Effect of Elevated Temperatures on the States of Water and Their Correlation with the Proton Conductivity of Nafion

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ABSTRACT: For the first time, we report the effects of elevated temperatures, from 80 to 100 °C, on the changes in the states of water and ion–water channels and their correlation with the proton conductivity of Nafion NR212, which was investigated using a Fourier transform infrared spectroscopy study. Experimentally, three types of water aggregates, protonated water (H+(H2O)n), nonprotonated hydrogen (H)-bonded water (H2O···H2O), and non-H-bonded water, were found in Nafion, and the existence of those three types of water was confirmed through ab initio molecular dynamics simulation. We found that the proton conductivity of Nafion increased for up to 80 °C, but from 80 to 100 °C, the conductivity did not increase; rather, all of those elevated temperatures showed identical conductivity values. The proton conductivities at lower relative humidities (RHs) (up to 50%) remained nearly identical for all elevated temperatures (80, 90, and 100 °C); however, from 60% RH (over λ = 4), the conductivity remarkably jumped for all elevated temperatures. The results indicated that the amount of randomly arranged water gradually increased and created more H-bonded water networks in Nafion at above 60% RH. From the deconvolution of the O–H bending band, it was found that the volume fraction \( \int f_i \) (i = each deconvoluted band) of H-bonded water for elevated temperatures (>80–100 °C) increased remarkably higher than for 60 °C.

INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) have attracted a great deal of attention as alternative and environmentally friendly energy sources for transportation, portable devices, and stationary power.1−12 Recently, increasing attention has been paid to higher temperature PEFC systems because of their higher power efficiency.13 The development of new materials for high-temperature proton-conducting membranes for PEFCs requires a better understanding of the working conditions of the membrane.14

Peron et al. worked on the proton conductivity of Nafion211 at elevated temperatures for varied relative humidities (RHs), though they reported the results for up to 80 °C only.15 In their study, at 80 °C, the conductivity increased from 0.0012 to 0.13 S/cm as RH is increased from 10 to 95%. Alberi et al.16 worked on the proton conductivity of Nafion117 at elevated temperatures (80−160 °C) as a function of RH. Though they found a very slight increase of the conductivity for 100% RH, in their another work,8,9 they observed that at 100% RH, some instability of Nafion starts for near 80 °C. From lower to 85% RH, they found almost identical values of conductivity for 80−140 °C (after it started to decrease). They considered that the expected growth of the conductivity was compensated by some kind of modification of the polymer matrix which decreases the mobility and the effective concentration of the charge carriers at those higher temperatures. Fourier transform infrared (FTIR) spectroscopy has been extensively applied to characterize the chemical structure of Nafion.10−12 Molecular level interactions that influence the states of water in Nafion materials have been investigated by the FTIR spectroscopy technique.14 States of water are the key factors for the proton conduction in electrolyte membranes. Lu et al. carried out dielectric relaxation spectroscopic study on Nafion117 in the acid (H+) form at several hydration levels and detected three
states of water, each exhibiting distinct dynamics. As the infrared (IR) spectrum shows a specific absorption pattern depending on the molecular structure, in many cases, it is used for structural and qualitative analyses of a substance. The sensitivity of IR spectroscopy toward water has made it valuable for the study of hydration. Kunimatsu et al. studied the states of water in Na− by ATR K of Aquivion at 35 °C and (0–50)% RH only and did not assign all of the deconvoluted peaks FTIR spectra only at ambient temperature. Laporta et al. worked on water distribution in Aquivion utilizing ATR—FTIR, and through a spectral deconvolution process of the O region into four peaks, and through the MD simulation, they could obtain valuable information on molecular interactions, especially those involving water molecules, particularly through the FTIR technique. Ping et al. worked on the states of water in different hydrophilic polymers through DSC and FTIR, and they showed that the absorbed water in the hydrophilic polymer develops two types of hydrogen bonds (H-bonds): one corresponds to the water molecules directly attached to the active site of the polymer to form the first hydration layer and another corresponds to the water molecules in the second hydration layer.

Kim et al. worked on the states of water on the physical and electrochemical properties of sulfonated poly(aryl ether sulfone) and Nafion and found that the states of water correlate with the proton conductivity. Some other groups have discussed the relationship between the states of water and the proton conductivity of Nafion at ambient temperature. Kunimatsu et al. studied the states of water in Nafion NR211 by ATR—FTIR, and from the analysis of the O–H bending region of water, they showed that the proton conductivity is closely associated with the growth of weakly H-bonded water. However, they did not discuss the O–H stretching band region, and also they measured and discussed FTIR results only for room temperature, not for higher temperatures. Hofmann et al. investigated the structure of water in Nafion membranes by IR spectroscopy and molecular dynamics (MD) simulation, and they were able to distinguish between the water molecules on the “surface” of the pores of the membrane as opposed to the bulk water molecules in the cavities of the system. They deconvoluted the O–H stretching (4000–2500 cm−1) band region into four peaks, and through the MD simulation, they assigned those peaks according to H-bonding. Ferrari et al. worked on water distribution in Aquivion utilizing ATR—FTIR, and through a spectral deconvolution process of the O–H stretching region (3700–2400 cm−1), they identified four different types of water species in Aquivion. However, they also measured FTIR—ATR of Aquivion at 35 °C and (0–50)% RH only and did not assign all of the deconvoluted peaks precisely, especially the peak at the highest wavenumber (3515 cm−1).

