

α -Relaxation and Morphology Transition of Perfluorosulfonate Ionomer Membranes

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ABSTRACT

Nafion α -relaxation has been the subject of intense investigations as it regulates the performance of electric actuators and polymer electrolyte fuel cells (PEMFC). Dielectric spectroscopy and atomic force microscopy (AFM) measurements of Nafion membranes allowed identifying the conformation transition of the polymeric aggregates as the process underlying the α -transition. The dielectric permittivity curves of Nafion showed that for temperatures $T > 120$ °C, the α -relaxation displaces to lower frequencies. Such unusual behavior was attributed to an elongation of Nafion polymeric aggregates occurring at $T \sim 120$ °C and is in agreement with both water uptake measurements and morphological changes inferred from AFM analyses.

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 [1,2]. Perfluorosulfonic acid membranes such as Nafion represent a remarkable advance in polymer membrane technology owing to its outstanding electrochemical and mechanical properties. Nafion α -relaxation has been the subject of intense investigations since it regulates the performance of electric actuators and polymer electrolyte fuel cells [3,4]. The α -relaxation temperature ($T_{\alpha} \sim 110 - 120$ °C) is the underlying parameter to control Nafion shape/temperature memory effects and the PEMFC performance at high temperature. 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 [2]. In this study, dielectric spectroscopy and atomic force microscopy measurements of Nafion membranes provided evidences for a conformation transition of the polymeric aggregates as the process underlying the α -transition. Such assignment of Nafion dielectric dispersion allows understanding the unusual shift of α and β relaxations to lower frequencies.

EXPERIMENTAL

Commercial Nafion membranes with different equivalent weight (EW), Nafion 105 ($EW = 1,000$ g mol⁻¹) and 115 ($EW = 1,100$ g mol⁻¹), were obtained from Dupont. The membranes were post-treated in three different solutions: HNO₃ (7 mol L⁻¹), H₂O₂ (3 vol.%), and H₂SO₄ (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. 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 [3,5]. The sample holder is capable of controlling both the temperature (from room temperature up to ~200 °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 to 3 MHz frequency (*f*) range with 100 mV *ac* amplitude. The electric modulus ($M^* = M' + iM'' = 1/\epsilon^*$) representation is used in order to minimize contributions from the electrode polarizations [6]. 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 [7]. Prior the dielectric spectroscopy analysis, both the impedance of the short-circuited sample holder and the resistance of the electrode-membrane interfaces were determined and subtracted from the DS data to eliminate the resistance of both the electrodes and the electrode-membrane interfaces, along with the parasitic inductance [3].

The water uptake as a function of temperature was determined by positioning a hydrated Nafion membrane in an air-tight humidity chamber used for the conductivity measurements. A hydrated Nafion membrane was positioned in the chamber and progressively heated in the temperature interval 100-180 °C with 10 °C steps at *RH* = 100%. After two hours of stabilization at each temperature plateau, the membrane was removed and kept in a beaker filled with water for water uptake gravimetric measurements.

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 oscillation amplitude ~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. AFM topology images were obtained at 25 °C and *RH* ~ 50% 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.

DISCUSSION

Figure 1a shows the dielectric permittivity and dielectric loss curves of N115 measured at *T* = 80 °C and *RH* = 100%, and the corresponding dielectric loss curve obtained by KK-transform. In order 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 *dc* conduction occurring at low frequencies ($f < 10^{-2}$ Hz) is required. Thus, **Figure 1b** shows the electric modulus representation of data from **Fig.1a**.

The dielectric loss as a function of frequency obtained from the KK-transform reveals a relaxation at $f \sim 10^{-3}$ Hz partially superposed with the α -relaxation ($f \sim 10^{-2}$ 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 data in **Fig.1a** [6]. Moreover, the crossover from *ac* to *dc* conductivity was identified in earlier reports at $f \sim 10^{-3}$ Hz [8,9,10]. Therefore, the relaxation observed at lower frequencies in Nafion dielectric spectrum can be attributed to ion-hopping dispersion (σ relaxation) [6,7]. The electric modulus representation is advantageous to study Nafion relaxations because it suppresses electrode polarizations and display the σ and α relaxations in a higher frequency range, as indicated in **Fig.1b**. The σ and α relaxations are observed at $f \sim 10^{-2}$ Hz and $f \sim 10^1$ Hz, respectively. **Fig. 2** shows the dielectric loss and electric loss modulus as a function of *T* and *f* for N115 at *RH* = 100%.

