Dielectric Relaxations and Conductivity Mechanism of Nafion: Studies Based on Broadband Dielectric Spectroscopy

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The electrical performance of Nafion was investigated from -155 to 155°C in the frequency range from 10 mHz to 10 MHz and for two different hydration conditions. The electrical responses are mainly due to conductivity, electrode polarization and relaxation phenomena. These features were correlated to the molecular and nano-scale structure of the material and to the transition/relaxation phenomena observed in both DSC and DMA studies.

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Introduction

Over the past 30 years, perfluorinated polymer electrolytes such as Nafion®, Aciplex®, Flemion® and Dow membranes were the most promising materials for application in polymer electrolyte membrane fuel cells (PEMFCs) due to their chemical stability, high degree of proton conductivity and remarkable mechanical properties. The major drawbacks to large-scale commercial use of these systems involve the high cost and low proton conductivities at high temperatures and low humidity (1, 2). To overcome these drawbacks, there is a need to perform fundamental studies on the correlations existing between the mechanism of charge transport and the structure, the molecular relaxations and the water uptake of ionomer membranes. The wide variety of investigations performed in order to fulfil these aims disclosed the extremely complex nature of Nafion and resulted in a widely discussed assignment of the transition/relaxation phenomena observed in both DSC and DMA studies (1-5). Recently, some interesting studies have been reported (3-7) which: a) reconcile the differences previously observed in the thermal behaviour of Nafion as measured by DSC and DMA; and b) provide more precise explanations on the molecular origins of endothermic DSC transitions and mechanical relaxations by vibrational spectroscopy, SAXS and \textsuperscript{19}F solid-state NMR analyses. To complete these knowledges, it is of crucial importance to understand the electrical response of Nafion in terms of dielectric relaxations. In this report, Broadband Dielectric Spectroscopic (BDS) measurements were carried out on dry and wet Nafion samples. The aim of this study was to correlate: a) the mechanism of proton migration in Nafion in terms of ion migration events and host medium reorganizations to the temperature and membrane humidification conditions; b) the transition/relaxation phenomena observed in both DSC and DMA studies (1-5) to those detected by BDS measurements.
Experimental

Membrane preparation

Nafion® 117 was purchased from Ion Power. Two samples were cut from the same commercial foil and activated as reported elsewhere (4, 6, 7). The “dry” sample was obtained by drying the polymer for 48 h under vacuum at 120°C. The “wet” sample was obtained by autoclaving the material at 120°C for 35 minutes at 100% RH and then by immersing it in milli-Q water overnight at room temperature.

Instruments and Methods

Modulated Differential Scanning Calorimetry (MDSC) measurements were carried out with a MDSC 2920 Differential Scanning Calorimeter (TA Instruments) equipped with the LNCA low-temperature attachment operating under a helium flux of 30 sccm. Measurements were collected with a heating rate of 3°C/min in the -100 < T < 400°C temperature range on ca. 7 mg of sample hermetically sealed in an aluminium pan.

Dynamic Mechanical Analyses (DMA) were carried out with a TA Instruments DMA Q800 system, using the film/fiber tension clamp. Temperature spectra were measured by applying to a rectangular film sample of ca. 25(height) x 6(width) x 0.18(thickness) mm³ an oscillatory sinusoidal tensile deformation at 1 Hz with an amplitude of 4 µm (0.05 N preload force). Measurements were carried out in the -100 < T < 210°C temperature range with steps of 4°C. The mechanical response data were analyzed in terms of the elastic (storage) modulus (E’) and viscous (loss) modulus (E”). tanδ = E”/ E’ was analyzed as a function of temperature to measure the material damping characteristics.

