Behavior of Water Molecules in PEFCs as Studied by ^{1}H NMR Spectroscopy

Atsuko Y. Nosaka* and Yoshio Nosaka

Department of Department of Chemistry, Nagaoka University of Technology, Nagaoka, 940-2188, Japan,

Water molecules confined in perfluorinated ionomer membranes which are extensively used for polymer electrolyte fuel cells, presented characteristic ^{1}H NMR spectra reflecting the difference in the morphology. For the hydrated membrane the water molecules at the distinct segments of the polymer undergo rapid exchange to give an apparent single signal. The signal shifts to the higher field with increasing the water content due to the increase of the fraction of the bulk water molecules. On shortage of bulk water the morphological conversion takes place. The membrane of such morphology exhibits a spectrum with separated regions at room temperature regardless of the water content, since the morphology prohibit the rapid exchange among the water molecules localized at the distinct segments. The characteristic spectral changes of water molecules associated with the chemical exchange among the water molecules in the different water domains and the change of the polymer morphology were demonstrated

Introduction

The studies on structures and properties devoted to swollen membranes have been extensively performed on perfluorosulfonated ionomer membranes such as Nafion due to their industrial interest in chlor-alkali production and polymer electrolyte fuel cells (PEFC) (1-25). Especially the application of the membranes to PEFC has been recently intensified from the energy and environmental viewpoints (1, 2). Nafion is the membrane developed by DuPont, in which hydrophilic perfluoroalkyleneether sidechains terminated with $-SO_3H$ are periodically attached to the hydrophobic fluorocarbon backbone. Although Nafion is known to possess exceptional thermal, chemical and mechanical stability, it has been acknowledged that it showed sometimes different properties after the long term storage (15). Recently from the observations of the variations in the ^{1}H NMR signals of water confined in Nafion we deduced that the polymer could undergo very slow morphological changes among distinct states depending on temperatures and hydrated conditions, and proposed a plausible scheme of the local conversion of the states of the water molecules associated with the morphological changes of the polymer (23-25). Slow morphological changes could influence seriously the accuracy of the measurements of the properties of the polymer and the evaluation of the performance of fuel cells. Some of the previous studies on the membranes may have been performed without being aware of whether the polymer was in a morphologically stationary state or a transitional state, which may account for the some unexpected experimental results for the membranes addressed so far. Therefore, it would be inevitable to identify whether the polymer is in a

morphologically steady or a transient state in advance. We demonstrated that ^{1}H NMR could be utilized for the identification to some extent, which might be difficult with the other alternative techniques (25). In the present study, we tried to obtain more detailed information on the exchange of water molecules at the distinct segments by observing the change of ^{1}H NMR signal under various conditions. Our observation suggests the potential to utilize ^{1}H NMR parameters such as the chemical shift value and peak area of the water molecules as a feasible measure of the water content of the hydrated membrane.

Experimental

Commercially available Nafion 112 and 1135 membranes (E. I. duPont de Nemours and Co.) were used as received. Although several pre-treatments of the membranes have been recommended (17), some steps significantly affected the spectral features. Therefore, we measured the membranes without any pre-treatment. The ^{1}H NMR spectra of the membranes were measured in the form of a single sheet. For the measurements of temperature dependence of the water signals, a membrane sheet of 2 x 50 mm was located in a 3 mm o.d. (55 mm high) glass NMR sample tube.

^{1}H NMR measurements were carried out on a Varian Infinity Plus 500 NMR spectrometer at 500 MHz in the temperature range of 25-85°C without sample rotation. The spectra were obtained after Fourier transformation of the FID signals following a single pulse excitation with pulse duration of 3.0 μs and a 5 s relaxation delay. To eliminate the background signal of the NMR probe, the spectrum measured with an empty NMR sample tube was subtracted from all the spectra. Chemical shifts were measured relative to DSS (sodium 2, 2-dimethyl-2-silapentane-5-sulfonate) as an external reference.

Results and Discussion

The water content of the as received Nafion membrane is about 5 %. The ^{1}H NMR spectra of water molecules in the hydrated Nafion membrane in the form of a single sheet presented apparently a single resonance line as shown in Figure 1 (a) at 25°C. The resonance line was considered to be broadened by the distribution of chemical shifts of the water with different structures and mobility in the chemically different environments in the membrane (23). Previously we demonstrated that the membrane presented the distinctive spectral features characteristic of the three different morphologies (designated hereafter as MI, MII, and MIII), depending on the water content and temperature. The single signal in Figure 1 (a) indicates that the polymer takes the morphology MI at 25°C.