As discussed above, until now, there are many reports on the proton conductivity and states of water in Nafion for ambient temperature up to 80 °C for varied RHs; however, to our knowledge, there is almost no report on the states of water at elevated temperatures (80–100 °C) simultaneously with varied RHs and their correlation with the proton conductivity. The possible reason of no report for elevated temperatures may be due to the unavailability of FTIR system for simultaneous measurement at elevated temperatures (up to 100 °C) and varied RHs (up to 100% RH), as this measurement system needs a high-temperature-, high-pressure-, and high-RH-controlled ATR—FTIR sample chamber and vapor-producing system. On the other hand, presently, the operating temperature of a fuel cell is 80 °C, so it is indispensable to investigate and know the hydrated morphology, states of water, and their correlation with the proton conductivity of Nafion at elevated temperatures (up to 100 °C), as those data will be helpful to design lower-cost perfluorinated polymer electrolyte membranes for PEFCs which can be used at higher temperatures (up to 100 °C). Therefore, we, with the engineering cooperation of several companies in Japan, developed a specially designed high-temperature-, high-pressure-, and high-RH-controlled ATR—FTIR system, through which we succeeded in controlling and measuring the ATR—FTIR spectra of polymer membranes for up to 100 °C while keeping the RH controlled up to 100% RH.

In the present paper, we first report the morphological changes, states of water at elevated temperatures (80–100 °C) and varied RHs (up to 100% RH), and their correlation with the proton conductivity in Nafion212, which are not published yet. We also performed ab initio molecular dynamics (AIMD) simulation on the states of water at an elevated temperature (80 °C) to support the experimental results of ATR—FTIR on the types of water in a Nafion212 membrane.

RESULTS

Number of Water Molecules per Sulfonate Group. The number of water molecules per sulfonic acid group (λ(H2O/−SO3H)) was plotted against RH and is shown in Figure 1. The λ value increased with increasing RH; however, λ was nearly identical for all temperatures. Therefore, the RH dependence can be used for the investigation of different hydration levels at each temperature.

Proton Conductivity. The proton conductivity of Nafion at varied temperatures is presented as a function of RH in Figure 2. The conductivity of the membrane depended strongly on the temperature and RH for all temperatures. The proton conductivities for 80 °C at 60 and 80% RH were found to be 0.05 and 0.1 S/cm, respectively. Dimitrov et al. investigated the humidity dependence of the proton conductivity for Nafion NR212, and their results (for 80 °C, σ ∼ 0.05 and 0.95 S/cm at 60 and 80% RH, respectively) were almost identical to our results. Figure 2 shows two distinct regions for conductivity; at a low RH, nondependency of the proton conductivity on temperature was observed; that is, the conductivity remained...
nearly identical for up to 50% RH for all temperatures. At a higher RH, that is, from 60% RH, the conductivity for elevated temperatures (>80 °C) was higher than that for 60 °C. When the RH was increased up to 70% and over, the difference became more remarkable. Surprisingly, we found that the proton conductivity above 80 °C did not increase anymore and the conductivities from 80 to 100 °C were almost identical. Until now, the proton conductivity of Naﬁon at over 80 °C with varied RHs is not reported yet by any researcher, and this new result is an important finding in the field of PEFC development.

Humidity-Dependent ATR−FTIR Spectra for Naﬁon NR212 at Varied Temperatures. The effect of humidity for varied elevated temperatures was investigated to understand the states of water in Naﬁon. Figure 3a shows the ATR−FTIR spectra of Naﬁon for 90 °C at varied RHs (the FTIR spectra for other temperatures can be found in the Supporting Information). The typical spectra of hydrated Naﬁon showed a broad absorption band at 3448 cm⁻¹ corresponding to O−H stretching, 28 1721 and 1633 cm⁻¹ corresponding to O−H bending, 24 1311 corresponding to CF₃ stretching, 29 1193 cm⁻¹ corresponding to asymmetrical C−F stretching, 24 1142 cm⁻¹ corresponding to symmetrical C−F stretching, 24 1055 cm⁻¹ corresponding to symmetrical S−O stretching with CCO bending, 30 967 cm⁻¹ corresponding to symmetrical S−O stretching with C−S stretching, 30 and 625 cm⁻¹ corresponding to the CF₂ rocking mode. 28 Although very weak, the O−H stretching band arising from non-H-bonded H₂O, 15,16,31−35 that is, OH groups without a donating H-bond, was identiﬁed at 3693 cm⁻¹ for temperature above 80 °C. 31,36 It was observed that O−H stretching and O−H bending band intensities increased signiﬁcantly with increasing RH and the bands at 1410 and 914 cm⁻¹ assigned to S=O and S−OH, respectively, 18 of SO₂H groups diminished with increasing hydration; however, the band at 625 cm⁻¹ remained constant for all RHs. For O−H stretching, appearance of a new shoulder peak at around 3223 cm⁻¹ was noticed with increasing RH. For all temperatures, similar results were found. Though the above-described spectra for varied temperatures above 80 °C resemble each other, a considerable variation in their band intensities and shapes was found from the data analysis. The above data are summarized in Table 1.

