturated with water vapor (RH = 100%) was passed for 1 h. It took 25 min to obtain one spectrum. The SFG spectra reversibility responded to RH change, indicating that the surface properties of the Nafion did not change by dry/wet cycles at least for the first 5 cycles.

#### 4. Discussions

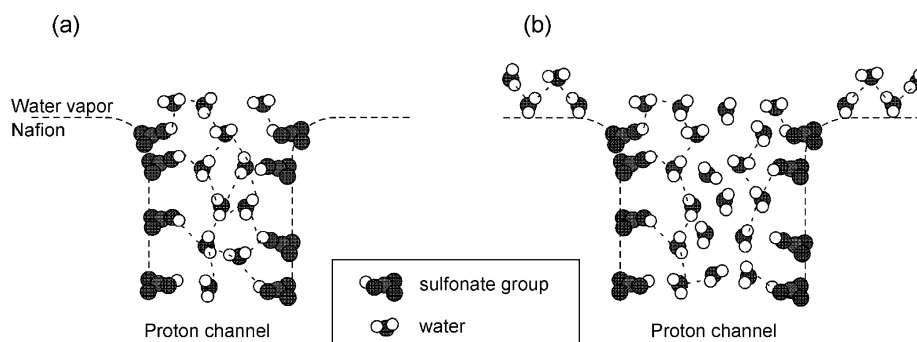
**4.1. Peak Assignment.** The position of peak A, 3720  $\text{cm}^{-1}$ , is close to that due to “dangling OH” or “free OH” of water molecules, which is usually observed when water molecules are in contact with a hydrophobic environment<sup>31,32</sup> and has been

observed at vapor/water interface.<sup>34</sup> Thus, peak A can be assigned to be due to water molecules exposed to the vapor phase at the Nafion surface.

The position of peak B, 3600  $\text{cm}^{-1}$ , is at a lower wavenumber than that of the “free OH” peak. Falk and co-workers reported that a peak at ca. 3520  $\text{cm}^{-1}$  is due to the water molecules, which are hydrogen bonded with sulfonate groups within the proton channel, based on the FT-IR measurements of the Nafion membrane in various cationic forms.<sup>15</sup> It is expected that the peaks due to water interacting with sulfonate groups should be strongly affected by exchanging proton with another cation. Figure 5 shows the SFG spectra in the OH stretching region of water molecules obtained at the Nafion thin film surface measured before (Figure 5a) and after (Figure 5b) immersing Nafion in LiCl solution for 1 h. It is clear that the intensity of the peak at 3600  $\text{cm}^{-1}$  was decreased by LiCl treatment, suggesting that peak B originates from water molecules interacting with sulfonate groups of the Nafion surface.

The position of peak C is in agreement with that of “ice-like” water. It is well-known that the SFG spectrum of the ice surface will give a broad OH stretching peak at around this low wavenumber region.<sup>22</sup> The shift of the SFG peak C toward lower wavenumber indicates a structuring of the hydrogen bonding network among water molecules. Such ordering of water molecules has also been observed at the octadecyltrichlorosilane (OTS)/water interface.<sup>31</sup> The highly hydrophobic nature of the surface should be the most important origin for the ordering of water molecules at the surface. The ordering of water molecules was also observed at the polytetrafluoroethylene (PTFE)/water interface, which has a similar chemical composition with the backbone structure of Nafion.<sup>35</sup> Thus, peak C should be due to water molecules adsorbed on hydrophobic, i.e., fluorocarbon, sites of the Nafion surface.

**4.2. Comparison between the RH-Dependent Structures of Water Molecules at the Surface and Inside of Nafion.** On the basis of the above-mentioned results, the RH-dependent behavior of water molecules at the Nafion surface can be summarized as follows. The presence of SFG peaks at 3600  $\text{cm}^{-1}$  (peak B), which is due to water molecules interacting with sulfonate groups, and at 3720  $\text{cm}^{-1}$  (peak A), which is due to non-hydrogen bonded water at the Nafion/vapor interface, and the very low intensity of the SFG peak at 3200  $\text{cm}^{-1}$  (peak C) at low RH condition suggest that water molecules adsorbed preferentially at sulfonate sites on the Nafion surface due to the hydrophilic nature of sulfonate sites but not at hydrophobic, i.e., fluorocarbon sites at low RH condition. As RH was increased to ca. 40%, the intensities of peaks A and B increased but that of peak C did not change, showing the increase of the amount of adsorbed water molecules only at the sulfonate site. Further increase of RH led to the adsorption of water molecules even at fluorocarbon



**Figure 6.** A model of the Nafion/water vapor interface in (a) low and (b) high RH environments.

sites on the Nafion surface as shown by the significant increase of the intensity of peak C at higher RH condition.