The measurement of complex conductivity spectra were carried out in the frequency range 10 mHz – 10 MHz, using a Novocontrol Alpha-A analyzer. The temperature range from -155 to 155°C was explored by using a home-made cryostat operating with an N₂ gas jet heating and cooling system. The measurements were performed using a closed home-made cell. This cell allowed us to maintain the membrane wet during the measurements as follows: the freshly-autoclaved membrane, sandwiched between two circular platinum electrodes, was located inside a cylindrical Teflon cell. The free volume was partially filled with 100 µL of bidistilled water in order to avoid drying during the measurements up to 155°C. The geometrical constant of the cell was determined by measuring the electrode-electrolyte contact surface and the distance between electrodes with a micrometer. No corrections for thermal expansion of the cell were carried out. The temperature was measured with an accuracy greater than +/- 0.05°C. The absence of water loss during measurements was checked by weighing the closed cell before and after measurements. The complex impedance $\tilde{Z}(\omega) = Z'(\omega) + iZ''(\omega)$ was converted into the complex conductivity $\sigma^{*}(\omega) = \sigma'(\omega) + i\sigma''(\omega)$ and permittivity $\varepsilon^{*}(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ spectra using equations $\sigma'(\omega) = k[Z'(\omega)]^{-1}$ and $\sigma''(\omega) = i\omega\varepsilon'(\omega)$, where $k$ is the cell constant in cm⁻¹ and $\omega = 2\pi f$ (f is the frequency in Hz).
Results and Discussion

Thermal analysis

The thermal behavior of Nafion membranes was studied collecting DSC measurements from -100°C to 400°C. The DSC profiles of dry and wet samples are shown in Figure 1 a) and b), respectively.

![DSC curves of dry a) and wet b) Nafion membranes. Dashed lines indicate the decomposition by Gaussian functions of the DSC profiles. Insets show the low-temperature region.](image)

Figure 1. DSC curves of dry a) and wet b) Nafion membranes. Dashed lines indicate the decomposition by Gaussian functions of the DSC profiles. Insets show the low-temperature region.

Two transitions were detected at -56°C and -40°C for both the dry and the wet samples (insets of Figure 1a and Figure 1b, respectively), which were attributed to the order-disorder molecular rearrangements in the hydrophobic perfluorinated domains of Nafion. This assignment was carried out considering that: a) the fluorinated domains of Nafion are similar to those of Teflon; b) the $T_g$ of PTFE was detected in a broad range of temperatures, from 160 to 240 K, with a midpoint at about 200 K (-73°C) (8, 9). An endothermic event was revealed at -5°C for both samples, which was ascribed to the melting of water. This latter event is much more intense in the wet sample with respect to the dry one. In accordance with other studies (4), Nafion membranes show three overlapping endothermic peaks which were indicated as I, II and III. Peak I was detected at 143 and 140°C, respectively for dry and wet Nafion. In accordance with other studies, peak I was assigned to the order-disorder molecular rearrangement transition which occurs owing to the polymer relaxation processes taking place inside the hydrophilic
polar clusters of Nafion. It can be observed that, with respect to the dry sample, Peak I is sharper in the wet Nafion. This evidence indicates that in the hydrated ionomer the –SO$_3$H terminal groups of polar domains are solvated by water molecules which are forming clusters with a more ordered structure. The different intensities shown by Peak I in the two samples suggest this attribution. Indeed, structural features based on hydrogen bonding and strong dipolar interactions such as those expected in hydrated polar cages should be energetically stronger than those generated by weak and disordered dipolar interactions, such as those expected in the polar cages of dry Nafion. Peak II was detected at 202 and 188°C in the dry and wet samples, respectively. Peak II was attributed to the endothermic decomposition of acid –SO$_3$H groups. Peak III was found at 235 and 223°C, in the dry and wet samples, respectively. In accordance with other studies (4), Peak III was assigned to the melting transition of hydrophobic microcrystalline fluorocarbon regions of Nafion membranes.

**Dynamic Mechanical studies**

The effect of water content on the mechanical properties of dry and wet Nafion membranes was investigated by DMA measurements carried out by subjecting a rectangular sample film to an oscillatory sinusoidal tensile deformation at 1 Hz with a mechanical elongation of 4 µm (see the Experimental section). The temperature spectra of storage (E’) and loss (E’’) modulus and tanδ are shown in Figure 2.

