DIELECTRIC RELAXATION SPECTROSCOPY STUDIES ON WATER-SATURATED NAFION 117 MEMBRANES

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ABSTRACT

Dielectric relaxation studies for water-saturated Nafion 117 membranes were carried out over the frequency range of $10^{-2} - 10^7$ Hz and at temperatures of $-140^\circ$C to 0°C. Gold-coated copper electrodes were used in a standard two-terminal cell. Nafion 117 samples were sandwiched between layers of polytetrafluoroethylene (Teflon™). The results obtained thus far recovered the intrinsic relaxations accurately and directly. Two main relaxation mechanisms were observed. The low frequency relaxation mechanism is due to the interfacial polarization, which takes place mainly at the interface between the Teflon blocking layer and the Nafion membrane. The activation energy for long-range proton motion was calculated to be 44.7kJ/mol. The high frequency mechanism is attributed to water relaxation, which takes place above $-120^\circ$C, probably reflecting the glass transition of the aqueous domains. An activation energy of 77.2kJ/mol was obtained for water relaxation in water-saturated Nafion 117 membrane.

1. INTRODUCTION

Although a great deal of effort has been made to replace Nafion as a PEM fuel cell membrane, the perfluorosulfonic polymer is the only one currently in commercial use. The unique properties of Nafion are related to its complex microstructure (1-3), which is characterized by microphase separation: a hydrophobic sub-phase formed by the fluorocarbon matrix and a hydrophilic sub-phase containing sulfonic groups, counter-ions, and water. One important feature of such a microstructure is that the hydrophobic part provides relatively good mechanical stability, even in the presence of water, while the hydrated hydrophilic domains provide for very high proton conductivity.

The proton conductivity of Nafion membranes is strongly associated with the water content. As water is added, Nafion membranes undergo a transition from being an insulator to being an ionic conductor. Wet Nafion, saturated with water vapor, has a high conductivity of about 0.06S/cm (4). Proton transport in Nafion membranes is evidently a very complicated process. It is generally believed that the excess proton mobility in water is connected to rotation of water molecules within a constantly changing network of hydrogen bonds (5,6). The dynamics of this network is particularly sensitive to a molecule’s hydrogen-bond environment. It is also clear that most of the water absorbed in these ionomers is very different from liquid water. Accordingly, knowledge of the
hydration state of Nafion membranes is expected to contribute to a basic understanding of proton conduction in this polymer.

The physical nature of water in Nafion has been characterized by several techniques. Infrared spectroscopy indicates a significantly reduced hydrogen bonding strength for absorbed water in these polymers compared to bulk water (7). Two water environments have been postulated as being associated with a void volume and an ion cluster region (8). Similar to the glassy behavior of water in confined environments at low temperatures (9), a glass transition of the water domains in Nafion was observed around 170-220K by $^1$H (10) and $^2$H (11) nuclear magnetic resonance (NMR) relaxation time measurements. In addition, differential scanning calorimetry (DSC) results for Nafion also showed the glass transitions at 180 to 210K (12).

Dielectric relaxation spectroscopy (DRS) is a powerful technique for studying the interaction of water with polymers. Several dielectric relaxation studies of Nafion membranes have been reported. In hydrated perfluorosulfonate polymers, dynamic mechanical and dielectric studies have been carried out by Yeo and Eisenberg (13). Dynamic mechanical measurements gave $\alpha$, $\beta$ and $\gamma$ relaxation processes; they were postulated to be related to main chain, polar regions, and a crankshaft motion of $-\text{CF}_2-$ groups, respectively. In isochronal dielectric measurements, two dispersions were observed in the $\beta$ relaxation region. The $\alpha$ relaxation is difficult to observe dielectrically, due to the fast desorption of water above room temperature. The $\gamma$ relaxation is shown to be dielectrically inactive. In a series of papers, Mauritz and co-workers (14-16) reported a linear segment in the low-frequency region of log ($\varepsilon''$) vs. log (f) plots, and suggested that the observed response was due to the existence of two types of hydrated clusters.

However, huge difficulties prevent the dielectric measurements for Nafion membranes. Since Nafion has high conductivity, the dielectric response is often masked by electrode space-charge effects, which arise from the motion of free charges. The frequency dependent features observed using a two-electrode geometry were shown to be consistent with well-characterized interfacial impedance and do not arise from ionic conduction in the membrane (17,18). These observations put into question the interpretation of Mauritz and co-workers.

The blocking-layer method has been used to avoid the electrode polarization (19). The method is based on the classical Maxwell-Wagner model of a layered capacitor (20). In response to the driving field, a space-charge layer develops at the sample/blocking-layer interface, where it cannot be discharged. In response to an applied sinusoidal field this space charge responds with a Debye-type relaxation at low frequency, from which a dc conductance can be derived. Teflon foils were used as blocking layers. It is a practically nonconductive, non-dispersive dielectric with a dielectric constant of 2.0.