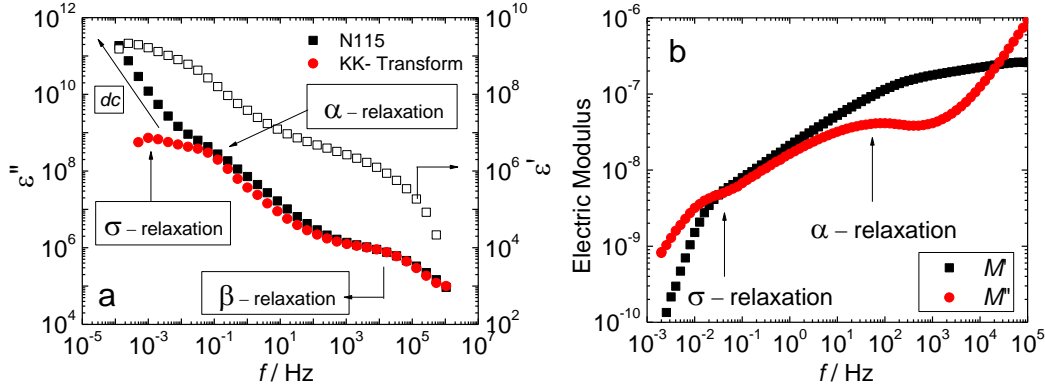


Figure 1. (a) Real and imaginary parts of dielectric permittivity as a function of frequency for N115 at 80 °C and at $RH = 100\%$. The KK transform of the real part of the dielectric permittivity is indicated. (b) Real and imaginary parts of the electric modulus as a function of frequency for N115 at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

In **Fig. 2a**, the β -relaxation 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 T can be better visualized in **Fig. 2b**. Previous DS studies of N115 revealed that the α and β relaxations exhibit an unusual shift to low f with increasing T [5,9,10]. The α and β relaxation dynamics shown in **Fig. 2** for N115 reproduces such behavior. Both relaxations displace to lower frequencies for $T > 120$ °C.