![Figure 2. Temperature spectra of storage (E’) and loss modulus (E’’) and tanδ of dry and wet Nafion117 membranes. The assignments of relaxation modes are reported.](image-url)
It can be observed that the irreversible elongation of samples occurs at temperatures above 170°C. The value of the storage modulus at room temperature, owing to the plasticizing effect of water: a) depends on the water uptake of Nafion; b) is higher for the dry membrane. Both dry and wet Nafion samples at T ~ 100°C exhibit the typical α-relaxation event. This latter mechanical relaxation mode, which was attributed to the motions in cluster aggregates of side chains (4), is the main feature of the tanδ profiles shown in Figure 2. The loss of energy corresponding to the α-peak is higher in the wet than in the dry sample, thus suggesting that the strength of hydrogen bonding network is higher in the wet than in the dry polar cages of host polymer. The two β relaxation modes revealed at ca. 4 and 24°C in the dry sample and at 0 and 20°C in the wet sample were assigned to the main chain motions of the fluorocarbon bulk domains of Nafion. The presence of two β peaks indicates that fluorocarbon chains are distributed in two different PTFE domains. In summary, water uptake influences the dynamics of host polymer decreasing β-relaxation events by 4°C (i.e., plasticizing effect of hydrophilic domains). Another relaxation event was detected at ca. -40°C and -72°C for the dry and wet Nafion, respectively which, in accordance with other studies (1, 2), was assigned to the γ relaxation mode of CF2 local motions.

Broadband Dielectric Spectroscopy studies

The real components of conductivity spectra (σ'(ω)) are shown in Figure 3 a) and b), respectively, for the dry and wet Nafion membranes.

Figure 3. Selected real conductivity spectra of dry (a) and wet (b) Nafion117 membranes. The measurements were carried out in the frequency region 10 mHz-10 MHz with a temperature step of 10°C.
The spectra of dry Nafion are reported from -155°C to 105°C owing to the collapse of the electrical response above 105°C. This conductivity breakdown in wet Nafion was observed at T > 145°C (Figure 3b). The values of \( \sigma'(\omega) \) of the dry membrane (Figure 3a) range from ca. 10^{-17} Scm^{-1} to 10^{-7} Scm^{-1}, thus indicating that in this condition Nafion is a dielectric material. At temperatures higher than 0°C, \( \sigma'(\omega) \) spectra of dry Nafion exhibit a frequency-independent feature. The \( \sigma'(\omega) \) values measured in this plateau correspond to the \( \sigma_{dc} \) values of bulk material (Figure 4). The analysis of \( \sigma'(\omega) \) profiles of Figure 3b shows that the wet Nafion membrane can be considered a dielectric material for temperatures lower than 0°C (\( \sigma'(\omega) < 10^{-7} \text{Scm}^{-1} \)). It should be observed that after the melting point of water (T > 0°C): a) the \( \sigma'(\omega) \) of the membrane increases abruptly; b) a new \( \sigma'(\omega) \) plateau is observed at high frequencies, which is thermally stimulated. In detail, the frequency profile of the conductivity spectra of the wet Nafion membrane at T > 0°C shows two different plateaus. The first is measured at \( \nu < 10 \text{ Hz} \) and the second at \( \nu > 10^5 \text{ Hz} \).

![Figure 4](image-url)

Figure 4. Dependence of \( \sigma_{dc} \) on the reciprocal of temperature for dry and wet Nafion membranes. Three conductivity regions are detected and singled out as VLT (very low temperature), LT (low temperature), and HT (high temperature). In VLT and LT regions the conductivity curves were fitted by Arrhenius-like equations (dotted lines), while in HT region by VTF relations.

The \( \sigma_{dc} \) values determined in the first and second plateau are reported in Figure 4 and are indicated respectively as \( \sigma_{dc1} \) (low-frequency plateau) and \( \sigma_{dc2} \) (high-frequency plateau).
The dependence on $1/T$ of $\sigma_{dc}$ values reported in Figure 4, reveals that: a) at temperatures lower than 0°C the $\sigma_{dc}$ values are determined only for the wet sample, which shows two different Arrhenius-like trends; b) the change in slope of the two Arrhenius-like trends is localized at -45°C, which corresponds to the Nafion glass transition event measured at -40°C in the DSC profiles; c) at $T > 0$°C both samples show a VTF-type dependence of conductivity on temperature; d) $\sigma_{dc2}$ presents values four orders of magnitude higher than those of $\sigma_{dc1}$. Taken together, the $\sigma_{dc}$ profiles shown in Figure 4 describe three different temperature regions, which are singled out as VLT (Very Low Temperature, from -155°C to -45°C), LT (Low Temperature, from -45°C to -5°C), HT (High Temperature, from 5°C to 155°C). Results suggest that in the VLT and LT regions the bottleneck of conductivity is the proton migration between different polar domains of bulk Nafion. It should be observed that in the VLT region: a) water is crystallized in polar cages; and b) perfluorinated chains are ordered in crystalline domains. Furthermore, in the LT region water is in its crystallized form and perfluorinated chains are above their $T_g$ value, thus they are in a more disordered and dynamic state. The activation energy of conduction in LT region is higher than that of VLT, probably owing to the inhibited segmental motion of fluorocarbon domains caused by crystallized water clusters present in side polar cages and interconnecting channels of the material. In HT the relaxation dynamics of both hydrophobic and hydrophilic domains are contributing to the overall conductivity. In this region, charge exchanges between polar groups are facilitated owing to a peristaltic-like modulation of polar domains caused by the relaxations of perfluorinated chains (4). The activation energies determined by the VTF and Arrhenius-like fits of the $\sigma_{dc}(1/T)$ curves in the above-described regions are reported in Table I.

