



Interplay between α -relaxation and morphology transition of perfluorosulfonate ionomer membranes



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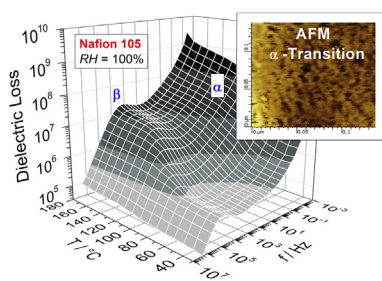
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HIGHLIGHTS

- Above α -transition electrostatic repulsions trigger conformation changes in Nafion.
- Below α -transition the motion of polymer chains is restricted by dipolar attraction.
- The dynamics of α -transition corresponds to a conformation transition of Nafion.
- AFM and DS confirm a conformation transition of Nafion polymeric aggregates.

GRAPHICAL ABSTRACT



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ABSTRACT

Nafion α -relaxation is the subject of intense investigations as it regulates the performance of electric actuators and polymer electrolyte fuel cells. Dielectric spectroscopy and atomic force microscopy measurements of Nafion membranes allow identifying the conformation transition of the polymeric aggregates as the process underlying the α -transition. The dielectric permittivity curves of Nafion membranes show that for relative humidity higher than ~60% and for temperatures higher than ~120 °C, the α -relaxation displaces to lower frequencies. Such unusual behavior is attributed to an elongation of Nafion polymeric aggregates occurring at high temperatures ($T > 120$ °C) and is in perfect agreement with morphological changes inferred from atomic force microscopy analyses.

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1. Introduction

Ionomers are high performance polymers in which the mechanical and electrical properties are controlled by the mesoscopic clustering of a small molar fraction of ionic groups [1].

Perfluorosulfonic acid membranes “such as Nafion” represented a remarkable advance in polymer membrane technology owing to its outstanding electrochemical and mechanical properties [2]. The long-standing application of Nafion membranes is largely due to its high proton conductivity, which provides a high power density output at low temperatures ($T < 100$ °C) in polymer electrolyte fuel cells (PEFC) [3,4].

Recently, the relation between the microstructure and electrical properties of Nafion at high temperatures ($T > 100$ °C) has been a

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subject of great interest [3,5,6]. Dynamic mechanical analysis (DMA) and dielectric spectroscopy (DS) data of Nafion samples show an intense energy dissipation, referred to as α -relaxation, commonly observed at $T_\alpha \sim 110^\circ\text{C}$ [7–9]. Several applications rely on the understanding of the nature of α -relaxation. The α -relaxation temperature is the underlying parameter to control Nafion shape/temperature memory effects [20], and the PEFC performance at high temperatures [3,5,6]. However, the overriding mechanism of α -relaxation is not fully understood and has imposed a challenge to various research groups for the last 30 years [1–3,5,7–9]. Furthermore, few research groups have dedicated on studying the relationship between the dynamics of α -relaxation and Nafion morphology [5,9,20]. Small angle X-ray scattering measurements showed that the Nafion morphology consists of a collection of adjacently-packed polymeric aggregates that are disorderly distributed in the matrix [27]. It has been reported that Nafion undergoes a morphology transition at high temperatures [31]. Nonetheless, a study devoted to characterize the relation between the morphology transition of Nafion and the α -transition is missing.

Previous characterizations of the α -relaxation of Nafion showed that it is markedly dependent on the electrostatic interactions among the sulfonic groups present at the end of side chains [9]. Based on these arguments, the α -relaxation as probed by DMA was assigned to the long range motion of main and side chains via destabilization of electrostatic interactions among sulfonic groups [9]. However, the DMA technique has a limited frequency range, which inhibits the full characterization of the dynamics of α -relaxation. The DS technique overcomes this limitation, and the DS measurements of Nafion were performed in a broad temperature and relative humidity range [8,9,15]. The DS measurements of Nafion membranes evidenced an unusual feature for the α and β relaxations of Nafion: both relaxations shift to lower frequencies with increasing annealing temperature [17,19]. The proposed assignment of α -relaxation to the motion of Nafion main and side chains via weakening of electrostatic interactions cannot account for the low- f shift observed at high T [8,9].

Furthermore, the relation between the dynamics of the polymer relaxations and the proton conductivity is obscured due to the lack of both an unambiguous identification of the polymer glass transitions (T_g) and a better understanding about the origin of the dielectric/mechanical relaxations of Nafion [7–9]. Typically, ionomers possess two distinct T_g , one associated with the segmental motion of the main chains within an electrostatically crosslinked framework, and the other one associated with the long-range motion of main chains without the mobility restrictions imposed by the ionic interactions [1]. At $T > T_g$, the dielectric and mechanical relaxations of other families of ionomers, such as perfluorocarboxylate ionomers, usually follow a Vogel-Tamman-Fulcher (VTF) thermal dependence, which is a signature of glass transition phenomena [1,8]. Detailed analyses revealed that α -relaxation in perfluorosulfonate ionomers does not exhibit the characteristic features of a glass transition and suggested that the α -transition can be linked to a morphological transition of the ionomer [5,8]. Therefore, the relationship between the morphology and the dynamics of α and β relaxations at high temperatures remains poorly understood.

More recently, the number of reports concerning the possible existence of condensed counterions in water-swollen Nafion membranes has increased considerably [10,11,15,26]. Small angle X-ray scattering (SAXS), fluorescence, and infrared spectroscopy studies of hydrated Nafion membranes revealed that a considerable fraction of protons is condensed in sulfonic acid groups [10,11]. Atomic force microscopy measurements of Nafion detected nanoscale surface-potential fluctuations, which were mainly derived from the ac ion-hopping conductivity, usually observed for

disordered ion conductors [16]. Moreover, recent dielectric spectroscopy measurements of Nafion solutions revealed that α and β relaxations are mostly associated with the fluctuations of condensed counterions along the longitudinal and radial directions of Nafion polymer backbone, respectively [15].

