



Nafion β -Relaxation Dependence on Temperature and Relative Humidity Studied by Dielectric Spectroscopy

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Nafion β -relaxation was studied by detailed dielectric spectroscopy measurements carried out in a wide range of both temperature and relative humidity. Cast and extruded Nafion were compared in the H^+ , Na^+ , and Cs^+ forms to evaluate contributions arising from membrane morphology and ionic interactions. The experimental data indicated that β -relaxation is associated with the motion of side chains of the ionomer. The unusual shift to lower frequencies of the β -relaxation was shown to be more pronounced for samples containing high water content and at temperatures above the α -relaxation, evidencing that the electrostatic repulsions between bare sulfonic groups reduce the side chain mobility. A pronounced increase of relaxation times was observed at relative humidity $>60\%$ suggesting a change of the morphology of the ionomer, in agreement with recent descriptions of the Nafion structure by small angle X-ray scattering analyzes.

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Nafion is considered one of the best proton conductors at low temperatures ($\sim 80^\circ\text{C}$) and has been extensively used as the electrolyte of Proton Exchange Membrane (PEM) and Direct Alcohol Fuel Cells (DAFC).^{1,2} More recently, such ionomer has been investigated as the polymeric matrix of composite electrolytes for fuel cells operating at higher temperatures ($\sim 130^\circ\text{C}$).^{2–4} It has been reported that at operating temperatures close to the water boiling point the performance of both PEM and DAFC are severely decreased as compared to the optimal operating conditions ($\sim 80^\circ\text{C}$).^{2,3} The main cause for the low performance at high temperatures is related to the low proton conductivity due to both the loss of water and the morphological instability associated with the polymer α -relaxation ($T_\alpha \sim 110^\circ\text{C}$).⁴ Therefore, understanding the properties of Nafion at conditions similar to the ones of fuel cell operation is a relevant issue that has attracted a great deal of attention.^{5,6}

In the last decades the structure of Nafion has been extensively investigated by small angle X-ray (SAXS) and neutron (SANS) scattering techniques as a function of both water content and temperature.^{7–11} Relevant information has been gathered evidencing the existence of ubiquitous TFE-like nanocrystallites and clustered ionic group-terminated side chains embedded in an amorphous hydrophobic matrix. Such a complex arrangement results in entangled dynamical properties of Nafion membranes that have been studied by dielectric spectroscopy (DS) and dynamic mechanical analysis (DMA) as a function of both temperature and membrane water content.^{12–15}

Nafion in the Na^+ form was probed by DMA and four distinct relaxation processes, namely γ , β' , β'' , and α , were identified with increasing temperature.¹⁶ The γ -relaxation occurring at $T_\gamma \sim -100^\circ\text{C}$ was attributed to the motion of backbone TFE segments. The β'' -relaxation, centered at $T_{\beta''} \sim -30^\circ\text{C}$, was associated with motions of the ether containing side chains. The β' and α -relaxations were assigned to the glass transition of the polymer matrix ($T_{\beta'} \sim 130^\circ\text{C}$) and of the ionic clusters ($T_\alpha \sim 240^\circ\text{C}$), respectively.¹⁶

However, both DMA and DS measurements revealed that the identification of α and β -processes were the most challenging ones owing to their dependence on both the membrane water content and the ionic form.¹⁷ It has been observed that β' and β'' relaxations shifted to lower temperatures with increasing water content as a result of a plasticizing effect, whereas both the α -relaxation intensity and T_α increased when Nafion in the acid form was gradually neutralized with Cs^+ counterions.¹⁷ Such features have cast doubts on the molecular origins of β and α -relaxation phenomena and have prompted the

reassessment of β and α -relaxations by different authors.^{12,13,18–20} In fact, the analysis of the dielectric spectra of Nafion is currently under debate.^{13,20} One of the main points discussed concerns the assignment of the dispersion at high frequency, which has been attributed to either a relaxation (β)¹³ or to electrode polarization.²⁰ Both interpretations consider crucial aspects and have presented convincing supporting arguments.

However, recent dielectric spectroscopy measurements over a wide temperature range revealed that the temperature dependence of β -relaxation times followed the Vogel-Fulcher-Tamman (VFT) behavior, typical of glass transition.^{12,13} Nuclear magnetic resonance (NMR) and DMA studies of Nafion neutralized with a series of protonated alkylammonium counterions evidenced that β and α -relaxations exhibit similar dynamics, suggesting that these relaxations are coupled.¹² In this context, the α -relaxation was attributed to the long range motion of backbone main and side chains via destabilization of the ionic cluster network and the β -relaxation accounted for the main chain segmental motions within the framework of the electrostatically cross-linked ionic groups.^{12,13}

Despite the information gathered about β -relaxation some unusual properties reported remain poorly understood.^{13,18,20,21} Previous DS measurements evidenced that the T -dependence of Nafion β -relaxation displayed an unconventional deviation of the thermal activated behavior in which a shift to low frequencies was observed for $T > 80^\circ\text{C}$.^{13,18} In addition, DS measurements on short side chain perfluorosulfonic acid polymers ($EW = 795 \text{ g} \cdot \text{mol}^{-1}$) revealed that the high frequency relaxations shifted to lower frequencies as the ionomer hydration increased from 45% to 100%.²¹ Such frequency dependence is unexpected from the standpoint of traditional polymer dynamics in which dipolar relaxation and dynamic glass transition are thermally activated processes, i.e., the increase of temperature at constant pressure increases the mobility of polymer chains and displaces the relaxation toward higher frequencies.²² Moreover, the plasticizing effect of water increases the polymer mobility thereby increasing the β -relaxation frequency.²³

The lack of consensus in the assignment of the β -relaxation motional mechanism and the absence of more detailed analysis of the unusual behavior observed at high RH and T indicate that an adequate description of the molecular nature and dynamics of β -relaxation is missing. Advancing the understanding of Nafion dynamics is useful to determine both the optimal operating parameters to avoid degradation of fuel cell performance and for the development of new Nafion-based membranes for high performance PEM and DAFC operating at high temperatures.^{24,25}

Therefore, the present study investigates the dielectric properties of Nafion in a wide range of frequency, temperature, and relative

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humidity. By measuring samples with different counterions in different experimental conditions, it was possible to propose a coherent mechanism for the β -relaxation of Nafion.

