Mater. Res. Soc. Symp. Proc. Vol. 972 © 2007 Materials Research Society 0972-AA08-07

State of Water in Nafion 117 Proton Exchange Membranes Studied by Dielectric Relaxation Spectroscopy

Georgios Polizos, Zijie Lu, Digby D. Macdonald, and Evangelos Manias
Materials Sci & Eng, Penn State University, University Park, PA, 16802

ABSTRACT

The dynamics and the nature of water environments in a fuel cell proton exchange membrane are studied experimentally. Specifically, the dynamics of water in Nafion 117 membranes, in the acid form, were investigated at two hydration levels and several temperatures by means of dielectric relaxation spectroscopy; two different dielectric spectroscopy experimental setups were employed for low (10^{-2}-10^{7} Hz, 25 to –80 ^{o}C) and microwave (0.045-26 GHz, 35 ^{o}C) frequency ranges. Three states of water were clearly identified: (a) water strongly bound to the sulfonic groups (in quantitative agreement with previous investigations) defining the first hydration layer; (b) loosely bound water, surrounding the first layer, and (c) free water, having similar dynamics as in the bulk/liquid water. This is the first time that the dynamics of loosely bound water are experimentally observed.

INTRODUCTION

Nafion® is the commercial name of the perfluorinated ionomers manufactured by E.I. DuPont, designed with high proton conductivity so as to be used as electrolytes in fuel cell applications [1]. The conductivity mechanism is generally believed to be controlled by the proton diffusion through the membrane's water network and, as a result, several studies have focused on exploring the nature of this water [2,3]. Infrared spectroscopy (IR) [4,5] and differential scanning calorimetry (DSC) [6] can detect distinct water types: bulk-like water, at high very high hydration levels; water bound –strongly or loosely– to the SO_3^- groups, via IR signatures; and hydrophobic water, entrapped in the fluorocarbon polymer chains under certain sample preparation conditions. In addition, solid state nuclear magnetic resonance (NMR) indicates a distribution of water environments [7]. Dielectric relaxation spectroscopy (DRS) can be used to detect all these water dynamics directly, however to date it has been employed mainly in the low frequency region (< 10 MHz) and focused on conductivity studies. There, and at low temperatures, a change in the activation energy of the conductivity mechanism was observed, due to water "freezing" at about –58 ^{o}C [8]; in addition, a relaxation attributed to the rotation of SO_3^-/water complexes (first hydration layer) has also been reported [9]. Here we report a systematic DRS study, combining both low and microwave frequencies, where all three water relaxation processes with distinct dynamics are measured and identified.

EXPERIMENTAL DETAILS

Nafion 117 membrane was purchased, purified as per ref. [10], and subsequently equilibrated at controlled relative humidity (by using saturated NaCl solutions in sealed vessels);

The membrane's water content λ was set to the desired value by controlling the relative humidity in an environmental vessel and equilibrating for 3 days (λ is defined as the number of absorbed water molecules per SO_3 site and was measured with respect to the dry weight of the membrane at the end of each experiment after drying the sample at 120°C under vacuum for 12 hours).

For dielectric measurements at low frequencies (10^{-2} to 10^{7} Hz, Novocontrol Alpha Analyzer) a specimen of 20 mm diameter and 0.17 mm thickness, was sandwiched between gold-coated brass electrodes and measured isothermally (25 to –80°C, controlled via Quatro Cryosystem). The complex permittivity (ε^*) is recorded as a function of frequency and temperature.

The complex permittivity values in the microwave frequency region (0.045-26 GHz, 35 °C, HP8510C network analyzer with a 10 cm coaxial waveguide) were obtained by using the transmission line method (the amplitude ratio of the transmitted wave to the incident wave is measured, and $\varepsilon^*(\omega)$ values are calculated [11]).

DISCUSSION

Low frequency dielectric relaxation spectroscopy

For Nafion 117 at low water contents, λ~1-2, the frequency and temperature dependence of the imaginary part (ε'', dielectric loss) of the complex permittivity [$\varepsilon^* = \varepsilon' - i\,\varepsilon''$] is shown in Figure 1a. As can be observed two modes clearly contribute to the $\varepsilon''(f)$, and both are shifted to lower frequencies with decreasing temperature.