In ion-containing polymers having condensed counterions, the application of an electric field is known to promote an induced dipole moment in which the diffusion of these counterions along the charged macromolecule polarizes the rodlike polymer backbone at characteristic length scales [12–14]. Such polarizations give rise to well-defined dielectric relaxations with a high dielectric increment ($\Delta\epsilon \sim 10^2$ – 10^4) [12–14]. The high dielectric increment observed in Nafion dielectric spectrum has posed a challenge to the determination of the origin of Nafion α and β relaxations, which have been ascribed to electrode polarizations, interfacial polarizations, and segment polymer relaxation [8,9,17,23]. However, none of these assignments allowed describing the dynamics of α and β in a broad range of both temperature and relative humidity, more specifically, to address the displacement to lower frequencies at high T of both relaxations.

Herein, we advance in the mechanistic interpretation of α and β relaxations of Nafion by characterizing the dynamics of such relaxations in a broad temperature and relative humidity range. We provide comprehensive evidence for the association of the α -relaxation with the polarization of the polymeric aggregates due to the diffusion of condensed protons, and the association of α -transition with a conformational transition due to the elongation process of polymeric aggregates. Such assignment of Nafion dielectric dispersion allows understanding the unusual shift of α and β relaxations to lower frequencies.

2. Experimental

Commercial Nafion membranes with different equivalent weight (EW), Nafion 105 ($EW = 1000 \text{ g Eq}^{-1}$) and 115 ($EW = 1100 \text{ g Eq}^{-1}$), were obtained from Dupont. The 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 form of the polymeric matrix. Samples were characterized in the hydrated form without previous thermal treatment to avoid morphological changes.

The dielectric spectroscopy (DS) measurements of Nafion films were performed using a specially designed airtight sample holder [3]. Temperature controllers connected to band heaters placed externally around the cylindrical chambers are monitored by thermocouples (type K) inserted inside the metallic walls. The 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 (electrically insulated from the chamber walls) with carbon cloth to facilitate water equilibration. A Solartron 1260 frequency response analyzer was used in the 4 mHz–3 MHz frequency (f) range with 100 mV ac amplitude. Further details of dielectric spectroscopy measurements are described elsewhere [3,17]. Dielectric permittivity representation ($\epsilon^* = \epsilon' - i\epsilon''$) was obtained by electrical impedance spectroscopy measurements ($Z^* = Z' + iZ''$) using Equations (1) and (2) [18]:

$$\epsilon'(f) = -\frac{d \sin(\theta(f))}{2\pi f \epsilon_0 S |Z(f)|} \quad (1)$$

$$\epsilon''(f) = -\frac{(d \cos(\theta(f)))}{(2\pi f \epsilon_0 S |Z(f)|)} \quad (2)$$

where ϵ' and ϵ'' are the real and imaginary parts of the dielectric permittivity; ϵ_0 is the vacuum permittivity ($\sim 8.854 \times 10^{-14} \text{ Fcm}^{-1}$); S is the electrode active area, d is the thickness of the membrane; $|Z|$ and θ are the modulus and phase retardation of impedance. The electric modulus ($M^* = M' + iM'' = 1/\epsilon^*$) representation is used in order to minimize the contribution of the dc conduction [20]. The ion conductivity of condensed protons was obtained from the relation: $\sigma^* = 2\pi f \epsilon_0 \epsilon^*$. By using the proton conductivities, the proton diffusion coefficient can be calculated with the Nernst–Einstein relation [15]:

$$D = \frac{\sigma k_b T}{ne^2}, \quad (3)$$

where k_b is the Boltzmann constant, T is the absolute temperature, e is the elementary charge, and n is the charge concentration. The charge concentration used in Eq. (3) takes into account the fraction of condensed counterions (0.8) previously estimated [10]. The real part of the dielectric permittivity is exempt from dc conduction contribution and the Kramers-Kronig (KK) transformation can be used to obtain the imaginary part of dielectric permittivity revealing the frequency dependent processes [22]. The following equation is the semi-analytical approach for KK transformations to obtain $\epsilon''(\omega)$:

$$\epsilon''(\omega) = -\frac{\pi}{2} \frac{d\epsilon'(\omega)}{d \ln \omega} \quad (4)$$

The water uptake as a function of temperature was determined by positioning a hydrated Nafion membranes in the cylindrical chamber at $RH = 100\%$. The chamber was heated from 100 to 180 °C with a 10 °C – step for 2 h. After this conditioning, the sample was removed from the chamber at each T and the water mass uptake (W_u) was extracted from the relative water content with respect to the dry sample (110 °C for 3 h). The water volume uptake (V_u) was estimated using the following relation:

$$V_u = \frac{\Delta V}{(1 + \Delta V)} \times 100, \quad (5)$$

$$\Delta V = \frac{\rho_N (m_{H_2O} - m_D)}{\rho_{H_2O} m_D}, \quad (6)$$

where m_{H_2O} and m_D are the wet and dry mass of the sample, respectively; ρ_N and ρ_{H_2O} are the mass densities of dry Nafion and of water, respectively.

Atomic force microscopy (AFM) experiments were carried out on an AIST-NT SMART microscope in intermittent (tapping) mode. A sharp silicon beam-deflection cantilever was used with an oscillation amplitude around 10 nm and a set point that was optimized for a large phase contrast. All experiments were conducted on multiple areas to confirm both the uniformity and the reproducibility of the encountered experimental conditions. AFM topology images were obtained at 25 °C for Nafion samples annealed *in situ* at 30 °C, 90 °C and 140 °C for 2 h. Rectangular films were cut respecting the extrusion direction (machine direction) and positioned vertically in the substrate. The relative humidity ($RH \sim 50\%$) was kept constant during the AFM measurements.

