Estimation of Water Contents of Polymer Electrolytes
By ^{1}H NMR Spectroscopy

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Water molecules confined in perfluorinated ionomer membranes
which are widely used for polymer electrolyte fuel cells, presented
apparently a single ^{1}H NMR peak in hydrated states because of the
rapid exchange among the water molecules at the distinct segments
of the polymer. The peak shifted to the lower field with decreasing
the water content due to the decrease of the fraction of the bulk
water molecules which present a peak at higher field. The chemical
shifts were found to be well correlated with the peak area. The
water peak for MEA (Membrane Electrode Assembly) showed also
similar behaviors to the membranes. From the relationship between
the chemical shift and the peak area of the confined water peak we
demonstrated the potential that the chemical shift could be utilized
to estimate the water content in the hydrated membranes and MEA.

Introduction

Perfluorosulfonic acid polymer electrolyte membranes such as Nafion (E. I. DuPont
de Nemours and Co.) are utilized extensively for polymer electrolyte fuel cells (PEFCs).
Nafion is a membrane in which hydrophilic perfluoroalkyleneether sidechains terminated
with $-SO_3H$ are periodically attached to the hydrophobic fluorocarbon backbone. 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 (1-26).
Therefore, it is of significant importance to understand the water behavior in the
membrane. Recently we demonstrated that ^{1}H NMR spectra of the water molecules
confined in the Nafion membranes presented characteristic features reflecting the changes
in the properties of the membranes (23-26). In this study on the basis of the changes of [1]H
NMR peaks of water molecules confined in Nafion and MEA (Membrane Electrode
Assembly) at higher temperature in an open system, we will discuss the adsorbability of
the water molecules at distinctive segments of the membrane and the chemical exchange
among them, and demonstrate that the ^{1}H NMR parameters could be exploited to estimate
the water content of the hydrated membranes and MEA.

Experimental

Commercially available Nafion 112 and 1135 membranes (E. I. duPont de Nemours
and Co.) were used as received. The water content of the as received Nafion membrane is

about 5 %. Although several pre-treatments of the membranes have been recommended (17), some treatment steps significantly affected the spectral features. Therefore, we measured the membranes without any pre-treatment.

MEAs (designated as MEA/112 or MEA/1135) were prepared by spray coating a Nafion 112 or a Nafion 1135 membrane with highly disperse carbon supported catalyst materials from platinum-ruthenium alloy on the anode and platinum on the cathode. The metal loadings were 0.5 mg/cm^2 both on the anode and the cathode.

^{1}H NMR measurements were carried out on a Varian Infinity Plus 500 NMR spectrometer at 500 MHz and on a JEOL ECA 400 NMR spectrometer at 400 MHz in the temperature range of 24-85°C without sample rotation. A single sheet of the membranes or MEA was located in a glass NMR sample tube and the ^{1}H NMR spectra were measured as described previously (23). For the observation of water vaporization, the measurements were performed without a cap of the NMR sample tube. Chemical shifts were measured relative to DSS (sodium 2, 2-dimethyl-2-silapentane-5-sulfonate) as an external reference.

Results and Discussion

MEA in the form of a single sheet presented a broad ^{1}H NMR peak as shown in Figure 1 (a) at 24°C. In an MEA, water molecules are expected to be adsorbed on the various parts, such as the carbon supported catalyst materials besides the polymer membranes and the polymer electrolytes in the catalyst layers. However, as shown in Figure 1 (b) and (c) no water peak was observed for Pt/catalyst (Ketjen carbon black) and
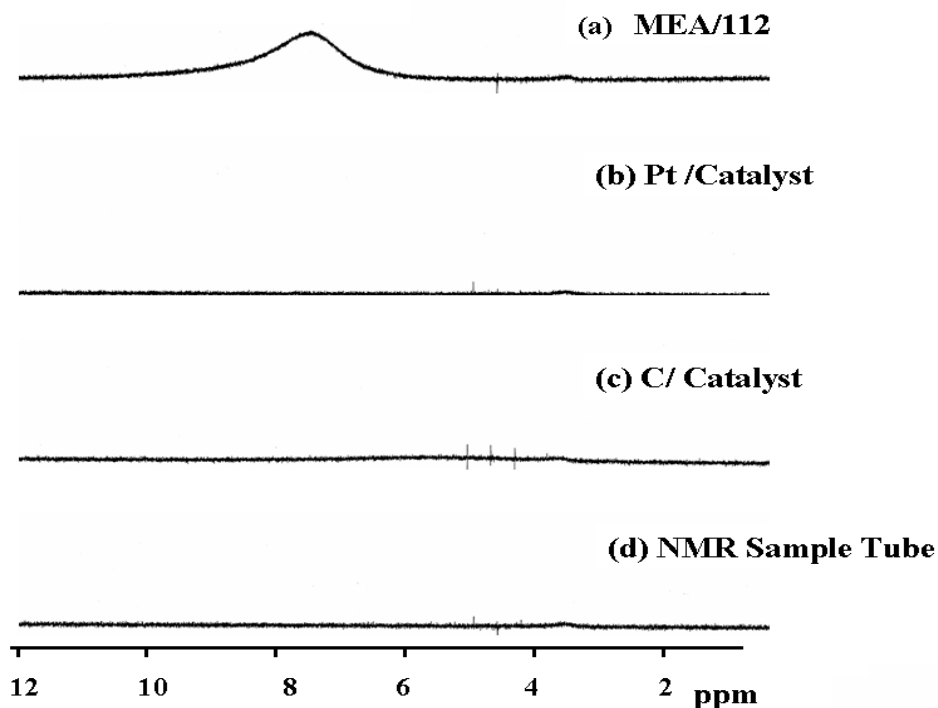