The behaviors of water molecules inside of the Nafion membrane have been investigated by several groups.<sup>7–9,36,37</sup> Water uptake gradually increases with RH initially and then drastically as RH becomes higher than 70–80%<sup>8,14</sup> and the RH-dependent total IR absorbance change was similar to the RH-dependent change of  $\lambda$ , i.e., the amount of water molecules per sulfonate group in the Nafion membrane,<sup>8</sup> supporting that IR mainly probes water in bulk Nafion. FTIR measurements showed two main broad peaks centered around 3500 and 3250  $\text{cm}^{-1}$  in the OH stretching region under various RH conditions and the latter peak increased first (up to RH = 47%).<sup>14</sup> The increase of the 3250  $\text{cm}^{-1}$  peak in FTIR spectra and the slow increase of water uptake with the increase of RH in the low RH region suggest that the amount of water molecules within the ion channel inside of Nafion increases with the increase of RH in this RH region. When RH was increased further to above 70–80%, the intensity and the position of the high wavenumber OH peak in FTIR spectra increased significantly and red-shifted, respectively. The position of the former peak finally reached the value of liquid water (3400  $\text{cm}^{-1}$ ) at RH = 96%. These results and very large water uptake suggest the evolution of more loosely bound water inside Nafion in the high RH region.

On the basis of these results, a schematic model for the RH-dependent structure of the Nafion membrane/water vapor interface is presented as shown in Figure 6. At very low RH environment, water molecules are present at the Nafion surface interacting strongly with the sulfonate site and in the proton channel, forming water clusters, inside of the Nafion membrane (Figure 6a). Recent theoretical studies of the distribution of water molecules in the Nafion membrane also suggest that water molecules are present close to the sulfonate group and form clusters at low RH conditions.<sup>38,39</sup> When RH is increased, the amount of water molecules increases at the sulfonate sites at the Nafion surface, resulting in the increase of SFG peaks at 3600 (peak B) and 3720  $\text{cm}^{-1}$  (peak A), and within the ion channel inside of Nafion, leading to the increases of IR peak at 3250  $\text{cm}^{-1}$ .<sup>14</sup> Further increase of RH to more than 70% leads to the uptake of a large amount of water into the Nafion membrane, resulting in the presence of bulk water as suggested by the increase of the IR peak at 3500  $\text{cm}^{-1}$ ,<sup>14</sup> and the adsorption of water molecules even at the very hydrophobic fluorocarbon site at the Nafion surface, resulting in the increase of the SFG peak at 3200  $\text{cm}^{-1}$  (peak C), i.e., “ice-like” water.

## 5. Conclusion

The RH-dependent structure of water at the Nafion thin film surface was studied for the first time by SFG spectroscopy. When the Nafion thin film was exposed to a low relative humidity (RH) environment, a peak at 3720  $\text{cm}^{-1}$  due to the “dangling OH” or “free OH” of water molecules and a peak centered around 3600  $\text{cm}^{-1}$ , which was assigned to be due to water molecules interacting with sulfonate groups of the Nafion surface, were observed. The intensities of these peaks increased as RH was increased. A broad peak centered around 3200–3300  $\text{cm}^{-1}$  due to water adsorbed on hydrophobic, i.e., fluorocarbon, sites of Nafion was observed when the Nafion thin film was exposed to high RH environment (RH > 60%). The behavior of surface water is compared with that of water in bulk Nafion and a schematic model for the RH-dependent structure of the Nafion membrane/water vapor interface is presented.

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**Supporting Information Available:** SFG spectrum of polytetrafluoroethylene (PTFE)/water interface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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