3. Results and discussion

3.1. Identification of the α -relaxation

Firstly, a detailed discussion concerning the dielectric spectra of Nafion is necessary for the investigation of the α -relaxation. Fig. 1a

shows the dielectric permittivity and dielectric loss curves of N115 obtained experimentally at $T = 80 \text{ }^\circ\text{C}$ and $RH = 100\%$, and the corresponding dielectric loss curve obtained by KK-transform [21,22]. To determine the characteristic frequencies of the α -relaxation and the frequency dependent conductivity (ac conduction peak) in the dielectric loss, the elimination of the upturn of the dielectric loss at $f < 10^{-2} \text{ Hz}$ due to the dc conductivity is required.

The dielectric loss as a function of frequency obtained from the KK-transform reveals a relaxation at $f \sim 10^{-3} \text{ Hz}$ partially superposed with the α -relaxation ($f \sim 10^{-2} \text{ Hz}$). Usually the position of the ac conduction peak in the dielectric loss curve coincides with the onset of dc conduction in the dielectric curve in agreement with the Fig. 1a [21]. The crossover frequency from ac to dc conductivity, identified in earlier reports at $f \sim 10^{-3} \text{ Hz}$ [17], is in good agreement with the onset frequency for dc conductivity, observed at $f < 10^{-3} \text{ Hz}$ [15,17,19]. Therefore, the relaxation observed at $f \sim 10^{-3} \text{ Hz}$ in Nafion dielectric spectrum can be attributed to a conductive dispersion (σ relaxation) [16,21].

Fig. 1b shows the electric modulus representation of Fig. 1a data. The electric modulus representation is advantageous to study Nafion relaxations because it suppresses both the dc conduction and electrode polarizations, and displays the σ and α relaxations in a higher frequency range. The σ and α relaxations are observed at

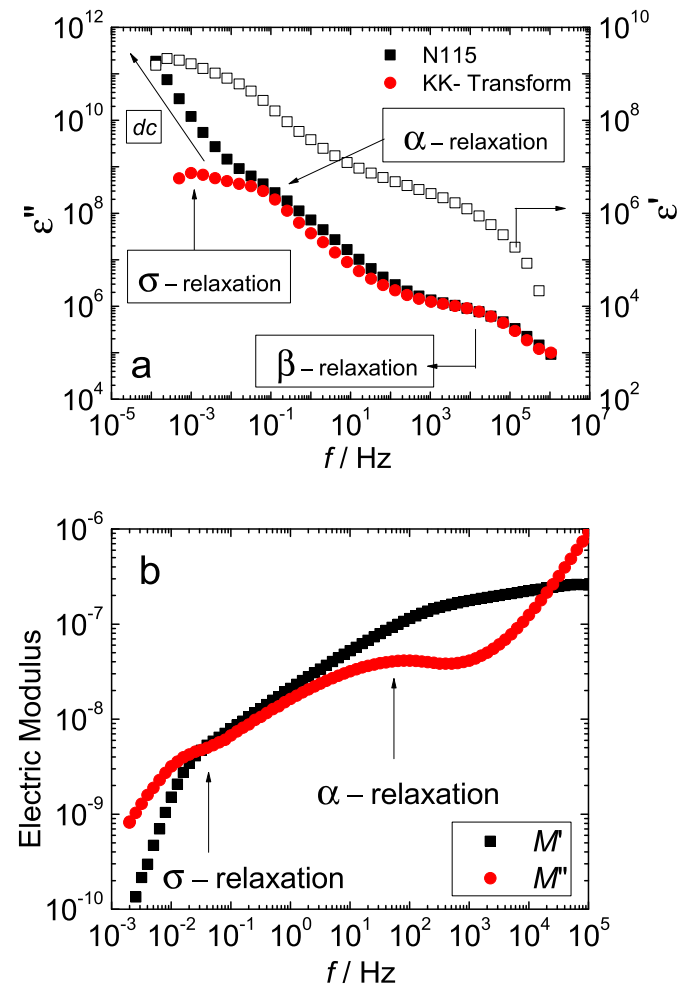


Fig. 1. (a) Real and imaginary parts of dielectric permittivity as a function of frequency for N115 at 80 °C and at $RH = 100\%$. The Kramers-Kronig transform of the real part of the dielectric permittivity is indicated. (b) Real and imaginary parts of the electric modulus as a function of frequency for N115 at 80 °C and at $RH = 100\%$.

$f \sim 10^{-2}$ Hz and $f \sim 10^1$ Hz, respectively.

The modulus representation of Nafion spectra allows monitoring the displacements of the α -relaxation in the frequency range, which is not possible in the dielectric representation due to overlapping phenomena. Previous reports emphasized that the electric modulus spectrum has contributions of high frequency electronic and vibrational polarizations, which can promote the broadening of the M'' peaks [33,34]. However, there are cases in which the observed relaxations can be predominantly an occurrence of ion-hopping [33,34]. In order to detect if electronic polarizations at high frequencies are changing the electric modulus, modulus curves taken at different relative humidity and temperatures can be normalized by the dielectric constant ($\Delta\epsilon'(\infty)$) and by the relaxation frequency (f_0), and collapsed into an universal curve [33,34]. If such scale law is not obtained, i.e., if there is no superposition of the electric modulus into an universal curve, it is likely that electronic and vibrational polarizations are taking place [33,34]. Fig. 2 shows the universal curves $M''(\Delta\epsilon'(\infty))$ vs ff_0 for both the relative humidity and temperature for Nafion 115. It is observed that the DS data collapses into universal curves, for both RH and T , indicating that the electric modulus is mainly due to the diffusion of ions [33,34].