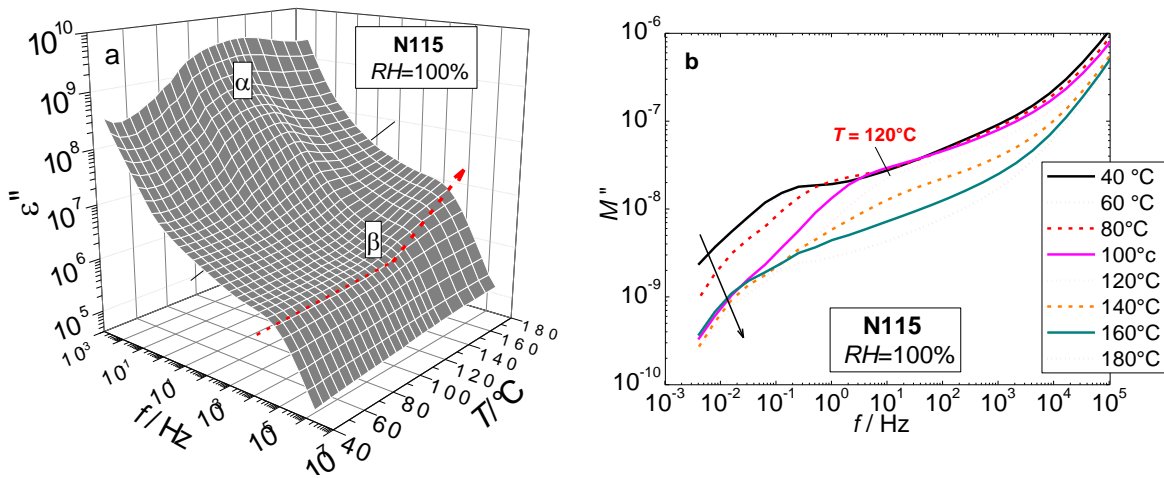


Figure 2. Dielectric loss (a) and modulus loss (b) dependence on T and f for N115 at $RH = 100\%$. In (a) regions in which α / β relaxations occur are marked and the dashed arrow indicates the β relaxation frequency. In (b) the arrow points to increasing measuring temperature and the α relaxation frequency at $T=120$ °C is indicated.

Such uncommon temperature dependence of the relaxation frequency can be contrasted with the usual shift to high f with increasing T of transitions observed in polymer/ionomer systems [6,7]. In ionomeric solutions, the increase of the polymer concentration leads to the displacement of β -relaxation to higher frequencies due to the decrease of the correlation length between the polymer chains [8]. In addition, the increase of the solution acidity displaces the α -relaxation to higher frequencies due to the decrease of the chain length resulting from

electrostatic screening of repulsive forces between sulfonic groups [8]. Therefore, the displacements of α and β relaxations of Nafion to lower frequencies with increasing T can be regarded as an inverse process. Such a process is related to a dilution due to the progressive increase of water sorption capacity at high T and RH . This dilution promotes the increase of the correlation length between the polymeric aggregates, which, in turn, 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 water content can be associated with an increase of the average length of Nafion polymeric aggregates. Thus, it is reasonable to assume that the unusual temperature dependence of the relaxation frequency is connected to a structural transition associated with the water sorption at high T . As the water content increases, dissociated ions induce strong electrostatic repulsion among sulfonic acid groups that promotes a conformation transition from a coiled state to more elongated polymeric aggregates.

Such a structural transition occurs at $T \sim 120$ °C in which an abrupt increase of the water uptake was observed, as shown in **Fig. 3**. The proposed scenario, in which the α -transition in Nafion membranes is related to the elongation of the polymeric aggregates, is further supported by the estimate of the end-to-end length as a function of temperature by considering the polarization of the polymeric aggregates due to the diffusion of counterions along the length scale (Eq.1). In ionomers, the frequencies of the dielectric dispersions associated with the α (f_α) and β relaxations (f_β) are related to the length (L) and average distance between the polymeric aggregates (ξ) according to [8,10]:

$$f_\alpha^{-1} \approx \frac{L^2}{6D}, \quad [\text{Eq. 1}]$$

$$f_\beta^{-1} \approx \frac{\xi^2}{6D}, \quad [\text{Eq. 2}]$$

where D is the proton diffusion coefficient at each temperature [13]. In **Fig.3**, the water content (**Fig.3a**) as well as the L and ξ values (**Fig.3b**) are shown as a function of temperature.

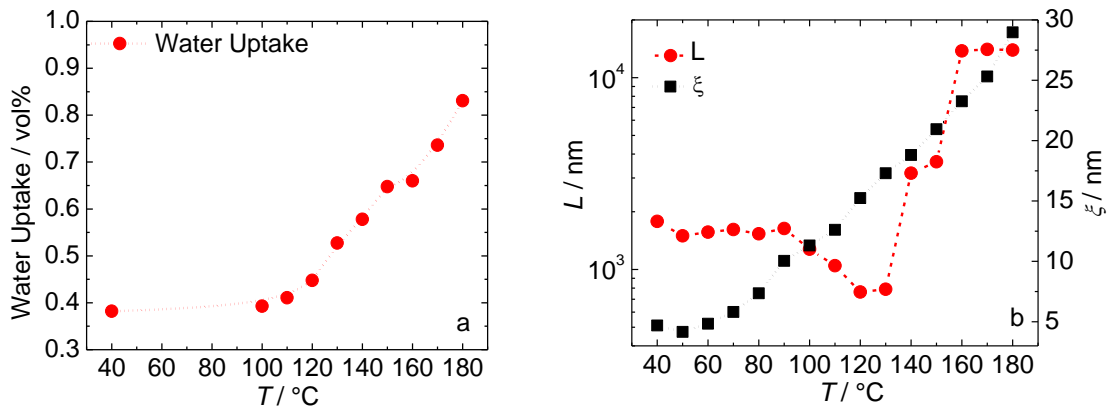


Figure 3. (a) Temperature dependence of water uptake and (b) the length (left axis) and correlation distance (right axis) of polymeric aggregates. Dotted lines are guide to the eye.