Figure 1 (b)-(d) shows the change of the signal with time when the temperature was heated at 85°C in an open system. With the evaporation of water molecules the signal intensity decreased, the resonance line became broader and the signal shifted substantially to the down field. After 3 h the peak area decreased by 80% as compared to that before the temperature increase. On decrease of temperature back to 25°C, the peak became too broad to be observable. This broad signal can be ascribed to the very rigid water molecules with restricted mobility which remained in the membrane after the vaporization

of volatile water molecules with narrow line widths. This result indicates that sharp and broad water signals cannot be discriminated at 25°C before temperature increase. On increase of temperature, with the vaporization of the mobile water the rigid water components remaining in the system would become dominant to contribute to the broader signal. On the basis of the assignment for ^{1}H MAS NMR spectra of dried Nafion reported by Giotto et al. (10), the remained broad signal could be reasonably assigned to the water molecules strongly associated with the sulfonic group of the polymer side chain with an electrostatic interaction.
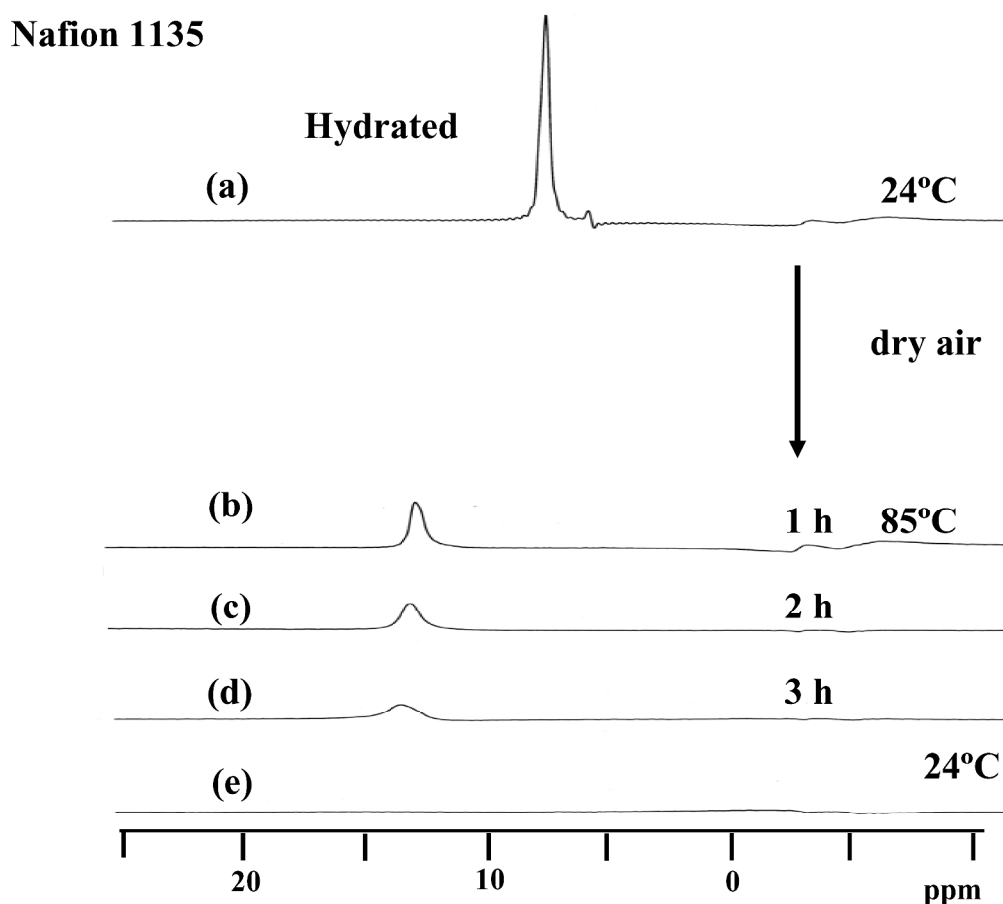
Nafion 1135

Hydrated

(a)   **24°C**

dry air

(b)   **1 h   85°C**

(c)   **2 h**

(d)   **3 h**

                                                                        24°C
(e)

| 20   10   0   ppm |

Figure 1 ^{1}H NMR spectra of hydrated Nafion 1135, measured at 500 MHz, at (a) 24°C, and 85°C (b) 1, (c) 2, (d) 3 h after the sample kept at 85°C in an open system. (e) The sample (d) was measured at 24°C.