### Table I. Activation Energies ($E_{\sigma_{dc}}$) determined by fitting VTF and Arrhenius Equations to the dependence on temperature of $\sigma_{dc}$ with $i = 1$ and 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{dc1}$</th>
<th>$\sigma_{dc2}$</th>
<th>$E_{\sigma_{dc1}}$/kJ·mol$^{-1}$</th>
<th>$E_{\sigma_{dc2}}$/kJ·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion117</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry</td>
<td>1</td>
<td>35.14±8.2 V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet</td>
<td>1</td>
<td>7.8±1.7 V</td>
<td>84.03±7.4 A</td>
<td>32.74±1.8 A</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.50±0.16 V</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$) HT, LT and VLT are the temperature ranges respectively of 155/-5, -5/-45, -45/-85°C.

$^b$) Activation energy determined by VTF equation: $\sigma_{k,i} = A_{\sigma_{k,i}} \cdot \Gamma(i,T) \cdot e^{-E_{\sigma_{dc}}/RT}$.

$^c$) Activation energy determined by Arrhenius-like equation: $\sigma_{k,i} = A_{\sigma_{k,i}} \cdot e^{-E_{\sigma_{dc}}/RT}$.

It can be observed that in the HT region the activation energy of the wet sample is about one order of magnitude lower than that shown by the dry Nafion. The three-dimensional representations of the imaginary component of permittivity curves, $\varepsilon''(\omega)$, are shown in Figure 5 a) and b) for the dry and wet Nafion membranes, respectively. In the case of dry Nafion it is possible to observe that when the temperature is ranging from -155°C to -45°C no significant relaxation is detected in $\varepsilon''(\omega)$ profiles. At temperatures above -45°C, a steep increase of $\varepsilon''(\omega)$ is observed at low frequencies which progressively increases in intensity as the temperature is raised. This electrical feature was ascribed to the interfacial Maxwell-Wagner electrode polarization phenomenon, which occurs in heterogeneous systems when they are endowed with boundaries between components characterized by a different dielectric constant. The fact that this latter event
is detected at temperatures above the $T_g$ of Nafion (see DSC results) confirms that the conductivity in this region is correlated to the segmental motion of fluorocarbon chains. Two further events are measured in this temperature region which are overlapped to the above-mentioned electrode polarization phenomenon of Nafion, and are indicated in Figure 5 a) as $\alpha$ (at lower frequencies) and $\beta$ relaxation modes. Both $\alpha$ and $\beta$ relaxation modes shift toward higher frequencies as temperature increases. The $\alpha$ mode was attributed to the relaxation of perfluorinated backbone chain dynamics, while $\beta$ mode corresponds to the relaxation of Nafion side chains bearing the sulfonic acid group. In summary, Figure 5 shows that in dry Nafion: a) the conductivity effects are detectable for temperatures higher than -45°C, i.e. after the glass transition of Nafion; b) the conductivity is associated to the interfacial electrode polarization phenomenon; c) the conductivity values and electrode polarization effects increase as the temperature rises; d) two relaxation phenomena ($\alpha$ and $\beta$) are detected, which shift toward higher frequencies as the temperature is raised.