AIMD Simulation on the States of Water. The AIMD simulation results for the O−H stretching region of the decomposed spectra are shown in Figure 4a. The decomposition of the stretching modes shown in the figure consisted of three major peaks. Hydrogen atoms in the W0 state represent dangling bonds and have a peak at 3750 cm⁻¹, which is close to the gas-phase values. The spectra for the WW and WS states have a strong peak at around 3500 cm⁻¹, which is in agreement with the main peak for liquid water. The spectra for the HW and HS states show a broad peak at 2800–3050 cm⁻¹. It is worth noting that several authors have reported the

Figure 2. Proton conductivity of Naﬁon NR212 as a function of RH for varied elevated temperatures. Unexpectedly, the conductivity above 80 °C did not increase anymore up to 100 °C, and the values for 80–100 °C were nearly identical.
presence of a peak at ~2900 cm$^{-1}$ in aqueous solutions of strong acids, which is assigned to the O–H stretching motion involving hydrated protons.17,18 Our result is consistent with these measurements.

The AIMD simulation results on the decomposed spectra for the O–H bending vibration region are shown in Figure 4b. The result for the bending modes shown in the figure is dominated by a strong peak at around 1600 cm$^{-1}$ and found to be rather insensitive to the hydrogen state, except for the HW protons which show a blue shift of 50–100 cm$^{-1}$ and a significant broadening. These HW protons correspond to the center of Zundel cations.

### DISCUSSION

As can be seen from Figure 3a, disappearance of the peaks at 1410 and 914 cm$^{-1}$ gave a clear indication of the dissociation of SO$_3$H groups with hydration, with the proton getting hydrogen-bonded to water. The red shift of the −SO$_3$ group from 1064 to 1055 cm$^{-1}$ gave the indication of H-bonding of water molecules with the −SO$_3$ group.

Types of Water in Nafion at Elevated Temperatures Analyzed from the O–H Stretching Region. Figure 3b (enlarged from Figure 3a) shows the ATR–FTIR spectra for the O–H stretching vibrational region for Nafion at 90 °C and varied RHs. It was noticed that up to 40% RH, the absorbance intensity increased systematically with increasing RH; from 40% RH, the intensity started to increase rapidly; and from 60% RH, the intensity increased remarkably. A new shoulder peak at 3223 cm$^{-1}$ appeared from 60% RH, indicating that the water networks spread out remarkably and a new type of water aggregates started to form from this RH. It was also observed that the very small peak at 3693 cm$^{-1}$ gradually diminished with increasing RH. The above results indicated that movement of water became dramatic at 90 °C and the polymer matrix also became highly mobile at this temperature, which affects the arrangement of large water aggregates in the membrane, and as a result, many smaller water aggregates develop. This tendency clearly started from a certain amount of water uptake (60% RH) in the membrane. However, it was difficult to clarify the difference in the states of water from those spectra. In this circumstance, as our purpose was to investigate the states of water, we decided to deconvolute the two main water bands, O–H stretching and O–H bending bands, to deduce the types and states of water quantitatively. The mass fraction of each water family can be obtained through a decomposition of the water band, which allows following separately the peaks related to each type of water molecules.22 Different states of water have been proposed to exist in Nafion membranes corresponding to different environments.39,40 Lu et al. observed the states of water, manifested through three population averages with distinctly resolved dynamical behaviors, and their changes with temperature (25–45 °C) and hydration level.14 To clarify the spectral variations in the O–H stretching region, the spectral shapes in the region were fitted using Gaussian functions. The deconvolution result of the O–H stretching region for 90 °C and 60% RH is shown in Figure 5. It was found that the O–H stretching region consisted of four water components, which correspond to four groups of vibrations. We assigned peak 1 (centered at 2923 cm$^{-1}$) to protonated water (such as H$_3$O$^+$ ions) bonded with sulfonate groups (−SO$_3$−H$_2$O).30,21,25,41 Peak 2 (centered at 3236 cm$^{-1}$) to symmetric and peak 3 (centered at 3465 cm$^{-1}$) to asymmetric O–H stretching vibrations, which were denoted as $\nu_1$(HO−H···O)24,42,43 and $\nu_\omega$(HO−H···O)24,42,43 respectively. Peak 4 (centered at 3604 cm$^{-1}$) was assigned to the stretching vibration of non-H-bonded water (hydroxyl groups of water attached to the C−F backbone of Nafion with weaker van der Waals force) denoted as $\nu$(HO−H···F).15,25 The indicated types of water for varied temperatures and RHs will be discussed in the next section.