Experimental

Commercial extruded Nafion 115 membrane (Nextr) was obtained from DuPont. Cast Nafion (Ncast) was prepared using the Nafion 5% solution (DuPont), which was evaporated at 80°C and redissolved in dimethylsulfoxide (DMSO – Aldrich). The resulting solution was kept under stirring for 24 h at room temperature. The homogenized mixture was poured in a Teflon mold for evaporation in a resistive furnace at 160°C. The studied membranes were post-treated in three different solutions: HNO_3 (7 mol L^{-1}), H_2O_2 (3 vol.%), and H_2SO_4 (0.5 mol L^{-1}) at 80°C for 1 h each, with intermediate washing steps with deionized water for organic solvent residues removal and to assure the proton (H^+) form of the polymeric matrix. The thickness of water swelled Ncast and Nextr were $190 \pm 5 \mu\text{m}$ and $160 \pm 2 \mu\text{m}$, respectively. To obtain samples in the Cs^+ and Na^+ forms, Nafion acid films were immersed in cesium or sodium hydroxide solutions (1 mol L^{-1}) at 80°C for 4 h. This step was repeated three times to assure the complete ionic conversion.

The dielectric spectroscopy (DS) measurements of Nextr and Ncast were performed using a specially designed airtight sample holder. The sample holder is based on two connected stainless steel chambers, the upper sample chamber and a water reservoir below, separated by a thermal insulator Teflon ring that allows an independent temperature control of each chamber.²⁶ Temperature controllers connected to band heaters placed externally around the cylindrical chambers are monitored by thermocouples (type K) inserted inside the metallic walls. The constructed sample holder is capable of controlling both the temperature (from room temperature up to $\sim 200^\circ\text{C}$) and the relative humidity (RH , from ~ 3 to 100%). Nafion samples were sandwiched between stainless steel spring-load contact terminals (insulated from the chamber walls) with carbon cloth to facilitate water equilibration. In this experimental apparatus, the RH of the sample chamber can be calculated by:

$$RH = \rho(T_r)/P(T_c) \times 100, \quad [1]$$

where ρ is the saturated vapor partial pressure, P is the vapor partial pressure, and T_r and T_c are, respectively, the water reservoir and sample chamber temperatures.

In the dielectric spectroscopy measurements as a function of RH and T preconditioning of the sample positioned in the sample holder is performed in order to ensure equilibrium conditions. For example, in temperature dependent measurements the sample was allowed to equilibrate with the water vapor for 24 h at 40°C ($RH = 100\%$) prior to dielectric measurements. In the case of measurements as a function of RH , the sample was stabilized for 3 h to reach the equilibrium with the sample holder chamber at very low RH . During the dielectric spectroscopy measurements the equilibrium condition was assumed to be attained when the electrical resistance of the sample at a given RH and T was constant as a function of time. For the DS measurements performed as a function of T at constant RH , the hydrated sample was positioned in the sample holder and the dielectric spectra were collected after 30 min of stabilization at each measuring temperature. For measurements as a function of RH at $T = 80$ and 130°C the dry sample was positioned in the sample holder; the sample holder and the water reservoir were heated to obtain the desired RH according to Eq. 1.²⁶ Then, the system was allowed to equilibrate for ~ 3 h until a constant sample electrical resistance was obtained. The DS measurement as a function of RH was carried out after 30 min of stabilization at each measuring RH with step of 5% or 10% with stabilization time of 30 min. A Solartron 1260 frequency response analyzer was used in the frequency (f) range of 0.1 mHz to 3 MHz applying an ac amplitude of 100 mV. Dielectric loss was measured as function of relative humidity at temperatures below (80°C) and above (130°C) the Nafion α -relaxation temperature ($T_\alpha \sim 110^\circ\text{C}$) to separate contributions arising from ionic phase and eventual crystallization.¹²

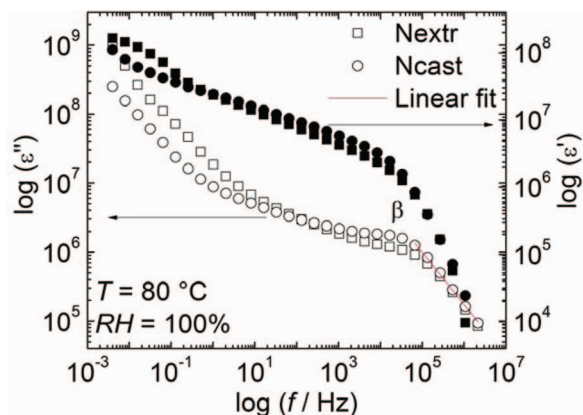


Figure 1. Dielectric permittivity loss (left axis) and dielectric constant (right axis) as a function of frequency for extruded and cast Nafion in the H^+ form measured at $T = 80^\circ\text{C}$ and $RH = 100\%$. The straight line corresponds to the high frequency fitting.