![Diagram of permittivity dependence on frequency and temperature for dry (a) and wet (b) Nafion 117 membranes.](image-url)
The $\varepsilon''(\omega)$ spectra of wet Nafion, shown in Figure 5 b), present an abrupt change at the water melting point and at $T < 0^\circ C$ reveal three relaxation modes. The latter are indicated in Figure 5 b) by arrows and labeled as $\alpha$, $\beta$, and $\gamma$ modes. $\alpha$ and $\beta$ relaxation events were assigned to the same molecular relaxations mentioned above for the dry Nafion sample, while $\gamma$ relaxation was ascribed to short-range motions of CF$_2$ groups composing the fluorocarbon backbone chains of Nafion. It should be noticed that with respect to the dry sample, in wet Nafion: a) the $\beta$ relaxation is shifted toward higher frequencies owing to the easier dynamics of sulfonic acid groups in polar cages; b) the $\gamma$ relaxation is observed as the movements of fluorocarbon backbone chains in these conditions are facilitated. At $T > 0^\circ C$ the $\varepsilon''(\omega)$ profiles of wet Nafion are dominated by two distinct polarization phenomena, localized in the low- and high-frequency wings of the $\varepsilon''(\omega)$ spectra, which are correlated respectively to the above-mentioned $\sigma_{dc1}$ and $\sigma_{dc2}$ values. In general, the value of $\sigma_{dc2}$ is higher than that of $\sigma_{dc1}$. The presence of two polarization events with two distinct conductivity values can be rationalized on the basis of the morphology of the material. Taken together, the polarization event peaking in the material at low frequencies was attributed to the interfacial polarization or Maxwell-Wagner phenomenon which occurs in heterogeneous systems when they are endowed with boundaries between components with different dielectric constants (10). Thus, when differences in the conductivity of the phases composing an inhomogeneous medium occur, an interfacial polarization is generated which corresponds to the buildup of space charges near the interfaces between the various phases. The high-frequency polarization event was ascribed to the electrode polarization phenomenon which gives rise to the conductive relaxations associated to ion accumulation processes near the electrodes rather than dielectric relaxations (11). This high-frequency polarization is observed only for the wet Nafion sample. Indeed, only in highly hydrated polar domains fast, long-range charge transport mechanisms can occur. In the $\varepsilon''(\omega)$ curves of wet Nafion at $T > 0^\circ C$ both $\alpha$ and $\beta$ relaxations, clearly observed at $T < 5^\circ C$ (see Figure 5b), were detected. Both modes are overlapped to the above-described electrode polarization phenomena. Figure 6 a) and b) shows the tan$\delta(\omega)$ profiles of the dry and wet Nafion samples.
Figure 6. Dependence of $\tan \delta(\omega) = \varepsilon'(\omega)/\varepsilon''(\omega)$ vs. frequency for selected temperatures of dry a) and wet b) Nafion117 membranes.

It is to be noticed that the above-mentioned relaxation events are easily detected in $\tan \delta(\omega) = \varepsilon'(\omega)/\varepsilon''(\omega)$ temperature spectra (Figure 6), where the contribution of electrode polarization phenomena is mostly negligible. Figure 6 a) confirms that in the temperature range between -155°C and -45°C the $\tan \delta$ values of dry Nafion are nearly frequency-independent. For temperatures ranging from -45°C to 5°C the peak assigned to the $\beta$ mode is revealed. At temperatures in the range between 5°C and 105°C both $\alpha$ and $\beta$ relaxations are easily observed. In Figure 6 b) the $\alpha$, $\beta$ and $\gamma$ relaxations of wet Nafion membranes are clearly observed. The abrupt change of $\tan \delta$ profiles occurring between -5 and 5°C clearly indicates that after the water melting transition in bulk Nafion membranes, the $\beta$ relaxation is shifted toward lower frequencies. This phenomenon is probably associated to polymer host reorganization events which occur owing to a decrease of Nafion porosity generated when the water melting process reduce the volume of the polar clusters of bulk polymer.

Conclusions

The BDS investigations carried out on Nafion117 in dry and wet conditions allowed us to detect the relaxation events responsible for long-range proton transport mechanisms along interconnecting channels and polar hydrophilic clusters of Nafion membranes. It was possible to determine that the conductivity in Nafion takes place owing to charge exchange processes occurring between different water domains embedded in the bulk...
material which are modulated by the segmental motions of fluorocarbon backbone domains of Nafion polymer. These results are confirmed by DSC and DMA studies.

Acknowledgments

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References