The ion-hopping predominance in the modulus spectra is probably associated with the low number density of ionic charges of Nafion ($\sim 10^{18}$ cm $^{-3}$) [33]. Changes of peak shape due to electronic contributions have been usually observed for materials containing high density of charge carriers ($>10^{22}$ cm $^{-3}$) [33]. Additionally, the predominance of ion-hopping is consistent with the high dielectric permittivity of perfluorosulfonate ionomers (Fig. 1) [15]. The dielectric constant at extremely high frequencies ($\Delta\epsilon' \sim 100$) is much lower than the dielectric constant of hydrated Nafion films, which suggests that the electronic polarizations display negligible contribution to the modulus spectra [33,34]. The absence of electronic polarization effects in the relaxations of Nafion in the studied frequency range allows the study of the dynamics of α relaxation as a function of both temperature and relative humidity using the electric modulus representation.

3.2. Frequency dependence of α and β relaxations

Fig. 3 shows the dielectric loss and electric loss modulus as a function of temperature and frequency for both N115 and N105 at $RH = 100\%$. In Fig. 3a and c, the β -relaxation (at 30°C) is observed at high frequencies ($f \sim 10^5$ Hz), whereas the α -transition is observed as a function of T at low frequencies ($f < 10^1$ Hz). The α -relaxation dependence on temperature can be better visualized in Fig. 3b and d. Previous DS studies of N115 revealed that the α and β relaxations exhibit an unusual shift to low f with increasing T , in perfect

agreement with data in Fig. 3 [17,19]. Both relaxations displace to lower frequencies for $T \geq 120^\circ\text{C}$ and $\geq 90^\circ\text{C}$ for N115 and N105, respectively. The displacement of α and β relaxations to lower frequencies for N105 (Fig. 3c and d) occurs in the temperature range between $T \sim 90^\circ\text{C}$ ($\sim 10^5$ Hz) and $T \sim 140^\circ\text{C}$ ($\sim 10^4$ Hz), whereas for N115 (Fig. 3a and b) the β -relaxation displacement develops at $T \geq 120^\circ\text{C}$.

To evaluate the dependence of the dynamics of α -relaxation on the water content of the sample, DS data were measured at different RH. Fig. 4 shows the electric modulus as a function of RH for N115. In Fig. 4, the α -relaxation is observed at $f \sim 10^{-1}$ Hz at $RH = 2.7\%$ (130°C). A progressive displacement of the α -relaxation to high f in the interval $RH \sim 3\text{--}60\%$ is observed. However, for $RH > 60\%$ the α -relaxation reverses the dependence on the RH, decreasing to lower f with increasing RH. The correspondence between the T and RH dependence for both α and β relaxations was observed in earlier reports of dynamic mechanical analysis (DMA). Such previous studies showed that the neutralization of acid Nafion shifted both α and β relaxations to higher temperatures in a similar temperature range [5,7].

It is worth noting that a typical transition identified as a peak in the dielectric loss as a function of temperature is mainly due to the thermally activated displacement of the relaxation, which is observed as a shift of the relaxation to higher frequencies with increasing temperature [21]. In contrast, the α -transition peak observed in the ϵ'' vs T plots at $f \sim 10^{-1}$ Hz of N115 (Fig. 3a) is formed from the displacement of α -relaxation to high f ($f > 10^{-2}$ Hz) in the $\sim 40\text{--}120^\circ\text{C}$ T -interval followed by a low f displacement at $T > 120^\circ\text{C}$. Such unusual behavior indicates that the α -transition cannot be ascribed to the polymer glass transition, which exhibits a Vogel-Tamman-Fulcher temperature dependence at high T [5].

Recently, it has been reported that the dielectric spectra of perfluorosulfonate ionomer membranes are dominated by ac conductivity of protons via ion-hopping in the $f \sim 10^6\text{--}10^{-3}$ Hz interval [2,15]. Moreover, the presence of α and β relaxations was associated to the diffusion of protons along different scales of the Nafion polymeric aggregates. The fast relaxation (β -relaxation) and the slow relaxation (α -relaxation) are attributed to the diffusion of ions along the radial and longitudinal directions of the polymeric aggregates, respectively [15]. The α and β relaxations are mainly a result of the longitudinal and radial polarizations due to the diffusion of condensed counterions. In this framework, the frequencies of α and β relaxations are dependent on the length and the correlation distance of the aggregates in the polymer matrix [13–15].

As the temperature and relative humidity promote the swelling of perfluorosulfonate ionomers, the displacement of α and β relaxations was previously shown to be mainly a result of the

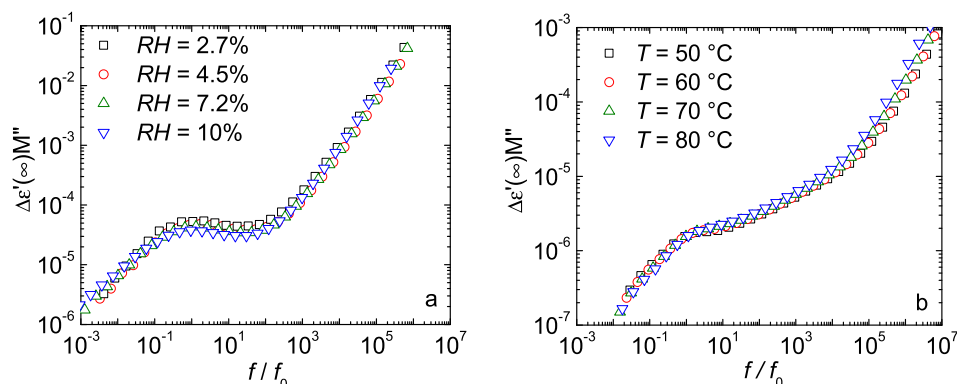


Fig. 2. Electric loss modulus for Nafion 115 as a function of frequency at (a) different relative humidity (at $T = 130^\circ\text{C}$) and (b) different temperatures (at $RH = 100\%$).