The Nafion β' and β'' -relaxations observed in DMA spectra have not a straightforward correspondence with the dielectric spectra; thus, in this study the β refers to the relaxation occurring at high frequency. The labels β' and β'' will be introduced latter in manuscript, following the same indications applied originally in the Ref. 27

Results

Figure 1 shows the f dependence of both dielectric constant (ϵ') and dielectric loss (ϵ'') at $T = 80^\circ\text{C}$ and $RH = 100\%$ for both extruded and cast Nafion in the H^+ form. It is worth mentioning that the high magnitude of the dielectric constant and loss observed in DS measurements of hydrated Nafion can be associated with induced dipole moment of Nafion main and side chains due to the presence of mobile counterions in water containing ionomers.^{28–30} Reported dielectric spectra of Nafion have shown three overlapping relaxations occurring over a broad f range ($10^{-1} < f < 10^6$ Hz) and conductivity/polarization losses occurring at very low f ($f < 10^{-1}$ Hz).^{18,31} The relaxation process occurring at $f_0 \sim 10^5$ Hz, is referred to Nafion β -relaxation and can be easily distinguished from other relaxations due to the fitted power law dependence of the relaxation onset ($\log(\epsilon'') \propto f^{-0.8}$).

Nevertheless, it is important to consider that the high-frequency dispersion ($f_0 \sim 10^5$ Hz) observed in Nafion spectrum has been alternatively ascribed to electrode polarization.²⁰ In order to evaluate electrode polarization contributions to Nafion dielectric spectra, DS measurements were carried out with samples with different thicknesses as shown in Figure 2a. It is well known that electrode polarization frequency decreases with increasing sample thickness and with decreasing sample conductivity.²⁰ The position of the high-frequency dispersion is essentially unaltered by the change of both thickness and electrical conductivity adding further evidence to the assignment for a dielectric relaxation. Electrode polarization effects occurs at frequencies lower than dc conductivity, since a long range ion motion is required to pile up the charges across the electrode/sample interface. DS measurements of Nafion were performed down to low frequencies (10^{-4} Hz) to study the dc conduction.

In Fig. 2b the Nafion spectrum at $T = 80^\circ\text{C}$ and at $RH = 100\%$ was displayed using the electrical conductivity representation ($\sigma^* = \sigma' + i\sigma''$). In σ' and σ'' vs f plots the conductivity is characterized by a linear decrease with decreasing frequency and any deviation from a linear dependence is usually ascribed to dispersions derived from bulk processes (dipolar relaxation, interfacial polarization, etc) or dispersions occurring in the electrode/electrolyte interface (electrode polarization, dc conduction, etc).²⁰ Conductivity measurements of Nafion as a function of frequency display three deviations from the linear dependence occurring at $\sim 10^5$ Hz, 10^{-1} Hz and 10^{-2} Hz assigned to, respectively, β -relaxation, α -relaxation and dc conductivity. In the

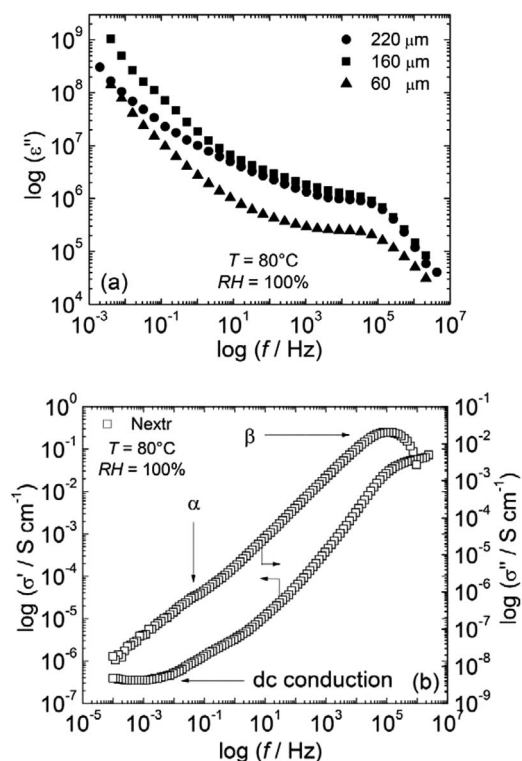


Figure 2. (a) Dielectric permittivity loss as a function of frequency for Nafion 212 (60 μm) Nafion 115 (160 μm) and Nafion 117 (220 μm); (b) real and imaginary components of conductivity as a function of frequency for Nafion 115 at 80°C and $RH = 100\%$.

studied frequency range electrode polarization contributions were not identified.

In order to evaluate the dynamics of the β -relaxation, the T dependence of ϵ'' was investigated in the 40–180°C T range with $RH = 100\%$. Figure 3 shows the dielectric loss dependence on both f and T for Nextr. Two main features can be clearly distinguished in Fig. 3: i) the β -relaxation shifts to lower f for $T > 100^\circ\text{C}$; and ii) a T -dependent maximum of the ϵ'' occurs at lower f ($< 10^1$ Hz). Such a maximum in ϵ'' occurring at low f can be ascribed to the α -relaxation of Nafion in analogy to previous DMA data.¹³ It is important to observe that the temperature in which β -relaxation reversed the frequency dependence is coincident with the α -relaxation temperature ($T_\alpha \sim 110^\circ\text{C}$).