The deconvolution results of the experimental spectra and simulated spectra were found to be consistent for the stretching region. The simulated W0 peak at 3750 cm$^{-1}$ is the

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**Table 1. Assignment of the Selected ATR–FTIR Peaks (4000−560 cm$^{-1}$) for Nafion NR212 at 90 °C**

| wavenumber (cm$^{-1}$) | band assignment | refs |
|------------------------|-----------------|-----|
| 3693                   | O–H stretching of non-H-bonded water | 31,36 |
| 3448                   | O–H stretching | 28 |
| 3223                   | O–H stretching | 24 |
| 1721                   | O–H bending | 24 |
| 1633                   | O–H bending | 24 |
| 1410                   | S=O of SO$_3$H groups | 18 |
| 1311                   | CF$_3$ asymmetric stretching | 29 |
| 1193                   | asymmetrical C−F stretching | 24 |
| 1142                   | symmetrical C−F stretching | 24 |
| 1055                   | symmetrical S−O stretching with CCO bending | 30 |
| 967                    | symmetrical S−O stretching with C−S stretching | 30 |
| 914                    | S−OH of SO$_3$H groups | 18 |
| 625                    | CF$_2$ rocking mode | 28 |

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**Figure 4.** AIMD simulation result for Nafion NR212 at 80 °C and 60% RH for the O–H stretching (a) and O–H bending (b) regions.
The combination of non-H-bonded water peaks (peak from monomeric waters and peak from waters attached to the C-F backbone), which corresponds to experimental Peak 4 at 3604 cm\(^{-1}\), the combined peak of WW and WS at 3500 cm\(^{-1}\) corresponds to the experimental combined peak of O–H symmetric stretching (at 3236 cm\(^{-1}\), peak 2) and O–H asymmetric stretching (at 3465 cm\(^{-1}\), peak 3), and the combination of broad peaks of HS and HW at 2800–3050 cm\(^{-1}\) corresponds to the protonated water peak at 2923 cm\(^{-1}\) (peak 1) of the experimental result (Figure 5). The consistency of the simulated peaks with the experimental peaks is shown in Table 2.

### Table 2. Consistency of AIMD-Simulated Peak with the Deconvoluted Peaks of the Experimental Spectra

| simulated peak | corresponding deconvoluted band (Figure 5) |
|----------------|------------------------------------------|
| W0             | peak 4                                   |
| WW             | peak 3                                   |
| WS             | peak 2                                   |
| HW             | peak 1                                   |
| HS             | peak 1                                   |

It is notable here that computer simulation result cannot perfectly reproduce the experimental spectroscopic data in general as found in many papers.\(^{44-46}\) Also in the present case, the calculated results do not correspond very well to the observed data about the vibrational frequencies. However, what we want to know from the computer simulation is how many types of water molecules subjected to the di-F backbone, which corresponds to experimental Peak 4, at 3604 cm\(^{-1}\), the combined peak of WW and WS at 3500 cm\(^{-1}\), corresponds to the experimental combined peak of O–H symmetric stretching (at 3236 cm\(^{-1}\), peak 2) and O–H asymmetric stretching (at 3465 cm\(^{-1}\), peak 3), and the combination of broad peaks of HS and HW at 2800–3050 cm\(^{-1}\) corresponds to the protonated water peak at 2923 cm\(^{-1}\) (peak 1) of the experimental result (Figure 5). The consistency of the simulated peaks with the experimental peaks is shown in Table 2.

To estimate the relative contents of these three water states, we have separated the observed band profiles, as shown in Figure 5. As already mentioned, the three states are assumed here. The integrated intensity of each component is expressed as \(A_i\). The fraction \(f_i\) of each band area \(A_i\) is calculated as

\[
f_i = \frac{A_i}{\sum_{j=1}^{3} A_j}
\]

However, it must be noticed here that the intensity fraction \(f_i\) is not equal to the molar fraction \((M_i)\) of each state. This is because we do not know the absorption coefficient \(\epsilon_i\) of these component bands. According to the Lambert–Beer’s law,

\[
A_i = \epsilon_i c l
\]

where \(\epsilon_i\) is the absorption coefficient, \(c\) is the concentration of each type of water (mol/L), and \(l\) is the length of light path (thickness of Naion) of each water component. \(M_i\) is given as

\[
M_i = \frac{\epsilon_i c}{\sum \epsilon_i c}
\]

Therefore, as long as the coefficient \(\epsilon_i\) is not known, \(M_i\) cannot be evaluated correctly. In the present paper, the change of different water aggregation states is discussed using \(f_i\), as a measure of \(M_i\).