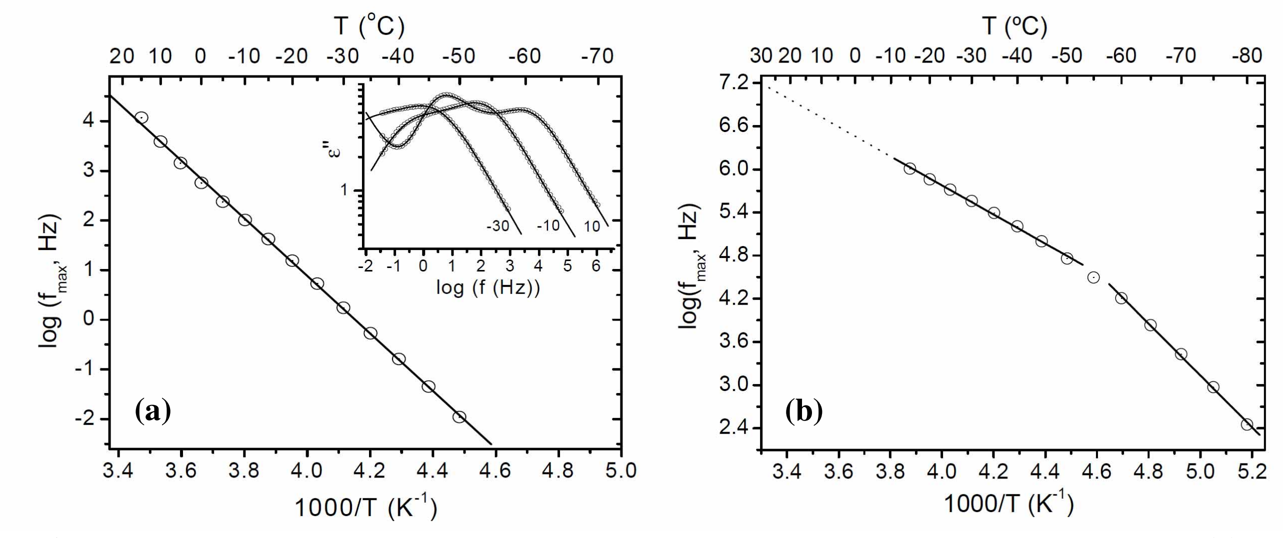

Figure 1. Dielectric spectroscopy data for Nafion 117 at two different low water contents: **(a)** λ~1-2, Arrhenius plot of the relaxation process associated with the SO_3/water complexes; this process is the high frequency relaxation (ε'' frequency peak) shown in the inset for selected temperatures. **(b)** λ=6, Arrhenius plot of the same relaxation process for a membrane that contains substantially more water. There are marked quantitative (four orders of magnitude speed-up) and qualitative (two distinct Arrhenius processes) changes in the water dynamics upon increased hydration of Nafion from λ~1-2 to λ=6 [*cf.* (a) *vs.* (b)].

Data analysis was done by the superposition of two Havriliak-Negami (HN) expressions and of a conductivity contribution [12], concurrently fitting both the real and imaginary parts of $\varepsilon^*(\omega)$:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_{i=1}^{2} \frac{\Delta\varepsilon_i}{\left[1 + \left(i\omega\,\tau_{0,i}\right)^{1-\alpha_i}\right]^{\beta_i}} - i\frac{\sigma_0}{\varepsilon_0}\omega^{-s} \tag{1}$$

where ω (= $2\pi f$) is the angular frequency, ε_0 the vacuum permittivity, $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ the relaxation strength, ε_s is the low frequency ε' limit and ε_∞ is the high frequency ε' limit, σ_0 is the low frequency conductivity, s reflects the frequency dependence of conductivity, α and β are shape parameters, and τ_0 (= $1/2\pi f_{max}$) is the relaxation time corresponding to the ε'' peak maximum ($\varepsilon''(f_{max})$) and is given by

$$\tau_{\max,i} = \tau_{o,i}\left\{\sin\left[\frac{(1-a_i)\beta_i\pi}{2+2\beta_i}\right] \Big/ \sin\left[\frac{(1-a_i)\pi}{2+2\beta_i}\right]\right\}^{\frac{1}{(1-\alpha_i)}} \tag{2}$$