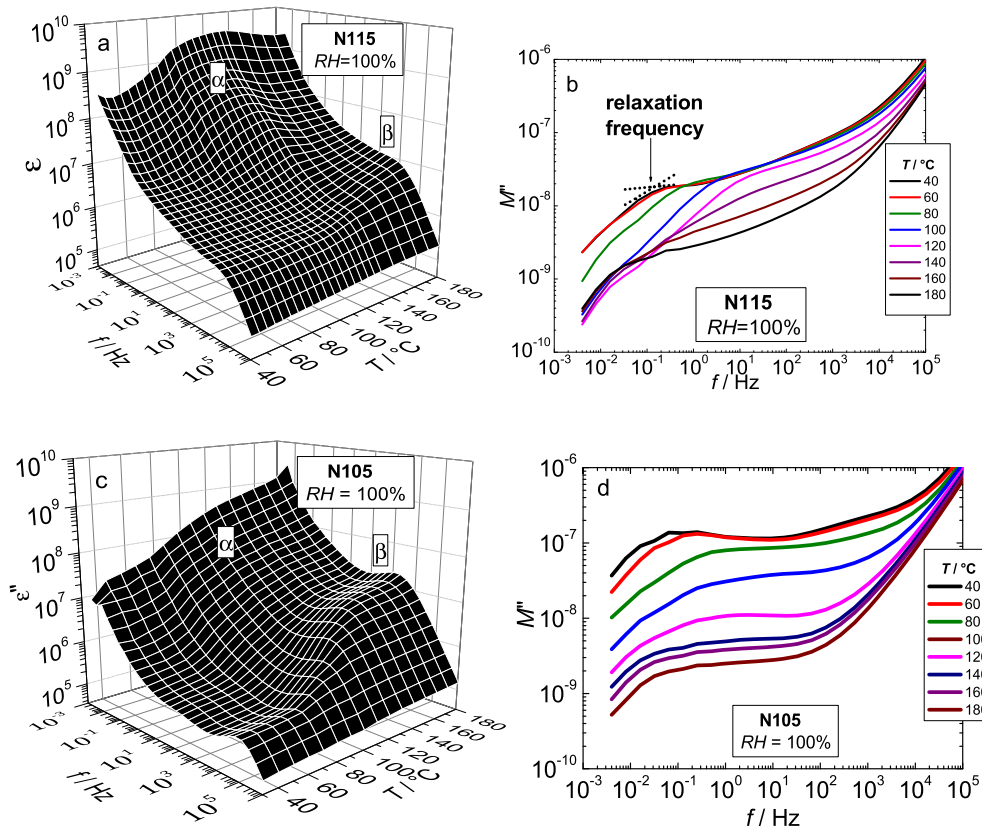


Fig. 3. Dielectric loss (a and c) and modulus loss (b and d) dependence on T and f for N105 and N115 at $RH = 100\%$. Temperature curves are in steps of 10 K.

interactions between the water molecules and the Nafion ionic domains [17]. Increasing the water content promotes the dissociation of protons, thereby increasing the electrostatic repulsions between sulfonic acid groups [17,24,25]. Therefore, the displacements of α and β relaxations of Nafion to lower frequencies can be understood as a dilution process due to the higher water sorption capacity at high temperatures and relative humidity. Such dilution promotes the increase of the correlation length between the chains,

which displaces the β -relaxation to lower frequencies. As the α -relaxation is dependent on the length of the main chains, the displacement to low f of the α -peak with increasing RH can be related to an increase of the average length of Nafion polymer backbone. Above a certain RH , as the water content increases, dissociated ions induce strong electrostatic repulsion among sulfonic acid groups, which promotes a conformation transition from a coiled state to a rigid rodlike polymeric aggregate. Owing to the higher density of side chains in the sample with lower EW the electrostatic repulsion is higher for N105 sample and the conformation transition occurs at lower $T \sim 80^\circ\text{C}$. Thus, the influence of the adsorbed water on both the length and the correlation distance of polymeric aggregates must be considered in order to understand the role of the electrostatic interaction in Nafion morphology.

According to the dielectric spectroscopy analysis (Figs. 3 and 4) and previous characterizations of the electrostatic interactions in hydrated Nafion membranes [10,11], at temperatures below the α -transition ($T_\alpha \sim 120^\circ\text{C}$), a fraction of the total amount of sulfonic groups contains condensed protons, which forms physical crosslinks via dipole–dipole attraction among the sulfonic groups, thereby restricting the mobility of the polymer chains. When the temperature approaches the α -transition an increase of the diffusion coefficient is observed, and thermal energy is enough to disrupt the electrostatic crosslinks. This result is in accordance with dynamic mechanical analysis reported by other groups [5]. Therefore, above the temperature of α -transition ($T > 120^\circ\text{C}$), the motion of the polymer backbone is no longer restricted by the dipolar attraction among sulfonic acid groups. This feature associated with the higher water content at high temperature ($T > 100^\circ\text{C}$) increases the degree of protonic charge dissociation as well as the electrostatic repulsions among sulfonic groups, thereby reducing the mobility of the polymer backbone.