The shift to low f of the β -relaxation can be better visualized in Figure 4, which shows the T dependence of β -relaxation times (τ_0) for Nextr and Ncast. The T dependence of the β -dispersion was similar

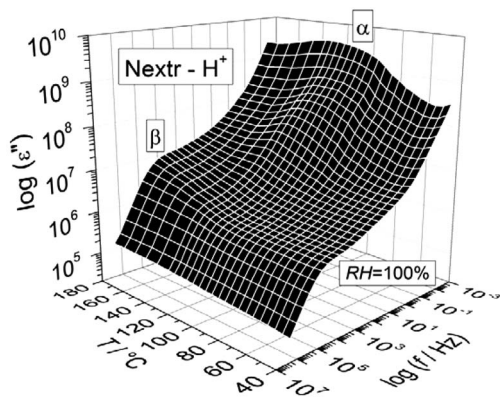


Figure 3. Dielectric permittivity loss as a function of temperature and frequency for extruded Nafion in the H^+ form at $RH = 100\%$.

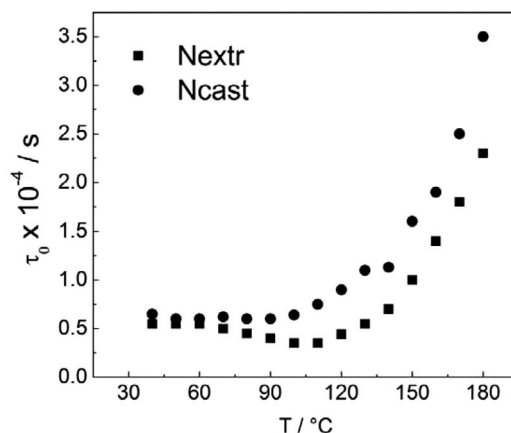


Figure 4. Temperature dependence of β -relaxation time τ_0 for Nextr and Ncast in the H^+ form at $RH = 100\%$.

for both extruded and cast samples. Up to 70°C the τ_0 of both samples are very close and have a weak dependence on T . For $T > 100^\circ\text{C}$, τ_0 values show a significant increase with increasing T , reflecting the shift to low f of the β -relaxation observed in Fig. 3. However, some features in Fig. 4 differentiate the cast and extruded samples: i) the increase of τ_0 occurs at a lower T for Ncast ($T \sim 100^\circ\text{C}$); ii) τ_0 values of Nextr membrane exhibit a minimum at $T \sim 110^\circ\text{C}$; and iii) above $\sim 70^\circ\text{C}$ Ncast τ_0 is appreciably higher than the Nextr. Such features are consistent with the different microstructures resulting from the fabrication methods.^{32,33} At constant RH Ncast absorbs a larger amount of water than Nextr and due to the plasticizing effect of water on the polar moieties of the ionic phase lower τ_0 values were expected for Nextr.

The displacement of β -relaxation to higher τ_0 is unexpected from the standpoint of traditional polymer dynamics, considering the thermally activated behavior of dipolar relaxation or dynamic glass transition and the plasticizing effect of solvent molecules in the polymer chains.^{22,23} In order to elucidate the mechanisms controlling such unusual behavior, DS measurements were carried out varying RH in the 3%–100% range at $T = 80^\circ\text{C}$ and 130°C , below and above the α -relaxation ($T_\alpha \sim 110^\circ\text{C}$), respectively, as shown in Fig. 5.

A careful analysis of Fig. 5 reveals some interesting features: i) at $T > T_\alpha$ the relaxation frequencies (f_0) are lower than the ones at 80°C (in agreement with Fig. 4); and ii) similar RH dependence of the β -relaxation is observed for both measured temperatures ($T > T_\alpha$ and $T < T_\alpha$). For RH up to $\sim 65\%$ the relaxation moves toward higher f , but for increasing RH ($> 65\%$) such behavior is reversed and the β -relaxation shifts to low f up to $RH = 100\%$.

The water absorption of Nafion has an appreciable dependence on the membrane fabrication process.⁸ Thus, as the dielectric behavior is strongly dependent on the water content, DS measurements of Nafion extruded and cast samples can provide further insights on the dynamics of the β -relaxation. Figure 6 compares the β -relaxation times (τ_0) of both Ncast and Nextr as a function of RH at $T = 130^\circ\text{C}$. Both polymers display similar relaxation dynamics up to $RH = 60\%$. However, with increasing RH the studied polymers have distinct critical RH in which β -relaxation reverses its dependence on the frequency. Such an effect is more marked for the extruded sample, which exhibits a clear increase of τ_0 for $RH > 60\%$ while cast Nafion displays a less pronounced dependence of τ_0 on the RH . Differently from the extruded membrane, the association-dissociation of the counterion plays an important role in the film morphology prepared during the solvent evaporation in the casting process.³² In this context, due to larger water uptake the electrostatic interactions is higher in Ncast shifting β -relaxation to higher τ_0 at $RH < 60\%$ (Fig. 6) and at $T > 80^\circ\text{C}$ (Fig. 4). The less pronounced decrease of the polymer segmental mobility of Ncast, indicated by the weak dependence of τ_0 for $RH > 60\%$, reflects the

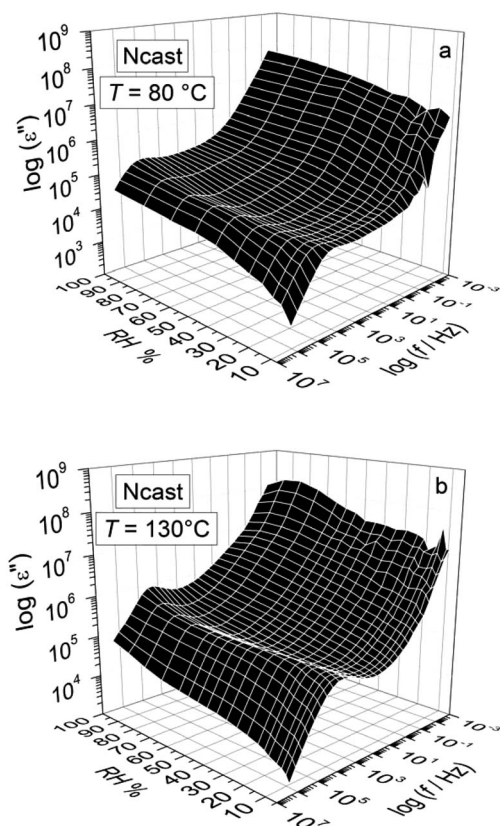


Figure 5. Dielectric permittivity loss as a function of relative humidity and frequency for cast Nafion in the H^+ form at 80 °C (a) and 130 °C (b).

higher degree of accommodation of polymer chains in the isotropic Ncast sample.

