Persistent Change in the Behavior of Water in a Perfluorinated Ionomer after Heating

Atsuko Y. Nosaka,*,† Satoru Watanabe,‡ Ichiro Toyoda,‡ and Yoshio Nosaka*,†

Department of Chemistry, Nagaoka University of Technology, Nagaoka, 940-2188, Japan, and Advanced Technology Research Center, Mitsubishi Heavy Industries, Ltd., Yokohama, 236-8515, Japan

Received March 8, 2006; Revised Manuscript Received April 25, 2006

ABSTRACT: To maintain the optimum performance of polymer electrolyte fuel cells by keeping the high ion conductivity of polymer electrolyte membranes, appropriate water managements of the membranes are required. ^{1}H NMR signals of water confined in the perfluorinated ionomer membranes used for PEFCs presented characteristic change after heating. At around 358 K, the resonance line reduced substantially, and the spectral feature was retained for a considerably long time (more than 18 days) after the temperature reverted to 297 K. The result suggests that the polymer structure was converted at around 358 K, so that the mobility of water molecules became higher and their chemical environments became more homogeneous, and that the structure was stable at room temperature. The structure is considered to be stabilized most likely by the interaction of water molecules to hold the structure even at 297 K, which keeps the mobility and homogeneity of water molecules high.

Introduction

Perfluorosulfonic acid polymer electrolyte membranes are applied widely to electrochemical devices and polymer electrolyte fuel cells (PEFC). Especially the application to PEFC has been intensified from the energy and environmental viewpoints. The membranes are composed of poly(tetrafluoroethylene) main chain with sulfoperfluoroalkyleneether side chains. The water molecules are known to play important roles for the membrane to exhibit high ion conductivity and for the cell to maintain its performance under operation.[1,2] The polymer electrolyte membranes lose their superior ion conducting properties when they are dry or under low humidified conditions. Therefore, careful water managements of the membrane are required for the cell to maintain its optimum performance under operation. For this purpose extensive efforts have been made in terms of modeling water transport and its management.[3−15] However, the detailed mechanism of the proton transport and the exact role of water in the membrane−proton interaction, which would assist to develop the membrane with improved performance, have not been clarified yet. NMR is one of the most powerful techniques to investigate the molecular dynamics and structures to characterize ionomers.[16] Numerous studies have been reported on the dynamics of polymer chains, the distribution of water in the polymer membrane, and ion or molecular diffusions by exploiting various techniques such as relaxation times, magnetic resonance imaging, and multi dimensional NMR.[6−21] ^{1}H NMR of water molecules absorbed in membranes often sensitively reflects the properties of the membrane besides the hydration level. In the present study on the careful observations of the changes of ^{1}H NMR signals against temperatures under the airtight condition, characteristic behavior of the proton signals was found, which could be applied to the efficient operation of fuel cells in the practical use.

* To whom correspondence should be addressed. E-mail: nosaka@nagaokaut.ac.jp.

† Department of Chemistry, Nagaoka University of Technology.

‡ Advanced Technology Research Center, Mitsubishi Heavy Industries, Ltd.

Experimental Section

Commercially available Nafion 112, 115, and 1135 membranes (E. I. du Pont de Nemours and Co.) were used as received (the extent of swelling is not known). 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 × 50 mm was located in a 3 mm o.d. (55 mm high) glass NMR sample tube without adding an excess of water, which was capped and carefully sealed with Teflon films to keep it airtight.

^{1}H NMR measurements were carried out on a Varian Infinity Plus 500 NMR spectrometer at 500 MHz in the temperature range of 297−358 K 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. For the measurements of the dependence of the proton signal on the applied field and the film thickness, a membrane sheet of 3 × 40 mm was located in a 5 mm o.d. glass NMR sample tube, and ^{1}H NMR measurements were carried out without sample rotation on a JEOL ECA400 and a Bruker Avance DRX 800 at 400 and 800 MHz, respectively. Chemical shifts were measured relative to DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as an external reference.