Figure 1 ^{1}H NMR spectra of (a) MEA / 112, (b) Pt/catalyst (Ketjen carbon black), (c) C/catalyst, and (d) NMR sample tube, measured at 400 MHz at 24°C.

C/catalyst. A small peak observed at around 3.5 ppm does not originate from MEA/112 and the carbon supported catalyst materials because it was also observed for the empty NMR sample tube (Figure 1 (d)). The small peak may be most probably ascribed to the water adsorbed on the NMR glass sample tube. Thus, the signal of the water molecules adsorbed on the carbon supported catalyst materials was not detected although very rigid water which could not be observed by NMR may exist. Therefore, the observed peak for MEA could be ascribed to the peak of water molecules confined in the polymer electrolytes, that is, in the Nafion membranes and Nafion in the catalyst layers.

The water molecules confined in the hydrated Nafion 1135 and MEA/1135 provide a broad ^{1}H NMR single resonance line as shown in Figures 2 (A) and (B). As stated above the peak for MEA could be ascribed to the water molecules confined in the polymer electrolytes contained in the MEA. However, the water peak for MEA is much broader than that of Nafion membrane for some reason. As reported previously, the peak of the water molecules in the hydrated Nafion membranes is considered to be broadened by the distribution of the chemical shifts of the various water molecules in the chemically different environments in the membrane (23). The broader peak for MEA may reflect the increased heterogeneity in the chemical environments of the water molecules, namely the heterogeneity of the morphology/structure of the polymer electrolytes (23).
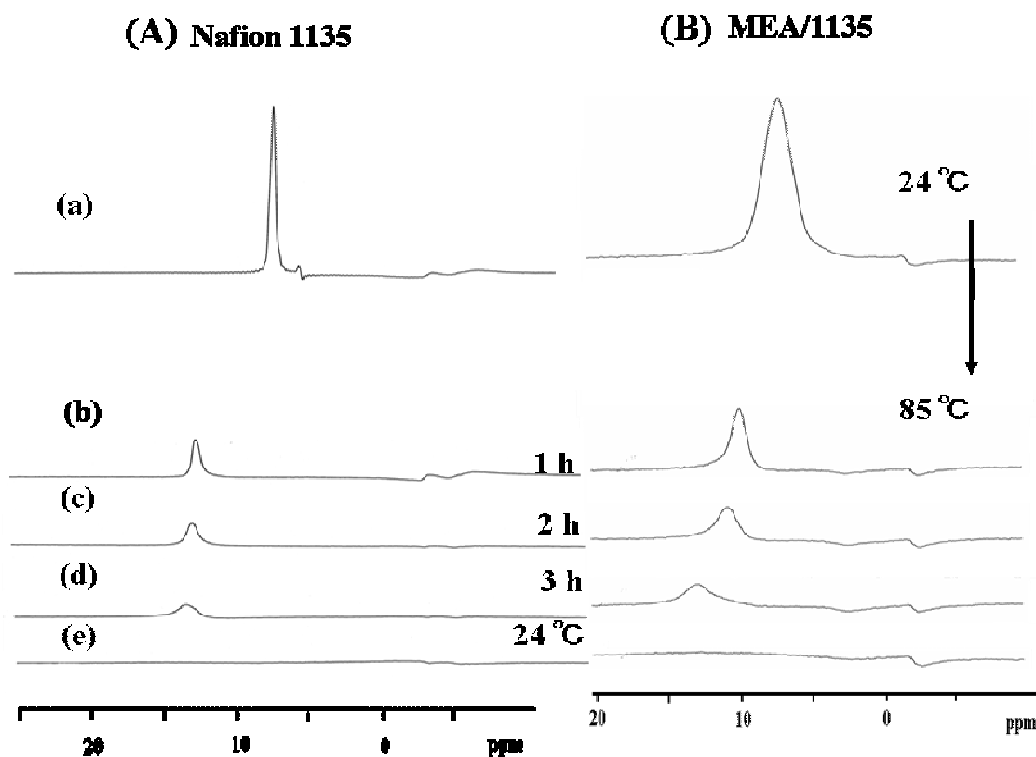