Changes in the above structurally different water aggregates at varied temperatures and RHs found from the O–H stretching band are shown in Figure 6. Figure 6a shows the relative fractional area, \(f_{\text{H}}(p1)\) (%), for the protonated water (p1) for varied RHs, and from the figure, it was found that the protonated water bonded with sulfonate groups (\(\text{H}^+ \cdot \cdots \cdot \cdot \cdot (\text{H}_2\text{O})\)) was nearly unchanged for up to 40% RH and, from over 40% RH, started to decrease with increasing RH and the areas for all temperatures were nearly identical. It was also found that the fraction \(f_{\text{H}}(p2)\) for H-bonded water (p2) showing symmetric stretching vibration, \(\nu_s(\text{HO}^+ \cdot \cdots \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot 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RH, after that, no di
(Figure 6b, upper part). Kunimatsu et al. also found increased amount of H-bonded water increased with increasing RH
of randomly arranged water gradually increased and created symmetrically ordered water was nearly unchanged, the amount
temperature and RH.

decreased, and the resultant H-bonded water increased with increased
the water clusters was also analyzed (not shown, see the
(Figure 6). We found more concrete information of the effect of
elevated temperatures on the states of water in Naﬁon from the
O–H band region. From the deconvolution, it was found that the O–H bending band consisted of three component bands with different peak positions: a slightly broad peak at 1836 cm
−1 (p1), an intermediate peak at 1711 cm
−1 (p2), and a sharp peak at 1630 cm
−1 (p3). We have assigned peaks p1 and p2 (decomposed from the experimental broad band centered at 1721 cm
−1) to protonated water, H3O
+(H2O)w. This band is composed of total protonated water (hydronium (H3O+), Zundel (H5O2+)
, Eigen (H4O3+), and possible stronger ions) in the bending region. Peak p3 at 1630 cm
−1 was assigned to H-
bonded water ((H2O)w), water hydrating –SO4
− groups. The AIMD simulated peaks (Figure 4b) were found to be consistent with the above experimental decomposed peaks of the bending band. The simulated peak at 1600 cm
−1 corresponds to the H-bonded water peak at 1630 cm
−1 of the experimental result (p3, Figure 7), and the simulated Zundel cation peak at around 1700 cm
−1 corresponds to the combined protonated water peak at 1836 (p1) and at 1711 cm
−1 (p2) of the experimental result (Figure 7).

Figure 8 shows the dependence of relative volume fraction
f(p_{3}+p_{2}) for the total protonated water (p1 + p2) found from the deconvolution of the O–H bending band (Figure 7). It was found that
f(p_{3}+p_{2}) for all temperatures decreased gradually with increasing RH. The fraction for all temperatures was identical for up to 60% RH; however, from 60% RH, it was remarkably lower for elevated temperatures (80 °C and 100 °C) than for 60 °C. Figure 9 (p3, lower part of figure) shows the dependence of relative volume fraction
f(p_{3}) for the H-bonded water. Again, we found that with increasing RH, the fraction
f(p_{3}) for H-bonded water was nearly unchanged and identical for all temperatures for up to 40% RH and started to increase from 40% RH. Though the fraction was identical for all

Figure 7. Gaussian deconvolution of the bending region of ATR–
FTIR spectra of Naﬁon NR212 for 90 °C and 60% RH: brown: experimentally observed; black: peak ﬁtting; green: deconvoluted peak 1; blue: deconvoluted peak 2; and red: deconvoluted peak 3.

Types of Water in Naﬁon at Elevated Temperatures Analyzed from the O–H Bending Band. Figure 3c (enlarged from Figure 3a) shows the ATR–FTIR spectra for the O–H bending vibrational region for Naﬁon at 90 °C and varied RHs. It was observed that the absorbance intensity of the protonated water band at 1721 cm
−1 increased for up to 20% RH, after that, no diﬀerence in the intensity was found for up to
40% RH, and then the intensity started to decrease from 60% RH. However, the intensity of the H-bonded water band at 1633 cm
−1 increased remarkably from 40% RH, and from 60%
temperatures for up to 60% RH, from above 60% RH, $f_{be(p3)}$ for elevated temperatures (80–100 °C) increased remarkably higher than 60 °C. This phenomenon, that is, when $f_{be(p2+p3)}$ is going down steeply from above 60% RH (Figure 8), $f_{be(p3)}$ is going up steeply from the same RH (Figure 9, lower part), implies that the water makes H-bond networks more effectively at a high water content for elevated temperatures. This result also supported the above O–H stretching band analysis result that the protonated water (p1 of Figure 6a) decreased and the amount of H-bonded water (p2 + p3 of Figure 6b) increased with increasing RH for all temperatures. However, though from the O–H stretching analysis, the effect of elevated temperatures and RH on the volume fraction for varied types of water could not be clarified so well, with the support of the O–H stretching band analysis results, we could distinguish the effect of temperature from the O–H bending band analysis well.

From the above discussion, we found that the O–H stretching band is composed of three types of water [protonated water (such as hydronium ion), H-bonded water, and non-H-bonded water] (Figure 5); however, the O–H bending band is composed of two types of water (protonated water with hydronium, Zundel, Eigen, and possible stronger ions and nonprotonated H-bonded water) (Figure 7).