Results and Discussion

The ^{1}H NMR spectra of PEFC membranes swollen with water presented broad resonance lines. The film thicknesses for Nafion 112, 1135, and 115 membranes are 50, 88, and 125 μm, respectively, and the ratio of ^{1}H NMR peak area of their water signals was 1.0:2.0:3.3. Thus, the observed signal intensities were well correlated with the film thickness. This indicates that not only signals of the water molecules adsorbed on the surface of the membrane but also those confined inside the membrane networks were detected by NMR. However, one must also take into the account for the existence of water molecules with highly restricted mobility confined in the polymer pores which cannot be detected by NMR. The line shape was not homogeneous Lorenzian, and the broad line showed large field dependence. For all the membranes, the line width measured at 18.8 T was

10.1021/ma060511r CCC: $33.50
Published on Web 05/25/2006

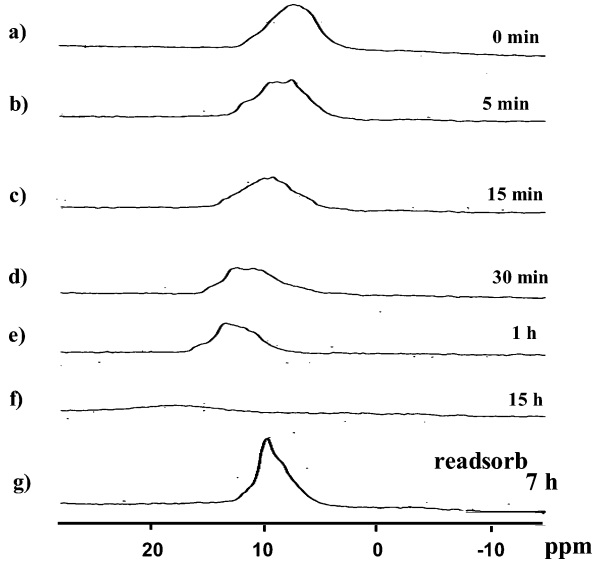

Figure 1. ^{1}H NMR spectra of Nafion 112, measured at 500 MHz at 295 K, after the sample was set under flowing dry air, for (a) 0 min, (b) 5 min, (c) 15 min, (d) 30 min, (e) 1 h, and (f) 15 h, and (g) then the sample was kept under ambient conditions at room temperature for 7 h.

about 1.6−3 times broader than that at 9.4 T. The line width of proton signals of absorbed water molecules in the membrane would be determined by the dipolar interaction between interacting protons or chemical exchange. If the resonance line is actually single and homogeneous, such large field dependence would not be observed. Therefore, the observed resonance line must be composed of the lines with different chemical shifts and line widths corresponding to the water molecules in the chemically different environments.

When the membrane sheet was kept under flowing dry air in a NMR probe, the signal intensity gradually decreased with increase of line width and the signal shifted to the downfield as shown in Figure. 1. After 15 h the peak area decreased substantially and the line width became significantly broad (Figure 1f). This broad signal could be ascribed to very rigid water molecules with restricted mobility, which remained in the system after the vaporization of volatile water molecules with narrow line widths. These results imply that sharp and broad water signals could not be clearly discriminated due to the signal overlap. Besides the signal overlap, the chemical exchange among the waters in various states could also make the discrimination difficult. With the vaporization of the mobile water the rigid water components remained in the system would become dominant to contribute to the broader signal. When the sample was kept under ambient conditions outside the NMR probe, water molecules in the air were reabsorbed gradually on the surface of the membrane to form mobile water domain. The signal intensity recovered gradually but with reduced line width (Figure 1g). The results show that the line width changes with humification conditions of the membrane. Thus, the water peak is comprised of the signals with different line widths and chemical shifts, which correspond to those of the water molecules with different structures and mobility in the different water domains in the polymer. The chemical exchange among the water molecules in the different chemical environments would be slow in the NMR time scale. The results are well consistent with the field dependence of the resonance line width stated above. Thus, the resonance line is apparently broadened by the distribution of chemical shifts. The heterogeneity of the proton signals of water molecules confined in the membrane may suggest the heterogeneity of the polymer structure.

When the sample was heated at high temperature of 358 K in an open system, the water molecules were rapidly evaporated and NMR signal intensity was substantially reduced. On the other hand, when the sample was heated gradually in a closed airtight system, the signal showed a characteristic temperature dependence. Figure 2 shows the spectral changes of the water molecules in Nafion 112 measured within the temperature range of 297−358 K. On increase of temperature, the signal shifted slightly upfield and the line width became sharper. The temperature was increased at the rate of 10 degree per 5 min.