To further investigate the β -relaxation dependence on membrane water content, DS measurements of Nafion in the salt form (Cs^+ and Na^+) were carried out. Such ion-exchanged Nafion samples have lower water sorption and increased glass transition temperature than the acid (H^+) form of the ionomer.¹⁷ In addition, the study of samples in the salt form can give relevant information about the role of the electrostatic interactions of the Nafion relaxation dynamics. The measured water content in the H^+ , Na^+ , and Cs^+ forms were found to be 23%, 17%, and 8%, respectively.³⁴ Figure 7 shows the dielectric loss dependence on the f at 80 °C for Nafion in the H^+ , Na^+ , and Cs^+ forms. The position of β -relaxation of Nafion in both Na^+ and H^+ forms were comparable ($f_{0(\text{H,Na})} \sim 10^5$ Hz) reflecting the relatively

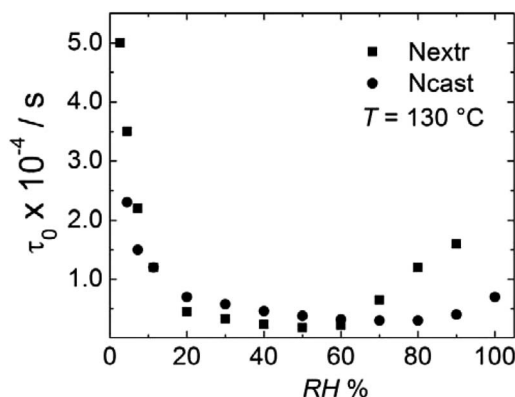


Figure 6. Relative humidity dependence of β -relaxation time τ_0 for Ncast and Nextr in the H^+ form at 130 °C.

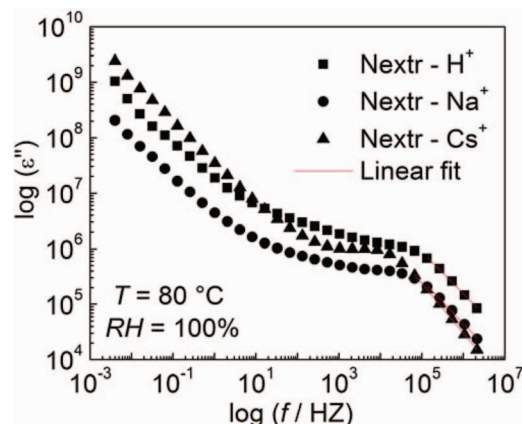


Figure 7. Dielectric permittivity loss as a function of frequency for extruded Nafion in the H^+ , Na^+ , and Cs^+ forms at $\text{RH} = 100\%$.

small difference of the water content, whereas for Cs^+ samples the β -relaxation occurred at lower $f_{0\text{Cs}} \sim 10^4$ Hz. The low f_0 of Nafion- Cs^+ sample is consistent with the lower water content that weakens the plasticization effect resulting in a decreased polymer segmental mobility.

Another relevant aspect of the β -relaxation is the separation of the two relaxations components β' and β'' , observed in DMA experiments.¹⁷ In order to distinguish the relaxation attributed to the dynamic glass transition (β') from the side chain orientation dynamics (β''), Figure 8 shows the dielectric permittivity loss as a function of temperature and frequency for the Cs^+ sample.

The T dependence of the dielectric loss of Nafion in both Cs^+ (Fig. 8) and H^+ (Fig. 3) forms display relevant differences. In the Nafion- Cs^+ form the β -relaxation remained stable over a large T range, showing a less pronounced dependence of f_0 with increasing T . The different dynamics of β -relaxation for ion-exchanged Nafion is in accordance with the results displayed in Fig. 4, which showed that the β -relaxation shift to lower f was observed to be more pronounced in H^+ samples at $T > T_g$.

The analysis of the Nafion in both the Na^+ and the Cs^+ forms enabled the separation of β components and contributed for discerning the side chain motion as the main mechanism responsible for the dielectric losses at high frequencies. Side chain dynamics can be identified by an Arrhenius-like dependence with typical activation energy, as opposed to glass transition dynamics, which follows a Vogel-Fulcher-Tamman thermally activated behavior above T_g .³⁵ Therefore, the β -relaxation dependence on T ($\text{RH} = 10\%$) of Nafion- Cs^+ above T_g ($\sim 130^\circ\text{C}$), as shown in Fig. 9, can be helpful to verify the mechanism involved in the β -relaxation dynamics.

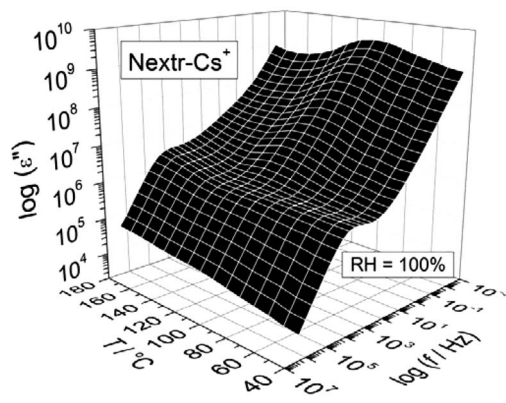


Figure 8. Dielectric permittivity loss as a function of temperature and frequency for extruded Nafion in the Cs^+ form at $\text{RH} = 100\%$.