Although as stated above the resonance line in the membrane taking the morphology MI was considered to be apparently broadened by the distribution of chemical shifts of the water with different structures and mobility in the chemically different environments in the membrane (23), this observation suggests that the distribution of the chemical shifts should be actually much larger. ^{1}H MAS NMR spectra

of dried Nafion consist of separated regions over 14 ppm (10). The hydrated membrane presented apparently a single signal because of the rapid exchange in the NMR time scale among the water molecules in the chemically different environments in the membrane. Therefore the chemical shifts and the line width changed in correlation with the change in the fraction of the each water component and the exchange rate among them. Thus, the line broadening and the chemical shift of the ^{1}H NMR signal of the hydrated membrane must be determined by the several factors such as, the mobility, the structure, the fraction, and the distribution of the chemical shifts of the water molecules in the chemically different environments in the membrane, and the chemical exchange among them. Therefore, the line broadening and the chemical shift alter sensitively with the water content and temperature. For the hydrated membrane, the bulk water molecules which move through the membrane relatively freely would present a signal with a narrow line width at higher field, supposedly around 5-4 ppm, by taking into the account that the chemical shift of the pure water solution is around 4.8 ppm at 25°C. On the other hand, the water molecules around the sulfonic group present a broad line at low field (around 9-14 ppm). On the increase of the water content, which would mean the increase of the bulk water, the apparent water signal of the hydrated membrane must become sharper and shift to the up field because of the increase in the fraction of the bulk water component in the membrane. This was evidently observed in Figure 2A.
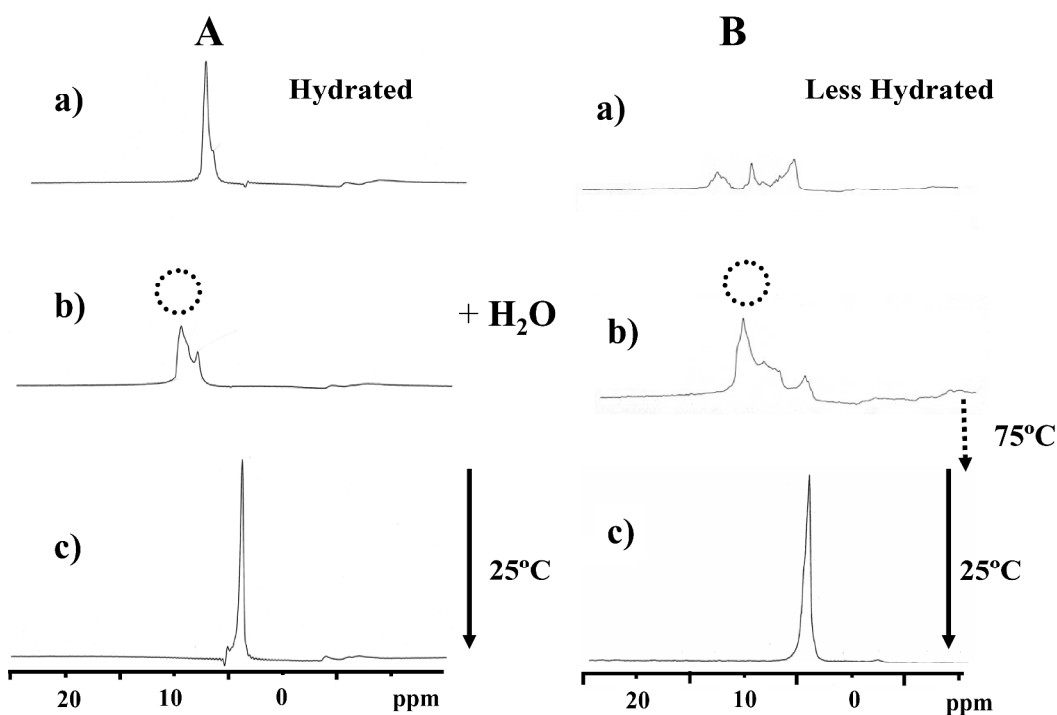

Figure 2 The ^{1}H NMR spectra of water molecules confined in Nafion membranes measured at 25°C at 500 MHz; A: (a) hydrated Nafion 1135, (b) immediately after the sample was soaked in pure water for 5 min and then wiped the excess of water on the surface with paper, (c) 20 h after the sample (b) was kept at 25°C under the air tight condition. B: (a) Less hydrated Nafion 112, (b) measured after the sample(b) was soaked

in water for 24 h and then wiped the excess of water on the surface with paper, (c) the sample was heated at 75°C under the air tight condition and measured at 25°C.