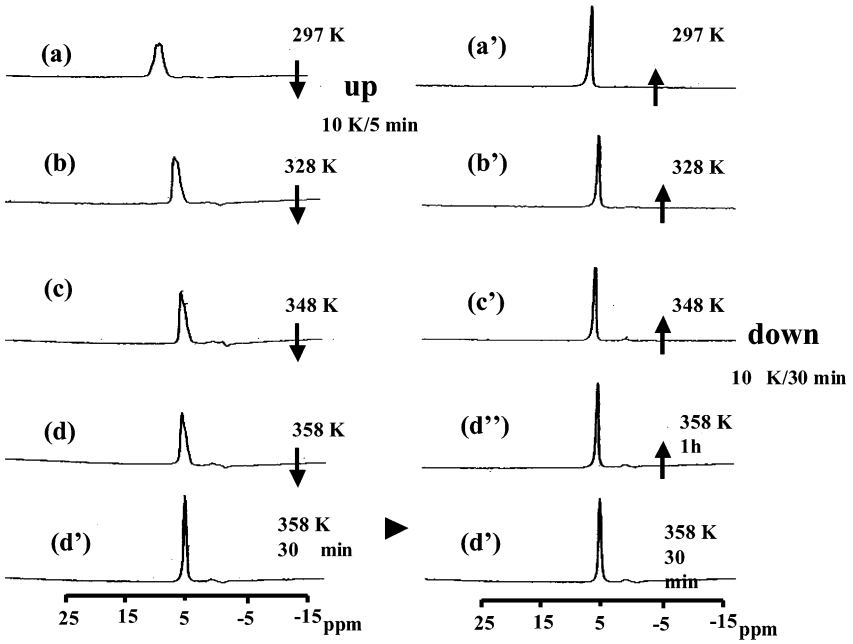

Figure 2. Temperature dependence of ^{1}H NMR spectra of water molecules contained in Nafion 112. The temperature was increased at the rate of 10 K/5 min to (a) 297 K, (b) 328, (c) 348, and (d) 358 K, and the temperature was kept at (d′) 358 K for 30 min. After the temperature was kept at (d″) 358 K for 1 h, the temperature was decreased at the rate of 10 K/30 min to (c′) 348, (b′) 328, and (a′) 297 K.

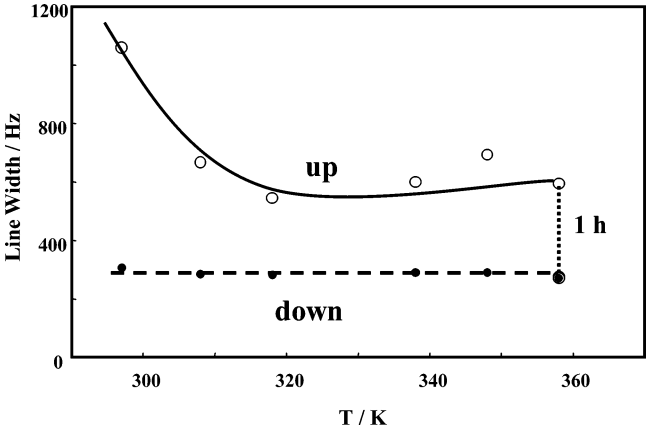

Figure 3. Temperature dependence of the line width of the ^{1}H NMR signal of water molecules contained in Nafion 112. The line widths of Figure 2 are plotted against temperature.

The line width was reduced to one-third of that before temperature increase when the sample was kept at 358 K for 30 min (Figure 2d). Furthermore, after 1 h, it did not become sharper. Then the temperature was gradually decreased at the rate of 10 K per 30 min. The line width however remained sharp after the temperature was decreased back to 297 K as shown in Figure 2a′ although it became a little bit broader. The change of the line width was plotted against the temperature in Figure 3. It is noted that the spectral feature still remained after 18 days at 297 K. On increase of temperature, the resonance line must become sharper partly because of the mobility gained. Taking into account that the resonance line is determined by the chemical shift distribution, the reduction of the line width could be also attributed to the increased homogeneity of the chemical environments of water molecules. This would mean that the polymer structure was thermally converted so that the chemical environments of water molecules became homogeneous and/or chemical exchange among water molecules became rapid. The fact that the resonance line remained sharp after the temperature back to 297 K suggests that the converted polymer structure should be stable at 297 K. This temperature dependence was reproducible. On the other hand, this characteristic phenomenon was not observed for an initial temperature increase to below 343 K. For this case, the water peak became sharper on increase of the temperature, but it became as broad as that before temperature increase shortly after the temperature was decreased back to 297 K. This fact suggests that the structural transition of the polymer membrane should take place at around 358 K. Once the polymer takes the specified structure, it must be stabilized, most likely by the interaction of water molecules since the phenomena were not observed under less humid conditions. This would mean that in the presence of enough amounts of water molecules to stabilize the structure, the polymer could hold the homogeneous structure at 297 K.