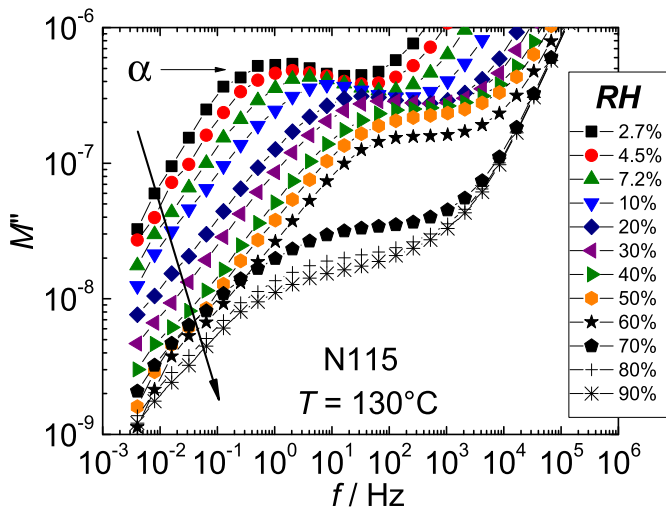


Fig. 4. Imaginary component of electric modulus as a function of frequency at different relative humidity values for Nafion 115 at $T = 130^\circ\text{C}$. The arrow indicates increasing RH .

3.3. Estimation of the polymer backbone length

The proposed scenario, in which the α -transition in Nafion membranes is due to the elongation of the polymeric aggregates, is further supported by the estimate of the end-to-end length of the polymer backbone using Eq. (7). In ion-containing polymers, the frequency of the dielectric dispersion associated with the radial (f_β) and longitudinal polarization (f_α) is related to the average distance between the chains (ξ) and to the length of the polyion (L) by the following equations [13,14]:

$$f_\alpha^{-1} \approx \frac{L^2}{6D}, \quad (7)$$

$$f_\beta^{-1} \approx \frac{\xi^2}{6D}, \quad (8)$$

where D is the diffusion coefficient of condensed counterions. In Fig. 5, the D values and the sample water content (Fig. 5a) as well as the L and ξ values (Fig. 5b) are shown as a function of temperature. In Fig. 5a, it can be seen that the water content of Nafion membranes increases substantially for $T > 100$ °C, in agreement with previous reports [26]. Although water is not considered a good solvent for Nafion compared to water-alcohol mixtures, the large amount of absorbed water indicates that a dissolution process is taking place.

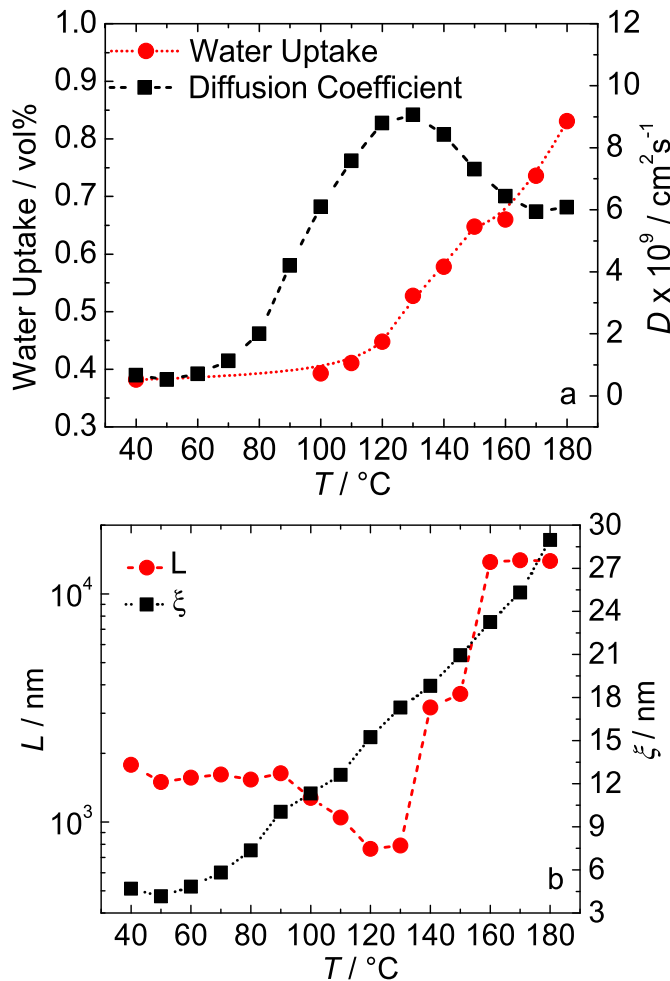


Fig. 5. (a) Temperature dependence of water uptake (left axis) and diffusion coefficient (right axis); and (b) the length (left axis) and correlation distance (right axis) of polymeric aggregates for Nafion 115 at RH=100%.

The diffusion coefficient D peaks at $T \sim 130$ °C followed by a reduction with increasing temperature. As the diffusivity of condensed counterions is coupled with the motion of the main and side chains [28,29], the reduction of D for $T > 130$ °C can be linked to the lower mobility of the polymer backbone due to increased electrostatic repulsion among sulfonic acid groups [27,28]. The increase of the repulsive forces among the fixed anionic charges is known to decrease the chain flexibility and is expected to increase with increasing water content at high T .

In Fig. 5b, the correlation distance between the Nafion chains increases from $\xi \sim 5$ nm ($T = 40$ °C) — a value in excellent agreement with the ones obtained by small angle X-ray scattering (SAXS) [27] — to $\xi \sim 29$ nm ($T = 180$ °C). The increase of ξ with increasing T ($T > 70$ °C) is expected to reflect the nearly linear dependence of the water volume fraction on the temperature.