For the purpose of determining the intrinsic dielectric response of Nafion membranes, the blocking-layer method was selected to conduct dielectric measurements. The purpose of this work was to investigate the viability of this method as well to explore methods for analyzing the raw data.
2. EXPERIMENTAL

The Nafion 117 membrane (E.I. DuPont de Nemours) was pretreated by: boiling in 3% H$_2$O$_2$, rinsing in boiling water, boiling in 0.5M H$_2$SO$_4$, and finally rinsing in boiling water (at least 1 hour for each step). The pretreated sample was stored in deionized water. A membrane treated in this manner is characterized by a water content of about $\lambda=22$ (the number of absorbed water molecules per -SO$_3^-$ site).

Differential scanning calorimetry (DSC) measurements were carried out using a TA Q-100 DSC. The sample was scanned from 25 to $-80^\circ$C to observe the water crystallization peak. The cooling rate was $10^\circ$C/min. The sample was loaded quickly in contact with the ambient atmosphere; no water loss was observed.

Dielectric relaxation spectra were collected using a Novocontrol Concept 40 broadband dielectric spectrometer. The frequency range was 0.01 Hz –10 MHz. Temperature control was accomplished using a Novocontrol Quattro Cryosystem. A very wide temperature range, -140 to 160$^\circ$C, is available. The standard 2-terminal configuration was used. Teflon films (0.0508mm thick) were inserted as blocking layers between the gold electrode and the Nafion sample.

Water loss was a problem. Tests at ambient temperature showed that almost half of the water were lost ($\lambda$ decreased to 12) during the experiment time. Thus an effort was made to minimize moisture loss by quenching the sample to low temperature (-140$^\circ$C) as soon as possible, and ending the experiment at 0$^\circ$C. The water loss during a typical experiment was thus reduced to less than 5.

3. RESULTS AND DISCUSSION

3.1 DSC results

The results of the DSC scans are shown in Figure 1. An exothermic peak, beginning at ca. $-20^\circ$C, is observed in the cooling scan, corresponding to the freezing of bulk water. The occurrence of the peak at lower temperatures is due to the depression of the freezing point of pure water by polar moieties (e.g. –SO$_3^-$) in a confined space (hydrophilic microphase).

For comparison, DSC measurement was carried out on a similar sample, which was dried in ambient environment for about 30 minutes (characterized by a water content of about $\lambda=13$). In contrast to water-saturated Nafion, no exothermic peak was observed (Figure 1). This indicated that a considerable fraction of water remains unfrozen on lowering the temperature. Water absorbed in Nafion membranes is usually considered to exist in two different states, bound and unbound. Approximately half of the absorbed water is bound to the Nafion membrane, and is not as easily desorbed as unbound water.
3.2 DRS results and equivalent circuit

A circular Nafion sample of 3.8cm$^2$ surface area was tested with Teflon blocking layers. The dielectric loss factor spectrum for water-saturated Nafion 117 membrane at different temperatures is shown in Figure 2. Two relaxation processes are observed: one occurs at low temperature and high frequency (high frequency (h.f.) relaxation (or peak)); the other occurs at lower frequency (low frequency (l.f.) relaxation (or peak)). Both relaxations move toward higher frequency with increasing temperature.

Figure 2 show that the low frequency peak has a maximum at about 100 kHz at a temperature of –10°C. Hydrated Nafion membranes showed a frequency-independent electric conductivity only at frequencies in excess of 10$^7$Hz at ambient temperature, when “standard” two terminal measurements were made (17,18). This indicated that the electric response at frequencies lower than 10$^7$Hz is dominated by ion motion and charge accumulation at the electrode interface, which gives rise to a linear increase of both the imaginary and real parts of complex permittivity. Our Nafion/Teflon sandwich is a Maxwell-Wagner two-layer capacitor. The Teflon blocking layers suppress the dc current, but induce interfacial polarization due to accumulation of free charge carriers. The low frequency relaxation in Figure 2 is just within this frequency region. This means that the low frequency relaxation of the Nafion/Teflon system may be due to interfacial polarization, which mainly takes place at the Nafion/Teflon interface.

The dielectric relaxation spectra of “dried” Nafion membrane (dried over P$_2$O$_5$) was also measured with the same procedure. Figure 3 shows the comparison of the dielectric response of these two membranes at –110°C. No high frequency peak is observed in the spectrum for the “dried” Nafion membrane. This indicates that the high frequency relaxation in water-saturated Nafion membrane arises from the water domains.
According to previous investigations (13), the water relaxation (occurring at high frequencies) together with the $\gamma$ relaxation constitutes the major softening process in the water-saturated polymer at low temperatures. The $\gamma$ relaxation was shown to be dielectrically inactive, as expected. Therefore, we attribute the h.f. relaxation to water relaxation. A detailed discussion of water relaxation is given in the following section.