The ionic conductivity of the membrane is closely related to the mobility of the water molecules in the membranes.[9] The attained structure must be favored to achieve the high ion conductivities of the membranes. A number of models on the polymer structures in relation to the proton conductivity and water transport have been proposed.[3−15] 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, contrary to the generally accepted inverse micelle type structure.[6] Present NMR results may indicate that at around 358 K, these aggregates resolved into more flexible structures with high mobility. Although the present results do not provide direct information on the actual structures of the polymer, they call for scattering and other investigations of the hydrated-polymer structure after heating to 358 K, or at 358 K. The analysis of the polymer structure at 358 K may give us a clue how to design the novel membranes to show high performance. The characteristic change in the water signals presented in this study could be also applied to improve the efficiency of the actual operation of the PEFC since the water conductivity attained at 358 K is expected to be retained for a fairly long time at room temperature.

Conclusions

^{1}H NMR signals of water confined in the perfluorinated ionomer membranes used for PEFCs presented characteristic change on increase of temperature around 358 K. On increase of temperature, the resonance line reduced to $^1/_3$ and became more homogeneous as compared to that before temperature increase (297 K). The spectral feature held for fairly long time (more than 18 days) after the temperature reverted to 297 K. This phenomenon could be explained by that the polymer structure was thermally converted so that the chemical environments of water molecules became homogeneous and water mobility became high, and/or chemical exchange among water molecules became rapid. The structure is considered to be stabilized most likely by the interaction of water molecules to hold the structure even at 297 K, which keeps the mobility and homogeneity of water molecules high.

Acknowledgment. This work was supported by Research and Development of Polymer Electrolyte Fuel Cells from New Energy and Industrial Technology Development Organization (NEDO), Japan.

References and Notes

(1) Miyatake, K.; Watanabe, M. *Electrochemistry* **2005**, *73*, 12.
(2) Savadogo, O. *J. Power Sources* **2004**, *127*, 135.
(3) Okada, T.; Xie, G.; Tanabe, Y. *J. Electroanal. Chem.* **1996**, *413*, 49.
(4) Gebel, G.; Lambard, J. *Macromolecules* **1997**, *30*, 7914.
(5) Gebel, G.; Moore, R. B. *Macromolecules* **2000**, *33*, 4850.
(6) Rollet, A.-L.; Diat, O.; Gebel, G. *J. Phys. Chem. B* **2002**, *106*, 3033.
(7) Dianoux, A. J.; Pineri, M.; Volino, F. *Mol. Phys.* **1982**, *46*, 129.
(8) Weber, A. Z.; Darling, R. M.; Newman, J. *J. Electrochem. Soc.* **2004**, *151* A, 1715.
(9) Paddison, S. J.; Paul, R.; Zawodzinski, T. A., Jr. *J. Electrochem. Soc.* **2000**, *147*, 617.
(10) Thampan, T.; Malhotra, S.; Tang, H.; Datta, R. *J. Electrochem. Soc.* **2000**, *147*, 3242.
(11) Springer, T. E.; Zawodzinski, T. A., Jr.; Gottesfeld, S. *J. Electrochem. Soc.* **1991**, *138*, 2334.
(12) Zawodzinski, T. A.; Jr; Derouin; C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. *J. Electrochem. Soc.* **1993**, *140*, 1041.
(13) Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, *23*, 4098.
(14) Hsu; W. Y.; Gierke, T. D. *J. Membr. Sci.* **1983**, *13*, 307.
(15) Yeager, H. L.; Steck, A. *J. Electrochem. Soc.* **1981**, *128*, 1880.
(16) McBriety, V. J.; Martin, S. J.; Karasz, F. E. *J. Mol. Liq.* **1999**, *80*, 179.
(17) Pak, Y. S.; Xu, G. *J. Electrochem. Soc.* **1993**, *140*, 1237.
(18) Chen, Q.; Schmidt-Rohr, K. *Macromolecules* **2004**, *37*, 5995.
(19) Giotto, M. V.; Zhang, J.; Inglefield, P. T.; Wen, W.-Y.; Jones, A. A. *Macromolecules* **2003**, *36*, 4397.
(20) Feindel, K. W.; LaRocque, L.; Starke, P.-A. D.; Bergens, S. H.; Wasylishen, R. E. *J. Am. Chem. Soc.* **2004**, *126*, 11436.
(21) Jayakody, J. R. P.; Khalfan, A.; Mananga, E. S.; Greenbaum, S. G.; Dang, T. D.; Mantz, R. *J. Power Sources*, on the Web. 2005.

MA060511R