As the relaxation frequency of the longitudinal polarization (α -relaxation) could not be precisely obtained due to the partial superposition with the σ relaxation, the relaxation frequency used to calculate the polymer chain length was obtained from the α -relaxation shoulder observed in the loss modulus curve as indicated in Fig. 3b. The estimated L in Fig. 5b is in accordance with previous reports ($L \sim 10^2$ – 10^4 nm) [35], and reflects the temperature dependence of the full length of the polymer aggregates. The L values increase substantially to $T > 120$ °C indicating that the displacement of α -relaxation to lower frequencies represents a conformation transition of perfluorosulfonate ionomer chains. The ionic dissociation increases the electrostatic repulsion among ions incorporated in the polymer backbone thereby increasing the end-to-end average distance of the polymeric aggregates [15,27].

3.4. AFM

In order to correlate the findings of the dielectric spectroscopy analysis with the morphology of the ionomer, tapping mode AFM measurements were carried out in Nafion 105. Fig. 6 shows the AFM topography and phase images of N105 samples at 30 °C and annealed at 90 °C and 140 °C.

The topography of Nafion at 30 °C displays a contrast of nanometer sized phases that can be attributed mostly to ionic and non-ionic phases. The depth of the contrasted regions is ~ 5 nm in agreement with previous AFM analysis [16,30]. In these images, the topography displays a rather irregular structure. Moreover, it is not possible to detect crystalline vs amorphous non-ionic regions considering the stiffness of the domains since the presence of stiffer chains in the vicinity of clustered ionic groups is also expected [27].

In general, it can be seen that the increase of the annealing temperature promotes a topological transition, which can be observed at $T \sim 90$ °C and ~ 140 °C (Fig. 6c and e) with respect to the sample annealed at $T \sim 30$ °C (Fig. 6a). The temperature range in which the topological transition is observed matches the temperature interval of the low- f shift of α -relaxation in N105 (Fig. 3c). Such correspondence suggests that the morphological evolution upon annealing is associated with the elongation transition of the polymeric aggregates, as evidenced in Fig. 5b.

When the annealing temperature is increased to $T_{ann} = 90$ °C the phase images display elongated structures very similar to reported images for annealed samples [31]. At $T_{ann} = 140$ °C, Nafion topography displays elongated features and the phase images display round structures ubiquitously distributed along the sample. A higher magnification image is provided in Fig. 7 and reveals that the darker spots consist of elongated domains occurring along elongated polymeric structures. This image is very similar to AFM images of annealed Surlyn[®] samples that showed nearly round ionic aggregates neighboring elongated polymeric structures [32].