Again, we found a difference in the increasing tendency of fraction of H-bonded water between the stretching and bending regions. The fraction of H-bonded water for the bending region for elevated temperatures remarkably increased from above 60% RH (Figure 9, lower part). This tendency could not be observed from the stretching region [Figure 6 (p2 + p3)]. The frequency of the OH stretching mode is very sensitive to its molecular surrounding. We consider that possibly the O–H bond stretching becomes slightly limited at a higher water content, which makes the difference of fraction of H-bonded water of the stretching region with the fraction of the bending region at elevated temperatures. As the protonated water for both stretching and bending bands decreased and non-H-bonded water was unchanged with increased temperature and RH, we considered that H-bonded water has a direct effect and is mainly responsible for the increase of the proton conductivity of Nafion. We found a clear effect of H-bonded water from the O–H bending mode, so we used H-bonded water of the bending mode to correlate the proton conductivity at elevated temperatures.

**Correlation between the States of Water and the Proton Conductivity at Elevated Temperatures.** Proton transport, both in bulk water and in Nafion, is intimately related to the structural dynamics of the hydrogen bond network of water. The conductivity of Nafion is highly dependent upon the states of water in the membrane. The correlation between the proton conductivity and the states of water at varied elevated temperatures is shown in Figure 9. From the figure, it was observed that the proton conductivity values for all temperatures for up to 50% RH were very similar, after that, from 60% RH, the conductivity for elevated temperatures increased remarkably higher than 60 °C, and the difference increased with increasing RH. We compared the proton conductivity result with fraction $f_{be(p3)}$ for H-bonded water found from the O–H bending analysis and observed a similar phenomenon that $f_{be(p3)}$ for H-bonded water for all temperatures was nearly identical for up to 60% RH and after that with increasing RH, the fraction for H-bonded water remarkably jumped for elevated temperatures (80–100 °C). From these results, the amount of increased H-bonded water can be correlated with the increased proton conductivity in Nafion. Kunimatsu et al. worked on the simultaneous measurements of proton conductivity and water uptake at room temperature, and from the analysis of the O–H bending band, they also suggested that the H-bonded water form water channels and increase of intensity from the H-bonded water band at 1630 cm⁻¹ caused the increase in the proton conductivity in Nafion.

The α-relaxation peak corresponds to the glass-transition temperature of the ionic domains of the neat Nafion in the acid form. α-Relaxation has been attributed to the onset of long-range mobility of both main chain and side chain giving rise to the gradual collapse of the static network and the subsequent evolution of a dynamic network. Hydrophilic ionic domains become extremely mobile at above the α-relaxation temperature, and thus the interconnected channels in Nafion may eventually be disrupted upon prolonged exposure to elevated temperatures. Sen et al. argued the possibility of a structural change within Nafion at around 80–90 °C based on a viscosity curve analysis. The α-relaxation temperature of Nafion NR212 is around 80 °C (onset 70–75 °C) (see also the Supporting Information). In our present study, we first found that proton conductivities of Nafion become maximum at 80
°C and do not increase with the increase of temperature up to 100 °C, so we focused our attention to clarify the phenomenon occurs at those higher temperatures. We suggest that from 60% RH, when the temperature increases from 60 to 80 °C, the vibrational motion of the polymer matrix and movement of water in Naﬁon increase, and gradually the system reaches equilibrium with thermodynamically and morphologically comparatively stable condition at around 80 °C. During this period of equilibrium, the randomly arranged water gradually became interconnected, created relatively broader H-bonded networks of water, and developed larger proton-conducting ion–water channels, which directly caused the increase of the proton conductivity. The pendant side chains, which anchor the sulfonate groups to the ﬂuorocarbon backbone, are labile enough to rearrange and stabilize water clusters as the amount of water increases. However, when the temperature increased above 80 °C, though the movement of water and polymer matrices increased more and became dramatic, the excess movement of water and possible morphological change were not favorable to make the H-bonded network larger anymore, and as a result, the proton conductivity also could not increase anymore. Again, though the weaker H-bonded water networks did not become larger at 90 or 100 °C, the H-bonds did not break; rather, the H-bond networks were maintained, so the proton conductivity did not decrease at those elevated temperatures.

CONCLUSIONS

Three types of water in Naﬁon212 at varied elevated temperatures and RHs were found from the experimental results (from the deconvoluted peaks for O–H stretching and bending bands of water), and AIMD simulation result supported the experimental results. From the O–H bending and stretching band deconvolution, we found that the content of protonated water [(H+)((H2O)n] was decreased, H-bonded water was increased, and non-H-bonded water was nearly unchanged with increasing RH for all temperatures. From the O–H stretching band analysis, it was found that the randomly arranged H-bonded water in Naﬁon212 gradually became interconnected and created more H-bonded water networks with increasing RH. From the O–H bending band analysis, interestingly, we found that from over 60% RH, the amount of H-bonded water jumped for temperatures above 80 °C, which clearly indicated that the randomly arranged water makes and spreads out the H-bonded water networks very fast from this RH. This result can be an important reference for the researchers working on the movement of water and H-bonding networks in perﬂuorinated membranes for fuel cells. The protonated water and non-H-bonded water had a negligible effect; however, H-bonded water had prominent contribution to the increase of the proton conductivity for Naﬁon212.