Figure 2 ^{1}H NMR spectra of water molecules confined in (A) hydrated Nafion 1135 and (B) MEA/1135 measured at 500 MHz, at (a) 24°C, and (b) 1, (c) 2 and (d) 3 h after the samples were kept at 85°C in an open system. (e) The samples (d) were measured at 24°C.

Although MEA/1135 presented a much broader peak than the Nafion1135, the water peak changed with time similarly to that of Nafion1135 (26) at higher temperature of 85°C in an open system as shown in Figure 2. At 85°C in an open system the water

molecules in the sample sheet evaporated gradually and after 3 h the peak intensity decreased significantly as compared to that before the temperature increase (Figure 2(d)). It is noted that the resonance line became broader and the signal shifted substantially to the down field. On decrease of temperature back to 24°C, the peak became too broad to be observable (Figure 2(e)) because of the reduced mobility of the water molecules due to the temperature decrease. This broad peak can be ascribed to the rigid water molecules with restricted mobility which remained in the polymer electrolytes after the vaporization of volatile water molecules with narrow line widths. The volatile water of narrow line width and the rigid water of broad line width cannot be discriminated at 24°C before temperature increase because of the rapid chemical exchange of the water molecules. At 85°C, with the vaporization of the mobile water molecules, the component of the rigid water molecules with the restricted mobility remained in the system would become dominant to contribute to the broader peak. On the basis of the assignment for ^{1}H MAS NMR spectra of dried Nafion reported by Giotto et al. (10), the remained broad peak could be reasonably assigned to the water molecules strongly associated with the sulfonate group of the polymer side chain with an electrostatic interaction.

Although as stated above the resonance line in the membrane 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), the distribution of the chemical shifts reported for dried Nafion which contains very small amount of water is actually much larger. ^{1}H MAS NMR spectra of dried Nafion consist of separated regions over 14 ppm (10). The water molecules in the different water domains localized around the polymer segments may be categorized to such as hydrophilic sulfonate groups, and 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). In the case of the dried Nafion, because of the shortage of the bulk water, the pendant group moiety of the polymer would become more rigid. Because 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 becomes slower, the membrane would present a spectrum with the distinct regions of broad water signals.

For the hydrated membrane and MEA the presence of enough amount of the bulk water enables the rapid exchange among the water molecules around the different segments in the NMR time scale. Consequently they presented apparently a single peak. 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. For the hydrated membrane, the bulk water molecules that are the most mobile component in the membrane would present a peak with the narrowest 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 24°C. On the other hand, the water molecules around the sulfonate group present a broad line at low field (around 9-14 ppm) (10, 26). Actually on the increase of the water content by adding water from outside to the membrane, which would mean the increase of the bulk water, the apparent water peak of the hydrated membrane became intensified and sharper, and shifted to the upper field because of the increase in the fraction of the bulk water component in the membrane (26). Thus for the hydrated membrane, the line width, the peak area, and the chemical shift of the water molecules altered sensitively in proportion to the water content.

