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

Zijie Lu, Hungoo Cho, Evangelos Manias, and Digby D. Macdonald
Center for Electrochemical Science and Technology
Department of Materials Science and Engineering
Pennsylvania State University
University Park, PA 16802

Dielectric relaxation spectra for hydrated and dry Nafion 117 membranes have been measured using the transmission line method over the frequency range of 45 MHz – 26 GHz and over the temperature range of 25 – 45°C. For hydrated Nafion 117 membranes (λ=12, 9, 6, 3; where λ denotes the number of water molecules per sulfonic acid group), the permittivity spectra show well-defined dielectric dispersions, and two dielectric relaxation processes were observed from the dielectric loss spectrum. A typical dielectric spectrum is shown in Figure 1, where the contribution of the conductivity, resulting from the long range motion of H_3O^+, has been subtracted from the dielectric loss, in order to obtain specific information about the state of water in the membrane. The dielectric relaxation process occurring at the higher frequency (about 18 GHz at 25°C) is attributed to the cooperative relaxation of hydrogen bonded networks of "free" water molecules. The lower frequency process (occurring at about 2 GHz at 25°C) is postulated to result from the motion of "hydration" or "bound" water.

The microwave DRS of membranes with lower water contents were also studied. Only one relaxation, corresponding to hydration water, was found for the membrane with a small amount of water (dried under vacuum at 30°C, λ~2), and no relaxation was observed for the dry membrane (dried at 150°C, λ=0). The static permittivity of the dry membrane was measured to be about 3.5.

The dynamics of hydration water and free water were analyzed from the effect of temperature on their relaxation times. The activation enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) were obtained from the Eyring equation, as shown in Table 1. $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the free water in the membrane have values that are characteristic of bulk water. The positive activation enthalpy (15.9kJ/mol) indicates that the relaxation of the "free" water involves the breaking and reforming of multiple hydrogen bonds, as expected. The positive activation entropy implies that the transition state for the rotational relaxation of "free" water molecules is a more random configuration than is the initial state. These results point to a significant degree of water-water bonding in the hydrated Nafion membranes. In contrast to the free water, the hydration water in Nafion 117 membranes shows distinct dynamics: negligible activation enthalpy and large negative activation entropy. The former suggests that the reorientation of the involved water molecules occurs readily with no H-bonds to break, and that the state of bonding in the transition state is similar to that in the initial state, while the latter implies that the transition state is a much more ordered configuration than is the initial state. The "hydration" water is assumed to comprise that associated with the sulfonic acid groups via dipole-dipole and ion-dipole interaction and that associated with hydrophobic hydration of the fluorinated side chains. The present work indicates that the hydrophobic side chains may participate in the relaxation process, which is consistent with previous infrared studies[1, 2]. Therefore, it may be concluded that a significant amount of water in hydrated Nafion 117 membranes is associated with the fluorocarbon side chain by hydrophobic hydration. Comparison of the activation energy for proton conduction with the activation enthalpies of the relaxations of hydration and free water indicates that it is the free water that controls the proton conductivity. Accordingly, optimization of the proton conductivity of the membrane requires optimization of the free water content in a manner that maintains the water in the membrane.

The fraction of free water in Nafion membranes is calculated from the dielectric dispersions. The percentage of free water increases with the total water content at each temperature. This explains the requirement of high water uptake for high conductivity. However, the most significant feature is that a larger amount of water (more than 50%) is used to hydrate the sulfonic acid group and the side chain than in facilitating proton conduction.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Michael Lanagan and Mr. Khalid Rajab for their help and discussion in 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.

REFERECENCES

1. M. Falk, *Can. J. Chem.*, **58**, 1495 (1980)
2. H.W. Starkweather and J.J. Chang, *Macromolecules*, **15**, 752 (1982)

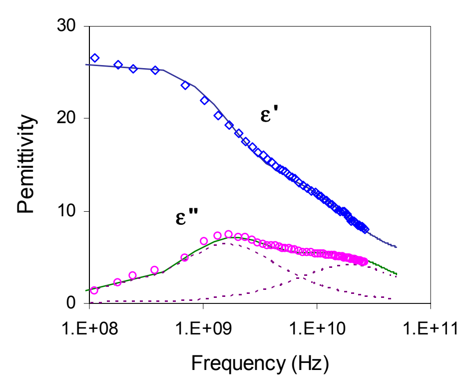

Figure 1. Permittivity ε′ (blue circles) and dielectric loss ε″ (red circles) for a Nafion 117 membrane equilibrated with saturated water vapor (λ=12) at 25°C. The contribution from conductivity has been subtracted from the dielectric loss. The solid lines are the calculated permittivity based on a two-Debye relaxation model.

Table 1. Activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, for free and hydration water relaxation in Nafion 117 membranes having different water contents per sulfonic acid group.

Sample	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (J/mol.K)
Free water	15.86	20.5
Hydration water		
λ~12	3.63	-41.07
λ~9	3.0	-35.02
λ~6	4.54	-26.64
λ~3	0.86	-37.9