For the ﬁrst time, we report the proton conductivities for Naﬁon for above 80–100 °C and varied RHs. We found that the conductivity increases up to 80 °C; however surprisingly, the conductivity did not increase after that and all values for elevated temperatures were identical. The reason for this phenomenon is discussed on the basis of the equilibrium of the hydrated Naﬁon system. We suggest that at around 80 °C, thermodynamically and morphologically, the system already reaches equilibrium and after that at more higher temperatures, the excess movement of water and polymer chains could not make the ion–water channels larger anymore. However, even up to 100 °C, the H-bonds did not break rather maintained, so the proton conductivity did not decrease at those elevated temperatures.

EXPERIMENTAL SECTION

Materials. Naﬁon NR212 membranes (thickness 50 μm) in the H+ form [ion-exchange capacity (IEC) 0.92 mequiv/g] purchased from DuPont were utilized for the measurements. The membranes were dried at 80 °C for 24 h prior to all experiments. The chemical structure of Naﬁon is shown in Scheme 1.

Scheme 1. Chemical Structure of Naﬁon in the H+ Form

FTIR Measurements. FTIR measurements were performed by our specially designed high-temperature, high-pressure, and high-RH-controlled ATR–FTIR system. The newly developed system can control and measure the ATR–FTIR of polymer membranes for up to 100 °C while keeping the RH controlled up to 100% RH. The schematic diagram of our ATR–FTIR system is shown in Scheme 2. The FTIR spectra were recorded through the ATR mode by using a PerkinElmer Spectrum 100 system with a Diamond ATR crystal operated with a deuterated triglycine sulfate detector and a zinc selenide (ZnSe) beam splitter for the range of 650–4000 cm⁻¹. Each spectrum was recorded with a spectral resolution of 4 cm⁻¹, 128 scans averaged per spectrum. The water vapor was produced in a specifically designed temperature- and high-pressure-controlled thermostatic vessel system shown in Scheme 2. The water in the vessel was heated by an electric heater, and the temperature of water was equilibrated by rotating a small blade fan in the vessel. Dry N₂ gas was passed into the vessel, and thus the water vapor was passed through a transfer tube into the speciﬁcally developed air-tight, high-temperature-, high-pressure-, and high RH-controlled ATR sample cell. A particular temperature and RH environment for the sample was made by the simultaneous control of the sample cell temperature, amount of N₂ flow, temperature of the water in the vessel, and the speed of the rotating blade fan. A high-temperature- and high-RH-resistant sensor (HN-CJ2, Chino Corporation, Japan) was inserted into the air-tight sample cell to monitor the temperature and RH of the Naﬁon sample. As the KBr window in FTIR was damaged due to high RH, we used a high-temperature- and high-RH-resistant window of ZnSe for the experiments. The size of Naﬁon NR212 film was 1 cm × 1 cm. A ﬂat-end screw gauge was inserted into the air-tight sample cell to attach the sample on the diamond ATR crystal. Before starting each ATR–FTIR measurement, the Naﬁon film was placed on the ATR crystal and kept ﬁxed at a particular temperature and RH condition environment for 20 min to reach equilibrium. The ﬁlm was then pressed by a screw gauge.
from the top, with an appropriate pressure on the surface of the film for perfect adhesion on the ATR crystal. The measured temperature and RH errors were ± 1 °C and ± 3% RH, respectively.

Water Uptake and Proton Conductivity Measurements. Water uptake and in-plane proton conductivity were measured using an isothermal absorption measurement system (MSB-AD-V-FC, BEL Japan Inc.) equipped with an impedance analyzer (Solartron SI 1260). The system enabled the simultaneous measurements of water uptake and in-plane proton conductivity of membrane in the same chamber. The impedance spectra were recorded with the help of ZPlot/Zview software under an ac perturbation signal of 10 mV over the frequency range of 10 Hz to 100 kHz. Each membrane sample (1 cm × 4 cm) was dried at 80 °C for 3 h under dry N₂ flow and then exposed to a humidified N₂ environment under a controlled temperature at 60–100 °C. After equilibration for several hours, we confirmed that there was no further weight change of each membrane, and membrane weight and proton conductivity were then measured sequentially. The membrane weight was measured by a magnetic floating balance in the same chamber. The impedance spectra were recorded with the help of ZPlot/Zview software under an ac perturbation signal of 10 mV over the frequency range of 10 Hz to 100 kHz. Each membrane sample (1 cm × 4 cm) was dried at 80 °C for 3 h under dry N₂ flow and then exposed to a humidified N₂ environment under a controlled temperature at 60–100 °C. After equilibration for several hours, we confirmed that there was no further weight change of each membrane, and membrane weight and proton conductivity were then measured sequentially. The membrane weight was measured by a magnetic floating balance under controlled humidity and temperature. Humidity conditions were changed stepwise from 10 to 100% RH. In this magnetic floating balance system, an electronically controlled magnetic suspension coupling is used to transmit the measured force from the sample cell to the microbalance. A free floating permanent magnet, which works as a suspension magnet, was held by a stationary electromagnet attached to the balance. The sample was hanged from the permanent magnet in a sample crucible. This magnetic suspension coupling transmits the measuring force in a noncontact manner from the sample chamber to the microbalance located in ambient atmospheric conditions outside the sample chamber. The proton conductivity was measured using a four-point probe cell fabricated with two platinum foil electrodes for outer current carrying and two platinum wire electrodes for inner potential sensing. The four-point probe cell was attached to the impedance analyzer (Solartron SI 1260) described above.