Figure 2A(b) shows the ^{1}H NMR spectrum measured immediately after the hydrated membrane was soaked in the pure water for five minutes. The signal shifted to the down field and two signals were observed. However, the spectral feature changed gradually to give a sharp intensified signal at the upper field within 20 h, as shown in Figure 2A(c). These phenomena can be explained as follows. The water molecules added would initially access the hydrophilic part of the polymer, namely the sulfonic group. Since the fraction of the water molecules around the sulfonic group increases, the signal becomes broad and shifts to the down field. The excess water molecules however gradually diffuse through the membrane to reach an equilibrium state where the fraction of the bulk water components becomes more dominant. Then the apparent signal becomes sharper and shifts to the upper field. The signal is intensified because of the increase in the total water content. Figure 2A(b) shows the transient spectrum of this process. Thus for the hydrated membrane, the line width, peak area, and the chemical shift of the water molecules change sensitively in proportion to the water content. Therefore, these parameters can be employed as a feasible measure of the water content of the hydrate membrane.

On the other hand, under less humidified conditions (less than the critical water content), the shortage of the bulk water causes the morphological conversion of the polymer (MI to MII) as reported previously. Different from that for MI, the membrane of MII presented a spectrum consisting of three distinct regions as shown in Figure 2B(a). Because of the shortage of the bulk water, the pendant group moiety of the polymer would become more rigid. Since the mobility of the water molecules around the distinct segments (hydrophilic sulfonic groups, and hydrophobic fluorocarbon main and side chains) becomes more restricted and the chemical exchange of the water molecules inter the distinct segments would become slower, the membrane presented a spectrum with the distinct regions of broad water signals. It is expected that the chemical exchange becomes rapid if the membrane is more hydrated by supplying water molecules. However, on supplying the enough amount of water by soaking the membrane in pure liquid water for 24 h at room temperature, the spectrum showed still three distinct regions although the low field region which can be assigned to the water molecules around the sulfonic group was notably enhanced. This fact indicates that the water molecules added do not diffuse through the membrane but are retained around the sulfonic group. The rapid exchange among the water molecules as observed for MI is not achieved in spite of the existence of the excess amount of water. Although MII is quite stable at room temperature, the morphological conversion from MII to MI takes place when the membrane is heated above 75°C with a supply of water molecules, as reported previously (25). Actually, after the sample in Figure 2B(b) was heated at 75°C, the membrane presented a similar spectrum to that of the hydrated membrane of MI (Figure2A(a)). This indicates that the morphological conversion to MI enables the rapid chemical exchange among the different water components. Therefore, MII is the morphology where the water molecules are highly localized at the distinct segments so that the rapid chemical exchange in the NMR time scale is not feasible.

The three distinct regions in the ^{1}H NMR spectrum in Figure 2B (b) may be categorized to the water molecules in the three different water domains localized around the polymer segments, such as hydrophilic sulfonate groups, and hydrophobic fluorocarbon main and side chains. Since the water added from outside would initially access to the hydrophilic part of the polymer, the lowest field region can be ascribed to that of the water in the vicinity of the sulfonate groups, and the other two regions to the waters around hydrophobic fluorocarbon main and side chains. By measuring the IR spectra of H_2O, D_2O and HDO in hydrated Nafion membranes, Falk reported that a substantial proportion of water molecules appeared to have an OH group (or occasionally both OH groups) exposed to the fluorocarbon environment (22).

When the samples is heated at 85°C under the humidified condition, MI and MII are converted to MIII where the chemical environments of water is more homogeneous and/or chemical exchange among water molecules is considerably rapid (23, 25), which enables the high conductivity of the polymer. The attained polymer morphology (MIII) is highly stabilized, most probably by the interaction with water molecules (23).

On the basis of the SANS (small angle scattering with neutrons) data of hydrated Nafion, Rollet et al. proposed polymeric aggregates surrounded by ionic groups and water molecules (6). On increase of temperature, the aggregates may resolve to convert to the homogeneous MIII. The bulk water spreads in the whole membrane, which enables the rapid chemical exchange among the water molecules in the whole membranes and enhances the mobility of water, resulting in the reduction of the line width of the water signal. Thus, to resolve the aggregates the provision of sufficient energy would be required by elevating the temperature up to the critical value of 75°C. The bulk water must play also an important role to attain the homogeneous state, since the conversion to MIII did not take place under less humidified conditions even at 85°C(23). The ionic conductivity of the membrane is closely related to the mobility of the water molecules in the membranes (9).