The dielectric relaxation spectra are due to the combined responses from the Nafion membrane and Teflon blocking layers. This effective response can be expressed as a sum of water relaxation and a Maxwell-Wagner interfacial polarization (Figure 2). A simple equivalent circuit, as shown in Figure 4, can be used to represent the dielectric response. The principal relaxation is represented by the series combination $C_2$, $G_2$. A dc conductance, $G_0$, is needed to describe effects of free charge carriers in Nafion. $C_\infty$ is the high-frequency limiting capacitance of the dispersion; it represents electronic polarization. $C_1$ is the aggregate capacitance of the blocking layers.

If we assume that the high frequency relaxation is a Debye relaxation, the complex admittance of Nafion in the test capacitor can be represented by

$$Y = G_0 + j\omega C_\infty + \frac{j\omega C_2}{1 + j\omega \tau}$$

[1]
The effective response of the test capacitor is given by

\[ Y_{\text{eff}} = \frac{j\omega C_1 Y}{j\omega C + Y} \]  \hspace{1cm} [2]

An algorithm has been developed to obtain the volume parameters from the effective dielectric response (19). The main parameters are the high frequency relaxation time \( \tau \) and the dc conductivity \( \sigma_0 \). The computation process is given in Reference 19.

3.3 High frequency relaxation

The plot of the calculated relaxation time for the high frequency peak versus reciprocal temperature (Arrhenius plot) is shown in Figure 5. For comparison, the relaxation times of water from \(^1\text{H} \) NMR measurements by other authors (10,21) are also shown in this figure. The good agreement of these values of relaxation time suggests that both relaxations may have the same origin. Thus we may attribute the h.f. relaxation to water relaxation.

The value of the activation energy \( E \) was calculated by least-squares fitting of the Arrhenius equation

\[ \tau = \tau_0 \exp\left(\frac{E}{RT}\right) \] \hspace{1cm} [3]
where $R$ is the gas constant and $\tau_0$ is the pre-exponential parameter. The activation energy for the water relaxation in saturated Nafion 117 membrane is found to be 77.5 kJ/mol. Starkweather et. al. (21) also observed water relaxation by the dielectric relaxation method. They observed peaks in $\varepsilon''$-f plots after subtracting the background due to the electrical conductivity, while we observed the peaks directly by using Teflon blocking layers. Starkweather’s dielectric relaxation time is also shown in Figure 5. Our h.f. peaks have lower relaxation time than that of Starkweather’s (Figure 5). This may be due to the difference in water content in the two membranes; our membrane has a higher water content ($\lambda=22$) than their membrane ($\lambda=15.6$). This indicates that the shift to higher frequencies upon increasing the water content is related to the change of the pre-exponential parameter, $\tau_0$, and not to a change in the activation energy. Similar phenomena have been reported by others (13,22). These features suggest that the water dynamics on a molecular scale are identical for different water content, but geometric restrictions for water relaxation within the heterogeneous microstructure become less important with increasing water content.

3.4 Comparison with the reported water relaxations

It is widely known that water displays a Debye relaxation in the microwave (GHz) region with an activation energy of about 20 kJ/mole (23). The rotation of water molecules in liquid water is a cooperative process due to the hydrogen bond network. In ice, the Debye relaxation time, $\tau$, is 7-8 orders of magnitude longer than that in liquid water (24). The relaxation time of pure ice versus reciprocal temperature is shown in Figure 6. Also shown in this figure are the relaxation times for HCl doped ice (25), water in porous glass (26), and water in poly(hydroxyethyl methacrylate) (27). The relaxation behaviors that have been reported are quite different from that of bulk water, as shown in Figure 6. This indicates that the dynamics of supercooled water is strongly influenced by the local environment of the water molecules, which includes the influences of ions and the confined geometry.

In our water-saturated Nafion membrane, a much shorter relaxation time and higher activation energy were obtained (Figure 5 and 6). The shorter relaxation time may be explained by the “structure-breaking” effect of protons (H$_3$O$^+$). Due to the ion-dipole interaction, a certain number of water molecules will be trapped and oriented in the immediately vicinity of H$_3$O$^+$ ions. This fraction of water is called primary hydration water. They are immobilized except in so far as the ion moves and contribute little to the dielectric orientational polarization. Water molecules far away from the ion keep their bulk state, and hence are called “bulk water” or “free water”. In the region between the hydration sheath and the bulk water, the water adopts a compromise structure due to the simultaneous orienting influences of the ion and the H-bond network. These water molecules rotate more rapidly than do those in bulk water. Their contribution to the total orientational polarization could thus reduce the principal dielectric relaxation time of the solutions. The difference between the Nafion membrane and dilute electrolyte solutions is that the fraction of bulk water is much lower in the membrane because of the high ion concentration. This is also supported by the FTIR measurements, from which a significantly reduced hydrogen bonding strength was found in Nafion membranes (7). Thus a shorter relaxation time is expected, as shown in Figure 6.
Figure 4: Equivalent circuits. (a) The layered capacitor used in this work. (b) Equivalent circuit representing the unresolved relaxation spectrum. (c) The resolved high frequency relaxation spectrum. (d) The resolved low frequency relaxation spectrum (Maxwell-Wager interfacial polarization).