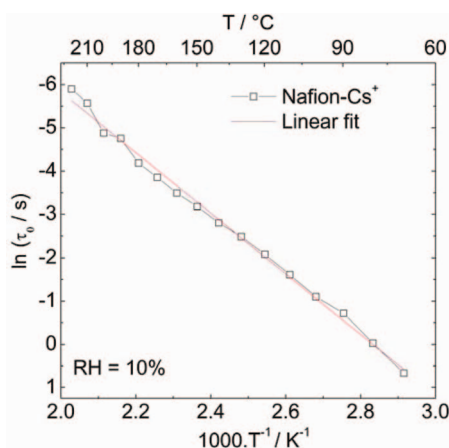


Figure 9. Arrhenius plot of Nafion in the Cs^+ form at $\text{RH} = 10\%$. The straight line indicates the best linear fit.

Discussion

At low RH , the shift of β -relaxation to higher f reflects the plasticizing effect of water, which increases the side chain mobility up to $\text{RH} \sim 65\%$. At high temperature ($T = 130^\circ\text{C}$) the β -relaxation is observed at lower f compared to the one at 80°C , and shifts further to lower f as the critical RH is exceeded. The similar shift to lower f at high RH ($>65\%$) observed for both measuring temperatures suggests that a critical amount of absorbed water is needed to promote the decrease of the polymer segmental mobility. Thus, it is reasonable to assume that the shift to low f of β -relaxation is related to the association–dissociation of the H^+ from sulfonic acid groups, which results in increased electric interaction between bare sulfonic groups that compete with the plasticizer effect of water. It is important to mention that the relaxation onset at high f is independent of the RH , exhibiting a constant slope ($\log(\epsilon'') \propto f^{-0.8}$) in the entire RH range. Changes of the relaxation width at half maximum were observed when the dipolar unit exists in an inhomogeneous molecular environment.³⁶ The counterion association promotes heterogeneous interactions among sulfonic groups with decreasing RH , as inferred from previously reported infrared and NMR data.^{37,38} Although β -relaxation dynamics is affected by the counterion association–dissociation in the sulfonic groups, the absence of changes in the relaxation width upon hydration indicates that the relaxing unit associated with β -relaxation cannot be exclusively ascribed to the dipolar group $\text{SO}_3\text{K}\cdot\text{H}_2\text{O}$ as proposed in earlier studies.¹⁹

β' -relaxation in both the Na^+ and Cs^+ forms occurs at higher temperatures ($T_{\beta'} \sim 130^\circ\text{C}$) as compared to the Nafion in the H^+ form ($T_{\beta'} \sim -20^\circ\text{C}$). The strong dipolar attraction between Nafion ionic groups in Na^+ and Cs^+ samples results in a considerable temperature increase ($>100^\circ\text{C}$) of both T_α and $T_{\beta'}$.¹⁷ Therefore, the backbone mobility at constant T of Nafion- Na^+ and Cs^+ samples is expected to be considerably reduced as compared to the H^+ form, and according to the time–temperature superposition principle the β -relaxation frequency should be lowered correspondingly.³⁹ However, the relatively small difference of β -relaxation f_0 values between the Nafion H^+ , Na^+ , and Cs^+ forms is mainly attributed to the water content, indicating that the process observed at high frequency for the different counterions probably refers to the same relaxation process. In addition, the β -relaxation onset for the three counterions has a similar slope of 0.8 for both H^+ and Na^+ , and 0.9 for Cs^+ form. Such features are inconsistent with the assignment of β -relaxation to the backbone segmental motion and a direct relationship with the polymer glass transition ($T_{\beta'}$) is not straightforward.

The marked shift to low f at $T > T_{\alpha\text{H}}$ and the weaker T -dependence at $T < T_{\alpha(\text{Na,Cs})}$ of β -relaxation suggests a link between the β -relaxation dynamics and the activated motion of Nafion ionic groups. The α -relaxation refers to the motion of Nafion main and side chains due to destabilization of sulfonic groups electrostatic interactions, and in the

Na^+ and Cs^+ forms it occurs at higher temperatures ($T_{\alpha(\text{Na,Cs})} \sim 240^\circ\text{C}$) than in the H^+ form ($T_{\alpha\text{H}} \sim 110^\circ\text{C}$).¹⁷ An important feature concerning the spectrum of Nafion- Cs^+ sample is the maximum identified in ϵ'' vs T at lower f ($f < 10^1$ Hz). The peak temperature is centered at $\sim 110^\circ\text{C}$ and can be associated to the previously observed temperature for β' -relaxation in DMA and DSC studies ($\sim 130^\circ\text{C}$).¹² Therefore, the β -relaxation components in the Nafion- Cs^+ can be separated, being the maximum occurring at low f identified in Fig. 8b attributed to the relaxation of polymer backbone molecules (β') and the relaxation observed at higher frequencies is likely to be related to Nafion side chain orientation (β'' -relaxation).