The higher frequency (faster) process can be described by a symmetric distribution of relaxation times and is typically attributed to the rotation of associated (hydrogen-bonded) sulfonic/water clusters [9], whereas the lower frequency process (slower) is attributed to interfacial polarization effects [9] and is of no interest here. The water molecules associated to the sulfonic groups form the first hydration layer and this layer's dynamics are thus depicted in the fast process; the corresponding Arrhenius plot is presented in Figure 1a, where no discontinuity or change in the time scale is observed, suggesting that this is the nonfreezing (non-crystallizable over the temperature range studied) water state. Thermodynamically, the completion of this strongly bound water layer occurs at λ~3, as confirmed by equilibrium water sorption data (not shown).

By increasing the water content to λ=6 this fast process seems to shift to faster times (the corresponding Arrhenius plot is in Figure 1b). This relaxation exhibits much faster dynamics than those of the first hydration water layer (Figure 1a), and is much slower than bulk water (normal ice) [13]; moreover, the activation energy change occurs at about –55 ^{o}C (Figure 1b) and is probably due to some kind of restricted/confined water crystallization/freezing [8,6]. Hence, the origin of this mode relates either to the *rotation* of the sulfonic/water complexes –same as seen in Figure 1a– but accelerated by excess amounts of loosely-bound water, or it relates to the *polarization* of these ion-rich domains (sulfonic/water/ proton clusters) [14]. A detail investigation at several water contents is in progress, in order to further our understanding of the exact origins of these low frequency relaxations.

In conclusion, broadband (10^{-2}-10^{7} Hz) dielectric relaxation spectroscopy can only probe those water dynamics that are due to water molecules associated with and affected by the SO_3 motions. Any other type of water is expected to exhibit substantially faster dynamics, which cannot be probed by this setup, and which are expected to shift to GHz frequencies at ambient temperatures. Such experimental studies, at much shorter times, are presented in the next section.

Microwave dielectric relaxation spectroscopy

Bulk/liquid water exhibits a relaxation time of 6.48 ps and ε_s value close to 75 (microwave dielectric measurements were performed on liquid water at 35 ^{o}C, data not shown here; the data analysis indicated a single Debye process ($1-\alpha=\beta=1$) with τ_o=6.48ps and ε_s~75 in