The major components of the water confined in the polymer electrolyte would be the bulk water that is most mobile and present a signal at higher field close to the water of pure water solution (4.8 ppm), and the water molecules in the vicinity of the sulfonate groups which undergo strong electrostatic interaction with the hydrophilic sulfonate group and present a broader signal at lower field around 9 ppm (25). Due to the chemical exchange the apparent signal is observed at around 5-8 ppm depending on the water content in the polymer electrolyte. The observed chemical shift would be determined by the relative fraction of the bulk water and the water around sulfonate groups. Because the fraction of the sulfonate groups in the polymer is fixed, the peak would shift to the lower field with a decrease of the fraction of the bulk water. This means that the peak shifts to the lower field with a decrease of the water content, which could be verified by the above experiments of the vaporization of water by heating the membrane and MEA at 85°C. When the sample was heated at 85°C in an open system, the most mobile water molecules, that is the bulk water was eliminated gradually from the system and the peak area decreased gradually with an increase of the line width and the signal shifted to the down field because of the decrease of the relative fraction of the bulk water. After the vaporization of the mobile bulk water the rigid water components around the sulfonate groups remained in the polymer became dominant, leading to the observation of the broader peak at the lower field. The peak area of the water signal measured with time after heating the sample relative to that before temperature increase in an open system was plotted against the chemical shift values in Figure 3. As shown in Figure 3, the chemical shift value is well correlated with the peak area which represents the water contents in the Nafion 1135 membrane and MEA/1135. This observation suggests the
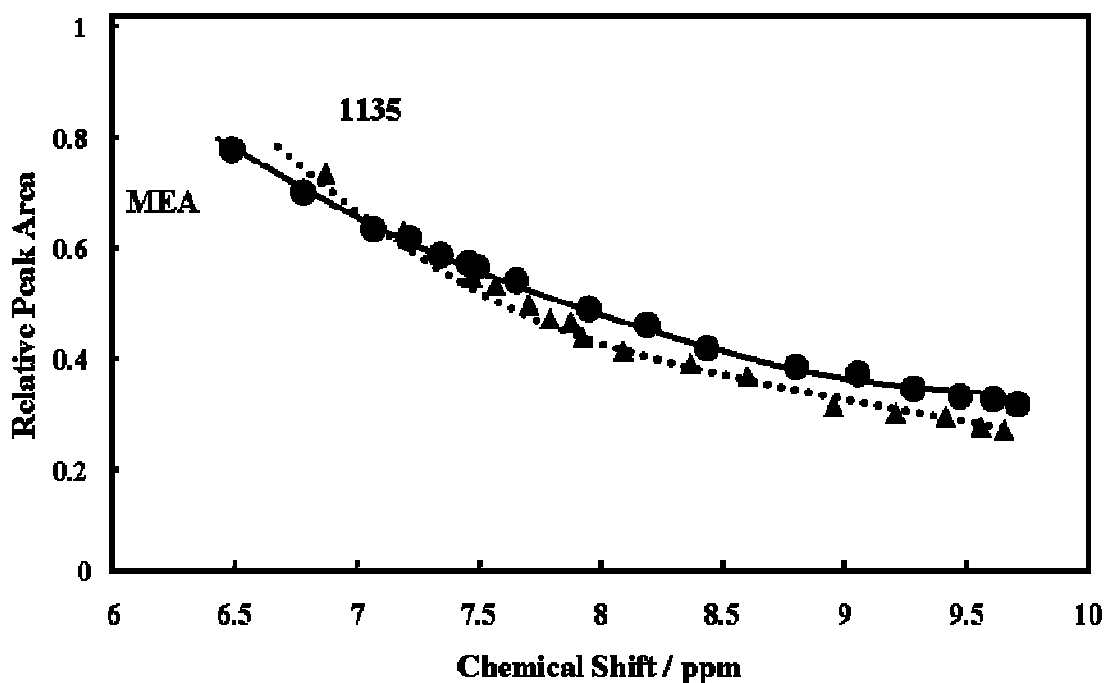

Figure 3 Relation of the chemical shift value and the relative peak area of
the water peak on heating at 85°C to that before temperature increase
in an open system, for a Nafion 1135 membrane (●) and an MEA/1135 (▲).

potential to utilize ^{1}H NMR parameters such as the chemical shift value and the peak area of the water molecules as a measure of the amount of water in the hydrated membrane and MEA. Although peak area is a direct measure of the water content, for the NMR measurements, it is affected by the sample size and magnetic field inhomogeniety. On the other hand chemical shift is barely affected by such factors. Therefore, chemical shift could be a practical measure for the estimation of the water contents.

Conclusion

Behaviors of water molecules confined in polymer electrolyte membranes and MEAs for PEMFCs were investigated by ^{1}H NMR spectroscopy. ^{1}H NMR peak of water molecules of MEA was ascribed to the water molecules confined in the polymer electrolytes contained in MEA. On evaporation the bulk water molecules in the polymer electrolytes gradually desorb from the membrane to leave water molecules around sulfonate groups. The chemical shifts changed sensitively reflecting the ratio of the fraction of the bulk water molecules to that of the water molecules around the sulfonate groups. The peak area which is a measure of the water content in the hydrated membrane was found to be well correlated with the chemical shifts. The results suggest that the chemical shifts of water peak could be exploited to estimate water content of hydrated membranes and MEA. Although peak area appears a direct measure of the water content, for the NMR measurements, it is affected by the sample size and magnetic field inhomogeniety. On the other hand chemical shift is barely affected by such factors. Therefore, chemical shift could be a practical and more precise parameter for the estimation of the water contents.

Acknowledgement

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