The β -relaxation of Nafion was resolved into β' (backbone motion at $T_{\beta'} \sim 130^\circ\text{C}$) and β'' (side chain motion at $T_{\beta''} \sim -30^\circ\text{C}$) at 1 Hz in DS measurements.^{16,17} However, for hydrated Nafion- H^+ ($4 \text{ H}_2\text{O}/\text{SO}_3\text{H}$) the independent analysis of underlying contributions to DS isothermal spectra arising from the main and side chains dynamics is difficult due to the proximity between the $T_{\beta''}$ (-85°C) and $T_{\beta'}$ (-70°C).¹⁷ As the side chains motion relaxes at a lower T than the backbone segments ($T_{\beta''} < T_{\beta'}$), it is reasonable to assume that the β'' -relaxation would occur at frequencies higher than the main chain relaxation. In this way, the β -relaxation measured at the highest frequency of Nafion- $\text{H}^+/\text{Na}^+/\text{Cs}^+$ spectra is possibly related to the side chain motion (β'' -relaxation). The β -relaxation fitting of Nafion- H^+ evidenced the presence of an additional relaxation at lower frequencies ($f \sim 10^4$ Hz) laying in an intermediary frequency between the β'' and α -relaxation,¹⁸ which according to the present work is probably related to the Nafion β' -relaxation.

The β -relaxation displays Arrhenius-type behavior with calculated activation energy $E_a \sim 13.8 \text{ kcal}\cdot\text{mol}^{-1}$, which is very similar to the reported values of E_a for side chain motion measured by DMA ($\sim 11 \text{ kcal}\cdot\text{mol}^{-1}$) for Nafion.¹⁶ The characteristic relaxation E_a and thermal dependence reinforce that the side chain orientation is the main relaxation process (β'' -relaxation) occurring at higher f in Nafion spectrum and the β' -relaxation, overlapped at lower f , is probably due to backbone segmental motion. Other reports attributed the measured β -relaxation of Nafion- H^+ spectrum to the matrix glass transition (backbone segmental motion) since it displayed a VFT-like dependence at $T > T_g$.¹³ As β -relaxation is composed of two overlapped relaxations it is reasonable to expect that the apparent relaxation dynamics will be determined by the process with the highest relaxation times. VFT thermal dependence exhibits higher relaxation times than Arrhenius for processes relaxing at the same T .⁴⁰ Considering that the side chains are attached to the polymer backbone and the relaxation temperatures are relatively similar, the motion of both processes are probably linked and the β'' -relaxation times will be limited by the less-mobile β' -process.⁴¹

In the present study, it is proposed that the shift to low f of β -relaxation is attributed to a lower mobility of side chain groups imparted by the increased electrostatic repulsion between bare sulfonic groups at $T > T_\alpha$ when enough water is available to dissociate the counterion ($\text{H}^+/\text{Na}^+/\text{Cs}^+$). This type of repulsion is present in polyelectrolyte and ionic solutions promoting significant changes in the polymer rigidity and conformation.^{42,43} In Nafion- Na^+ NMR studies of the interaction of Na^+ ions with relatively fixed anionic sites in the polymer was discussed, in agreement with the present description of increased rigidity of polymer chains above a critical RH .³⁸ Tensile stress-strain and stress relaxation measurements evidenced that hydrated Nafion membranes are stiffer than dry ones above a critical water content and $T > 90^\circ\text{C}$.⁴⁴ Furthermore, the SANS pattern of fully hydrated Nafion films was reported to resemble the scattering of Nafion solution.⁴³

In this context, at high T ($T > T_\alpha$) and high RH it is supposed that the repulsion between the charged sulfonic groups changes the main chain conformation assuming a rigid rodlike structure. This interpretation is in accordance with previous SANS measurements of Nafion films evidencing that upon hydration the Nafion structure can be considered a dissociation of entangled rodlike particle aggregates which is in perfect agreement with the features observed in the dielectric spectroscopy data discussed in the present study.⁴³

Summary

The β -relaxation was studied for extruded and cast Nafion, in both the acid and salt forms. Detailed DS measurements in a wide range of temperature, relative humidity, and frequency provided a coherent description of β -relaxation dynamics. The main focus was to advance the understanding of the mechanisms controlling such relaxation with special attention to its unusual frequency dependence. The experimental results evidenced that β -relaxation of acid Nafion can be separated as a sum of two overlapping relaxations in which the measured dielectric loss at high frequency was associated with the motion of the ether containing side chains. The shift to low f of the β -relaxation is closely related to the lowered mobility of side chains imparted by strong electrostatic repulsion among bare sulfonic groups, occurring above a critical water content. The DS data analysis is in agreement with previous reported spectroscopic data of Nafion that indicated the dissociation of rodlike polymeric aggregates with increasing water sorption. The inferred morphological changes found at high relative humidity and high temperature must be taken into account for the stable operation of PEM fuel cells in such conditions.