Conclusion

^{1}H NMR signals of water molecules confined in Nafion membranes with different water contents were measured under various conditions. The characteristic spectral changes of water molecules associated with the chemical exchange among the water molecules in the different water domains and the change of the polymer morphology are illustrated in Figure 3. (a) The water molecules in the hydrated membrane which takes morphology MI presents a single ^{1}H NMR signal because of the rapid exchange among the water molecules. (b) The shortage of the confined water molecules causes the morphological conversion of polymer from MI to MII. For this membrane in less hydrated states, owing to the shortage of the bulk water, the chemical exchange among the water molecules in the distinct domains is considered to be slow in the NMR time scale and three signal regions were observed, which could be attributed to the water molecules localized around sulfonate groups, fluorocarbon side and main chains. (c) On addition of water to this membrane, the water molecules initially access to the hydrophilic groups and the peak intensity of the low field region notably increased. But the three regions hold still in the spectrum since the morphology MII prohibits the rapid

chemical exchange among the water molecules at room temperature. (d) On increase of temperature above 75°C, MI and MII convert to the more homogeneous morphology MIII under humidified conditions. The morphology MIII must be favored to achieve the high ion conductivities of the membranes.
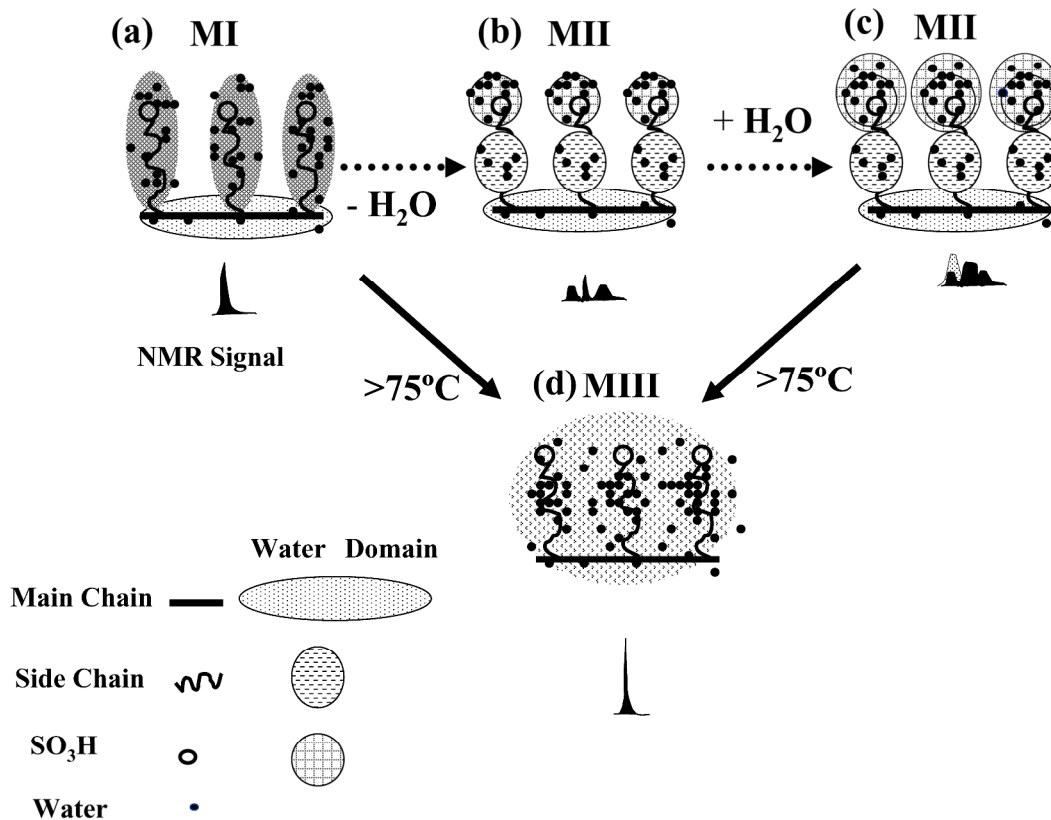

Figure 3 The characteristic spectral changes of water molecules associated with the chemical exchange among the water molecules in the different water domains and the change of the polymer morphology

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