Figure 5: Arrhenius plot of the calculated relaxation time for the high frequency relaxation. For comparison the values found in the literature are also given in this figure. The NMR data were taken from the minimum $T_1$ (10,21). Also shown in the figure are the results of Starkweather and Chang (21).
The activation energy reflects the strength of local interactions around a water molecule. For liquid water, an activation energy of 20 kJ/mole was found for the dielectric relaxation, which reveals the number of H-bonds associated with a water molecule is about 4 (equals to the activation energy divided by the H-bond energy, about 5 kJ/mole). The higher activation energy for Nafion membrane can be explained by some stronger interaction of water molecules. The ion-dipole interaction between $\text{H}_3\text{O}^+$ and adjacent water molecules or between the sulfonic acid groups and water may provide such a strong interaction. The interaction of absorbed water molecules with the polymer matrix may also contribute. The contribution of the polymer matrix is most probably associated with the deficit of water molecules required for the formation of an extended H-bond network (26).

3.5 Low frequency relaxation (Maxwell-Wagner model)

In the low frequency region, dielectric loss is negligible, and $G_0$ dominates the response [Figure 4(d)]. The relaxation time for the low frequency peak is obtained by

$$\tau_{l.f.} = \frac{C_1 + C'_2}{G_0} = \frac{\varepsilon_0 (\varepsilon_1 / d_1 + \varepsilon_2 / d_2)}{\sigma_0 / d_2} = \frac{\varepsilon_0 (g \varepsilon_1 + \varepsilon_2)}{\sigma_0} \quad [4]$$

where $g = d_2 / d_1$ [Figure 4(a)]; $C_1 = \varepsilon_0 \varepsilon_1 (A / d_1)$, is the aggregate blocking layer capacitance; $C'_2 = \varepsilon_0 \varepsilon_2 (A / d_2)$, is the bulk capacitance of Nafion sample; $G_0 = \sigma_0 A / d_2$ is the bulk conductance of Nafion sample, $\sigma_0$ is the dc conductivity; and $\tau_{l.f.} = 1/2 \pi f_{m.l.f.}$.

The frequency of maximum loss, $f_{m.l.f.}$, which is read directly from Figure 2, versus reciprocal temperature for the low frequency relaxation is shown in Figure 7. The calculated activation energy is 44.7 kJ/mole. From Equation [4], $\sigma_0$ is proportional to $f_{m.l.f.}$. Hence, the dc conductivity, which is due to the long-range proton motion, also has an activation energy of 44.7 kJ/mole. This value is close to Cappadonia’s result (28) of 0.53eV (51.1kJ/mol) for soaked Nafion 117 membrane at temperatures below 0°C. The $\sigma_0$ values calculated from Equation [4] are shown in Table 1.

| Table 1 Extracted conductivities of Nafion 117 at different temperatures |
|-----------------|-----|-----|-----|-----|
| T, °C           | -80 | -40 | -20 | -10 |
| $\sigma_0$, S/m | 5.86×10⁻⁸| 3.50×10⁻⁶| 1.98×10⁻⁵| 4.67×10⁻⁵|
Figure 6: The relaxation time versus reciprocal temperature plots for comparison with data in the literature. 1) In the work of Feldman, water was absorbed in porous glass, which was treated by immersion in KOH solution and had a pore size of 50-70 nm (26). 2) In the work of Johari et al. (27), water (about 58% by weight) was absorbed into poly(hydroxyethyl methacrylate) (PHEMA). 3) HCl doped ice data were for single crystal fast grown from HCl solution (25). 4) The pure ice data were for the water molecule rotation (24).

Figure 7: Arrhenius plot of the maximum frequency of the imaginary part of complex dielectric constant for the low frequency relaxation.
4. CONCLUSION

The method of blocking-layers has been successfully demonstrated for determining dielectric bulk parameters of ionomers with high dc conductivity. The results obtained thus far recovered the water relaxation accurately and directly without subtracting the dc conductivity background, as did by Starkweather and Chang (21). Further, by analyzing the low frequency Maxwell-Wagner relaxation, the dc conductivity and its activation energy were obtained. However, great care must be paid to make the blocking layers and Nafion membrane microscopically smooth, uniform in thickness, and tightly adhering to each other and to the electrode surfaces, in order to eliminate artifact relaxations at high frequencies.

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