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References

1. P. Colombari and A. Novak, *J. Mol. Struct.*, **177**, 277 (1988).
2. G. Alberti and M. Casciola, *Annu. Rev. Mater. Res.*, **33**, 129 (2003).
3. Y. Shao, G. Yin, Z. Wang, and Y. Gao, *J. Power Sources*, **167**, 235 (2007).
4. B. R. Matos, E. I. Santiago, J. F. Q. Rey, A. S. Ferlauto, E. Traversa, M. Linardi, and F. C. Fonseca, *J. Power Sources*, **196**, 1061 (2011).
5. L. Ghassemzadeh, K. D. Kreuer, J. Maier, and K. Muller, *J. Phys. Chem. C*, **114**, 14635 (2010).
6. P. W. Majsztrik, A. B. Bocarsly, and J. B. Benziger, *Macromolecules*, **41**, 9849 (2008).
7. K. Schmidt-Rohr and Q. Chen, *Nature Mater.*, **7**, 75 (2008).
8. M. Kim, C. J. Glinka, S. A. Grot, and W. G. Grot, *Macromolecules*, **39**, 4775 (2006).
9. G. Gebel, *Polymer*, **41**, 5829 (2000).
10. M. K. Mistry, N. R. Choudhury, N. K. Dutta, and R. Knott, *Langmuir*, **26**, 19073 (2010).
11. K. A. Page, F. A. Landis, A. K. Phillips, and R. B. Moore, *Macromolecules*, **39**, 3939 (2006).
12. K. A. Page, K. M. Cable, and R. B. Moore, *Macromolecules*, **38**, 6472 (2005).
13. S. J. Osborn, M. K. Hassan, G. M. Divoux, D. W. Rhoades, K. A. Mauritz, and R. B. Moore, *Macromolecules*, **40**, 3886 (2007).
14. M. K. Hassan, A. Nalawade, A. Abukmail, Y. Patil, and K. A. Mauritz, *ECS Trans.*, **41** (1), 1359 (2011).
15. V. Di Noto, E. Negro, J.-Y. Sanchez, and C. Iojoiu, *J. Am. Chem. Soc.*, **132**, 2183 (2010).
16. T. Kyu, M. Hashiyama, and A. Eisenberg, *Can. J. Chem.*, **61**, 680 (1983).
17. S. C. Yeo and A. Eisenberg, *J. Appl. Polym. Sci.*, **21**, 875 (1977).
18. D. W. Rhoades, M. K. Hassan, S. J. Osborn, R. B. Moore, and K. A. Mauritz, *J. Power Sources*, **172**, 72 (2007).
19. C. Tsionos, L. Apekis, and P. Pissis, *J. Mater. Sci.*, **35**, 5957 (2000).
20. V. Di Noto, G. A. Giffin, K. Vezzu, M. Piga, and S. Lavina in: *Solid State Proton Conductors: Properties and Applications in Fuel Cells*. P. Knauth and M. L. Di Vona, Editors, ch. 5, p.109, Wiley, New York (2012).
21. Z. D. Deng and K. A. Mauritz, *Macromolecules*, **25**, 2739 (1992).
22. A. Schönhal, in *Dielectric Spectroscopy of Polymeric Materials: Fundamentals and Applications*, J. P. Runt and J. J. Fitzgerald, Editors, p. 86. American Chemical Society, Washington, DC (1997).
23. N. G. McCrum, B. E. Read, and G. Williams. *Anelastic and Dielectric Effects in Polymeric Solids*, p. 413. Wiley, New York, (1967).
24. M. K. Hassan and K. A. Mauritz in *Fuel Cell Chemistry and Operation*, A. M. Herring, T. A. Zawodzinski Jr., and S. J. Hamrock, Editors, p. 113. ACS Symposium Series, Vol. 1040. American Chemical Society, Washington, DC (2010).
25. V. Di Noto, E. Negro, and S. Lavina in *Fuel Cell Chemistry and Operation*, A. M. Herring, T. A. Zawodzinski Jr., and S. J. Hamrock, Editors, p. 98. ACS Symposium Series, Vol. 1040. American Chemical Society, Washington, DC (2010).
26. G. Alberti, M. Casciola, L. Massinelli, and B. Bauer, *J. Mem. Sci.*, **185**, 73 (2001).
27. I. M. Hodge and A. Eisenberg, *Macromolecules*, **11**, 289 (1978).
28. J. G. Kirkwood and J. B. Shumaker, *Proc. Nat. Acad. Sci.*, **38**, 855 (1952).
29. A. S. Michaels, G. L. Falkenstein, and N. S. Schneider, *J. Phys. Chem.*, **69**, 1456 (1965).
30. a) L. Aras and I. Kocak, In: *Structure and Properties of Ionomers*, M. Pineri and A. Eisenberg, Editors, p. 547. Nato Science Series C, Springer (1987); b) H. I. Kocak and L. Aras, *Polymer*, **31**, 1328 (1990).
31. K. A. Mauritz and M. K. Hassan, *ECS Trans.*, **25**, 371 (2009).
32. R. B. Moore and C. R. Martin, *Anal. Chem.*, **58**, 2570 (1986).
33. G. Gebel, P. Aldebert, and M. Pineri, *Macromolecules*, **20**, 1428 (1987).
34. G. Suresh, Y. M. Scindia, A. K. Pandey, and A. Goswami, *J. Mem. Sci.*, **250**, 39 (2005).
35. A. Eisenberg, M. King, and M. Navratil, *Macromolecules*, **6**, 734 (1973).
36. R. H. Boyd and F. Liu, in *Dielectric Spectroscopy of Polymeric Materials: Fundamentals and Applications*, J. P. Runt and J. J. Fitzgerald, Editors, p. 113. American Chemical Society, Washington, DC (1997).
37. S. R. Lowry and K. A. Mauritz, *J. Am. Chem. Soc.*, **102**, 4665 (1980).
38. R. A. Komoroski and K. A. Mauritz, *J. Am. Chem. Soc.*, **22**, 7487 (1978).
39. N. G. McCrum, B. E. Read, and G. Williams. *Anelastic and Dielectric Effects in Polymeric Solids*, p. 127. Wiley, New York, (1967).
40. A. Arbe, J. Colmenero, and D. Richter, in *Broadband Dielectric Spectroscopy*, F. Kremer and A. Schonhals, Editors, p. 707, Springer Verlag, Berlin (2003).
41. H. Sasabe and S. Saito, *J. Polym. Sci.: P. A-2*, **6**, 1401 (1968).
42. W. K. Kim and W. Sung, *Phys. Rev. E*, **83**, 051926 (2011).
43. L. Rubatat, G. Gebel, and O. Diat, *Macromolecules*, **37**, 7772 (2004).
44. M. B. Satterfield and J. B. Benziger, *J. Polym. Sci.: Part B. Polym. Phys.*, **47**, 11 (2009).