The in-plane proton conductivity (σ) based on the four-point probe was calculated from the impedance data according to the following equation:

\[ \sigma = \frac{d}{A \cdot R} \]  

where \( A \) is the cross-sectional area, \( d \) is the distance (1 cm) between two gold electrodes, and \( R \) is the resistance value measured.

Number of Water Molecules per Sulfonate Group. The number of water molecules per sulfonate group at each RH, \( \lambda[H_2O/SO_3H] \), was calculated using the IEC value of Nafton with the following equation:

\[ \lambda = \frac{\text{water uptake (\%) × 10}}{\text{IEC} \times \text{MW}_{H_2O}} \]  

where MW\(_{H_2O}\) is the molecular weight of water (18.01 g mol\(^{-1}\)).

Spectral Deconvolution. Spectral deconvolution was performed using a commercial software, GRAMS/AI Version 9.1 (Thermo Fisher Scientific Inc., USA). The background-subtracted FTIR spectra were first imported to GRAMS/AI software and smoothed with a Savitzky–Golay function (polynomial = 2 and points = 31). Then, the region for deconvolution was selected, and the base line was corrected with a multipoint function. For the estimation of the minimum number and peak position of component bands of water in the deconvoluted region, the first derivative of the FTIR data and several references were taken into consideration. In the initial step of curve fitting, for the lowest RH data to be deconvoluted, all parameters (peak position, height, and full width at half-maximum) of each component band were allowed to vary, except for the peak shape which was fixed to Gaussian function. Gaussian function was found to be better for the best fitting of the component bands. For the deconvolution of all successive higher RH data, the peak positions of the component bands were kept constant; however, the height and full width at half-maximum were allowed to vary.

AIMD Simulation. We have performed AIMD simulations of hydrated Nafton for 60% RH using a model system containing 2 Nafton molecules with 4 terminating sulfonate groups and 17 water molecules, which is equal to the model used in our previous studies. All calculations were based on the generalized gradient approximation in the Perdew–Burke–Ernzerhof form. Separable norm-conserving pseudopotentials were used, and only the Γ-point was used to sample the Brillouin zone. The orbitals were expanded by the adaptive finite element basis functions at the average cutoff energy of 74 Ry and were quenched to the Born–Oppenheimer surface at
Each AIMD step. We exploited the mixed precision algorithm to improve the performance of this procedure. Experimental masses were used for all catalysts to reproduce the experimental spectra. The simulation lasted for 50 ps using a time step of 0.726 fs, and the average temperature was 67 °C. Other details of the simulations are given elsewhere. The trajectory of our simulations was used to investigate the structural and vibrational properties of our model system. In Table 3, we show the probabilities of hydrogen atoms to take different states defined by the donor and acceptor oxygen atoms. We note that all sulfonate groups are fully dissociated, and thus the donor oxygen is limited to those of H₂O and H₃O⁺. The remaining 1% of the hydrogen atoms exists in the form of isolated H⁺. The vibrational properties are investigated using the power spectra defined by

\[ P(\omega) = \sum_k \int \langle \mathbf{v}_k(t) \cdot \mathbf{v}_k(0) \rangle \exp(i\omega t) \, dt \]  

(6)

where \( \mathbf{v}_k(t) \) denotes the velocity of atom \( k \). Only hydrogen atoms are considered here because our interest is the high-frequency region of the spectra. In this work, we used a simple method for decomposing the power spectra into contributions from different hydrogen states as follows. Let us assume that \( s \) denotes the five hydrogen states defined in Table 3. Then, the spectra for state \( s \) is given by

\[ P_s(\omega) = \sum_k w_k(s) \int \langle \mathbf{v}_k(t) \cdot \mathbf{v}_k(0) \rangle \exp(i\omega t) \, dt \]  

(7)

where \( w_k(s) \in [0, 1] \) denotes the probability that atom \( k \) takes state \( s \) during the simulations.

**ASSOCIATED CONTENT**

○ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01765.

α-Relaxation, humidity-dependent ATR–FTIR spectra for other elevated temperatures, relative fraction (%) of varied types of water in Nafion212 for the O–H stretching region, and schematic illustration of the five hydrogen states (PDF)

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Notes
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was financially supported by the Ministry of Economy, Trade and Industry (METI) and New Energy and Industrial Technology Development Organization (NEDO), Japan. We would like to thank Dr. M. Yamaguchi, Dr. H. Hasegawa, Dr. K. Shinohara, Dr. Y.-K. Choe, and Dr. T. Ikeshoji for their valuable discussions and cooperation related to this paper.

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