Images displayed in Figs. 6 and 7 show the sample surface,

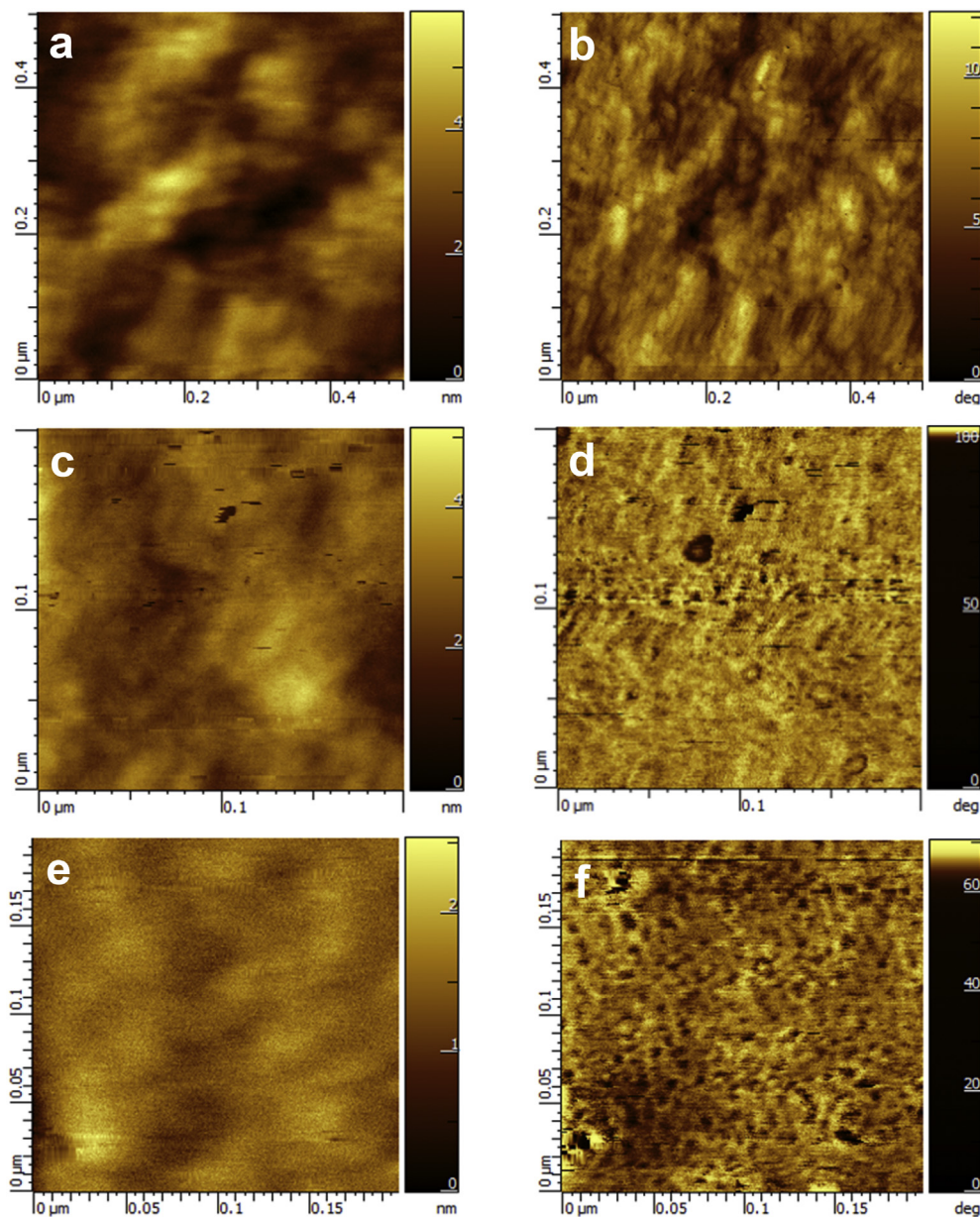


Fig. 6. AFM images of Nafion measured at room temperature at (a and b) 30 °C and at two different annealing temperatures (c and d) 90 °C and (e and f) 140 °C. The scan range is 500 nm by 500 nm for (a and b), and 200 nm by 200 nm in (c–f). The extrusion direction is in the vertical direction. Left: topography, right: phase images.

whose extrusion direction is placed vertically, the elongated polymeric aggregates must be oriented in the vertical position according to previous anisotropic studies of Nafion by SAXS [1,2]. The anisotropic orientation of the Nafion microstructure is in accordance with Fig. 7 that evidences the presence of elongated structures in the vertical position. In order to compare the correlation distance among the elongated structures with the ones obtained by DS (Fig. 5b), the average distance was estimated in Fig. 7b. The average distance between the elongated structures (~9 nm) is larger than the correlation distance between the polymeric aggregates obtained by SAXS [27], and DS (Fig. 5b) for non-annealed samples (~5 nm). However, such a difference follows the trend observed in Fig. 5b in which annealing increases the correlation distance among the polymeric aggregates. Thus, the AFM images in the noncontact mode confirm the presence of elongated structures of samples annealed at high temperature and is in perfect

agreement with the morphological transition inferred from dielectric spectroscopy measurements.

4. Conclusion

Careful dielectric spectroscopy analysis along with atomic force microscopy images provided valuable insights to advance the understanding of the properties of Nafion. The characterization by dielectric spectroscopy and atomic force microscopy of Nafion 105, which has a higher density of sulfonic acid groups, allowed identifying contributions arising predominantly from electrostatic interactions. The α -relaxation was shown to be due to the longitudinal polarization of condensed counterions in the vicinity of anionic groups distributed along the polymer backbone. The displacement of this relaxation in frequency represents conformation changes of the polymer backbone. At high temperatures the

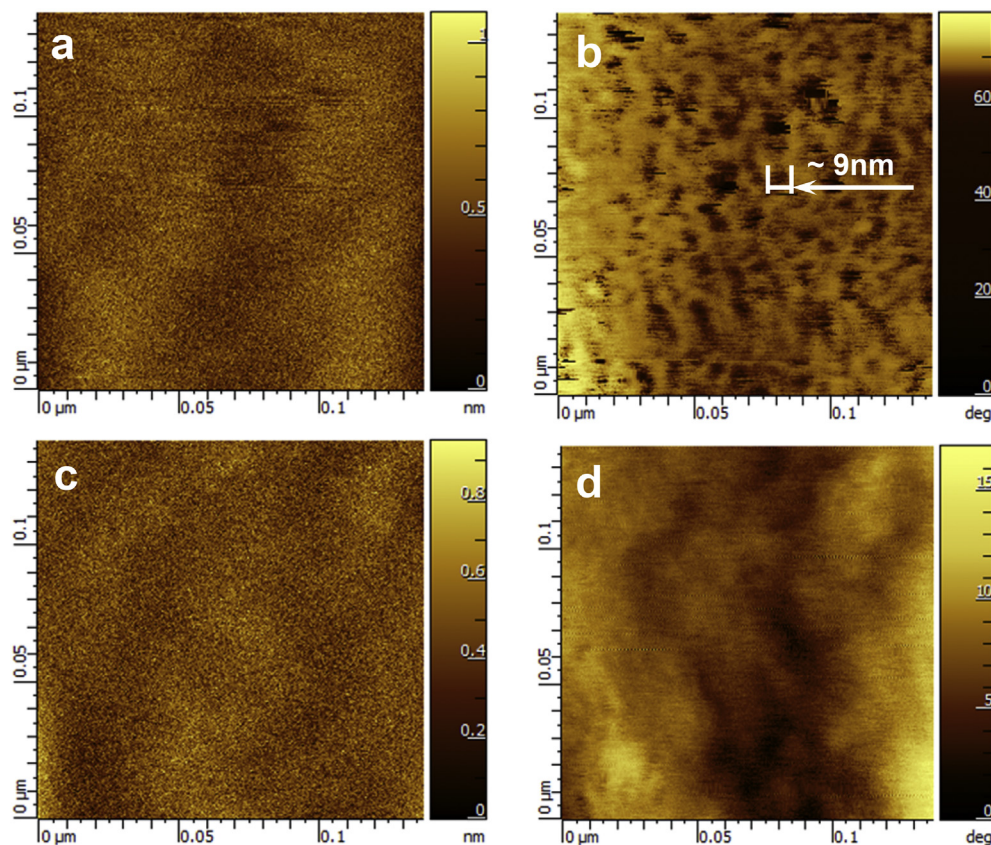


Fig. 7. AFM images of Nafion annealed at 140 °C, (a and b) tapping mode, (c and d) non-contact mode. The scan range is 150 nm by 150 nm.

α -relaxation displaces to lower frequencies indicating the elongation of the Nafion polymer aggregates, as confirmed by atomic force microscopy.

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