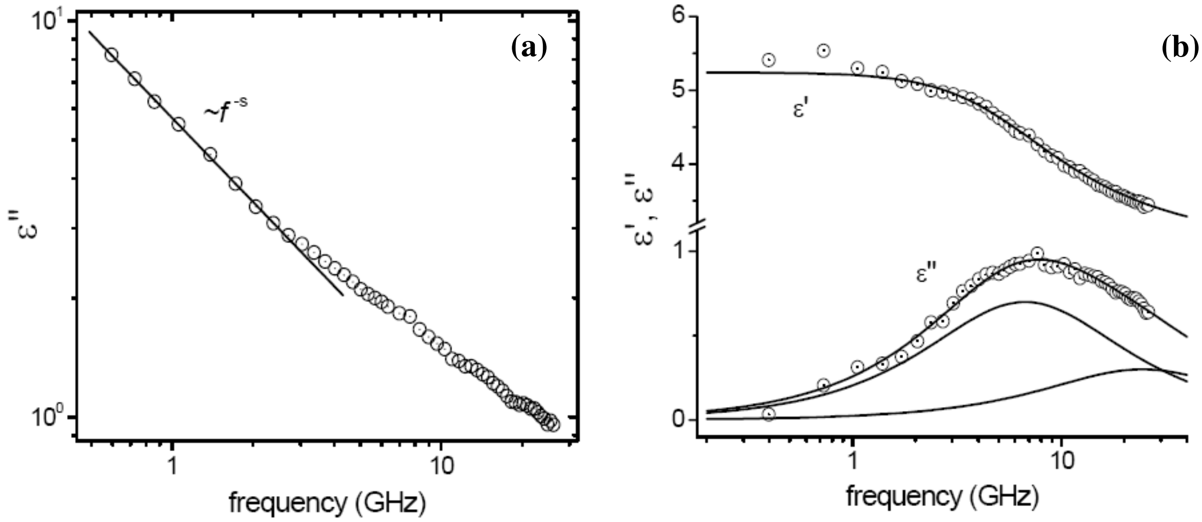

Figure 2. Real and imaginary parts of permittivity for Nafion 117 with water content $\lambda = 6$, measured in the microwave frequencies at 35 °C. **(a)** The imaginary part $\varepsilon''(f)$ including the conductivity term (indicated on the plot at the low frequencies, as $\propto f^{-s}$). **(b)** Imaginary part after conductivity subtraction, ε'', and real part, ε', of permittivity. The best simultaneous fitting to ε' and ε'' are shown as lines through the experimental points. The two components used for the ε', ε'' fit [*i.e.* the two Debye peaks in (b) under the $\varepsilon''(f)$ curve] are added to get the total ε'' and are integrated to get the total ε'. Given that dry Nafion does not exhibit any relaxations in this frequency range, *i.e.* has no ε'' peaks, these two process must correspond to water relaxations.

excellent agreement with literature [15] data). For the same temperature, 35 °C, the dielectric losses for Nafion 117 at $\lambda = 6$ are shown in Figure 2a. The low frequency linear divergence is the conductivity contribution, which results from the long-range motion of protons and can be described by a power law expression (*cf.* last term in equation 1). The exponent s takes values between 0 and 1 depending on the membrane's structure, on proton transport mechanism, and on ionic cluster and water channel formation, as suggested by several models [3]. The s = 1 value corresponds to well-interconnected clusters –water pathways– giving rise to a dc (frequency independent) conductivity, whereas lower s values correspond to ion diffusion in less-percolated/more-tortuous pathways [14]. In the plot above, s is *ca.* 0.7 for $\lambda = 6$ and reduces to *ca.* 0.5 for λ~1-2 in the low frequency (10^{-2} Hz) region. After the conductivity subtraction from the $\varepsilon^*(\omega)$, according to equation 1 and with the s mentioned above, the dielectric dispersions ($\varepsilon'(\omega)$ and $\varepsilon''(\omega)$) can be plotted (Figure 2b).

The best fitting to the experimental data were obtained by employing two Debye relaxations with high and low frequency components as shown in Figure 2b. The higher frequency component (faster mode) is relaxing at about 18 GHz and exhibits similar dynamics with liquid bulk water when measured at the same temperature. This fast mode can therefore be safely attributed to the membrane's bulk-like (free) water, which has been proposed to exist in the center of the ionic clusters and in the channels connecting them [e.g. 3, and references therein]. The lower frequency component (slower relaxation time) corresponds to a stronger peak, whose relaxation distribution at higher frequencies overlaps with the faster relaxations attributed to liquid bulk water. This slower process can result from the relaxations of water layer spatially located between the first hydration shell and the bulk water. The observed relaxation times for this water type are about ten times slower than those of the bulk water, but much faster (by more than a thousand times) than the relaxation times of the first hydration level (*cf.* Figure 1b). This water type should correspond to the water that is termed as loosely bound water or second hydration level, and its dynamics are affected by the interactions with both of the other two water environments – bulk-like and strongly bound to SO_3. This water should be freezable (an exotherm is detected in the DSC, data not shown here) and should exhibit a very broad distribution of relaxations/ dynamics that spans from the 10 MHz range to 10 GHz at ambient temperatures.

Finally, the enumeration of the relative water molecule populations within the various types of water is also possible. Specifically, the relaxation strength of the peaks ($\Delta\varepsilon$, proportional to the ε'' peak area and equal to the change in ε' before and after the process frequency) is a good measure of the density of the relaxing units and thus of each mode's population. For example, for $\lambda = 6$ the amount of bulk water is less than the loosely bound water as can be clearly seen in Figure 2b, and the values derived from the fitting analysis are $\Delta\varepsilon = 0.5$ and 1.6 respectively, or equivalently there is a *ca.* 3/1 ratio of water molecules that exhibit slower/bulk-like dynamics. The detailed study of such populations as a function of the hydration level λ can provide insights on the temporal distribution of water in Nafion and can bridge to the spatial distribution of water in the membrane, when combined with characterization studies (AFM, SAXS).

CONCLUSIONS

In this dielectric spectroscopy study of acid-form hydrated Nafion 117 we combine two different experimental set-ups which can explore time scales from 1ns to 100s (10^{10} to 10^{-2} Hz). Focusing on the water dynamics in these membranes, three relaxation processes were identified attributed to three different water states. The slowest process resulting from water molecules strongly bound to the sulfonic groups (first hydration layer) was observed in the low frequency region (10^{-2} to 10^{7} Hz), in quantitative agreement with prior work from various groups and techniques. In the GHz frequency region, two more distinct relaxations were detected for the first time: one (the fastest process) that involves dynamics similar to bulk/liquid water and is due to the membrane's free water, and a slower one due to a second hydration layer, loosely-bound to the SO_3/water clusters.

ACKNOWLEDGMENTS

The authors thank Dr. Michael Lanagan for his help and advice on microwave dielectric measurements. The authors also gratefully acknowledge the support of this work by International Fuel Cells, Inc, through Subcontract No.3540OB and the US Department of Energy through Contract No. DE-FC04-02AL67608.

REFERENCES

1. M. Rikukawa and K. Sanui, *Prog. Polym. Sci.* **25,** 1463 (2000).
2. M.A.F. Robertson and H.L. Yeager, ″Structure and Properties of Perfluorinated Ionomers″, in: *Ionomers, Synthesis, Structure, Properties and Applications*, ed. M.R. Tant, K.A. Mauritz and G.L. Wilkes (Chapman & Hall, 1997) pp.290-330.
3. S.J. Paddison, *Annu. Rev. Mater. Res.* **33,** 289 (2003).
4. W.A.P. Luck, ″Structure of Water and Aqueous Systems″, *Synthetic Membrane Processes*, ed. G. Belfort (Academic Press, 1984) pp.21-72.
5. E.E. Boakye and H.L. Yeager, *J. Membrane Sci.* **69,** 155 (1992).
6. H. Yoshida and Y. Miura, *J. Membr. Sci.* **68,** 1 (1992).
7. R.S. Chen, J.P. Jayakody, S.G. Greenbaum, Y.S. Pak, G. Xu, M.G. McLin and J.J. Fontanella, *J. Electrochem. Soc.* **140,** 889 (1993).
8. M. Cappadonia, J.W. Erning and U. Stimming, *Journal of Electroanalytical Chemistry* **376,** 189 (1994).
9. C. Tsonos, L. Apekis and P. Pissis, *J. Mater. Sci.* **35,** 5957 (2000).
10. S.J. Paddison, D.W. Reagor and T.A. Zawodzinski Jr., *J. Electroanal. Chem.* **459,** 91 (1998).
11. M.J.C. van Gemert, *Phillips Res. Repts.* **28,** 530 (1973).
12. S. Havriliak and S. Negami, *J. Polym. Sci., Polym. Symp.* **14,** 89 (1966).
13. Ya. Ryabov, A. Gutina, V. Arkhipov and Yu. Feldman, *J. Phys. Chem. B* **105,** 1845 (2001).
14. Z.D. Deng and K.A. Mauritz, *Macromolecules* **25,** 2369 (1992).
15. U. Kaatze, *J. Chem. Eng. Data* **34,** 371 (1989).