In **Fig.3a**, it can be seen that the measured water content of Nafion membranes increases substantially for $T > 120$ °C, in agreement with previous reports [12]. As the water content

increases a higher degree of dissociation of the protonic charges from the sulfonic acid groups is expected to result in increased repulsive forces among the dissociated ionic groups. The large amount of absorbed water indicates that a dissolution process is taking place with increasing T . In **Fig. 3b**, the increase of the water uptake is reflected in the increase of ζ with increasing T , a feature more marked at $T > 80$ °C. The correlation distance between the Nafion polymeric aggregates increases from $\zeta \sim 5$ nm ($T = 40$ °C), which is in good agreement with the values inferred from small angle X-ray scattering (SAXS) [13], to $\zeta \sim 29$ nm at $T = 180$ °C. **Fig. 3b** shows the temperature dependence of the length (L) of the polymeric aggregates. The sharp increase of L is observed to occur in a similar temperature range ($T > 120$ °C) in which the water uptake increases substantially. Such behavior adds evidence to the scenario in which the displacement of α -relaxation to lower frequencies is associated with a conformation transition of polymeric aggregates due to repulsive forces among sulfonic acid groups. The increased ionic dissociation due to water uptake increases the electrostatic repulsion among ions incorporated in the polymer backbone thereby increasing the end-to-end average distance of the polymeric aggregates [8,13].

In order to correlate the DS analysis with morphological features, tapping mode AFM measurements were carried out in N105 membranes ($EW = 1000$ gmol⁻¹) as shown in **Fig. 4** and **5**. The topography of Nafion was previously shown to exhibit a contrast of nanometer sized phases —nearly circular-shaped features with dimensions of $\sim 4 - 10$ nm— that can be attributed mostly to ionic and non-ionic phases (**Figs. 4a** and **4b**) [14].

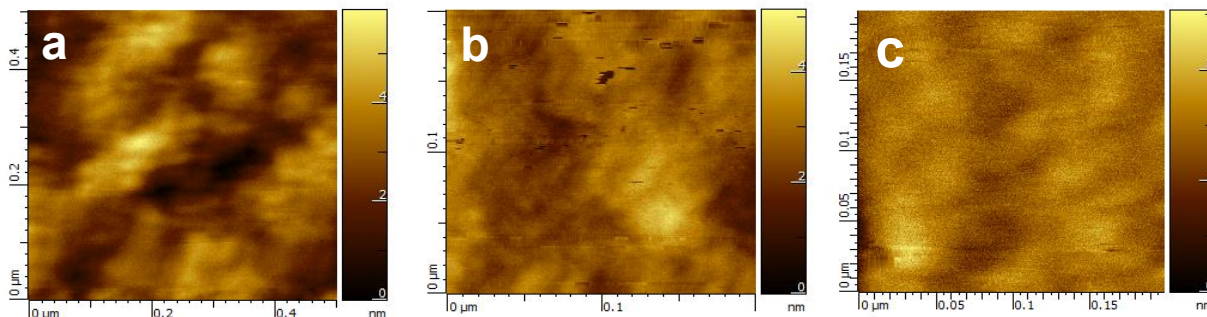


Figure 4. AFM topography images of Nafion annealed at 30 °C (a), 90 °C (b) and 140°C (c).

In **Fig. 4**, the depth of the contrasted regions is ~ 5 nm in agreement with previous AFM analysis [14,15]. Differently, the topography of Nafion annealed at $T = 140$ °C (**Fig. 4c**) exhibits elongated features.

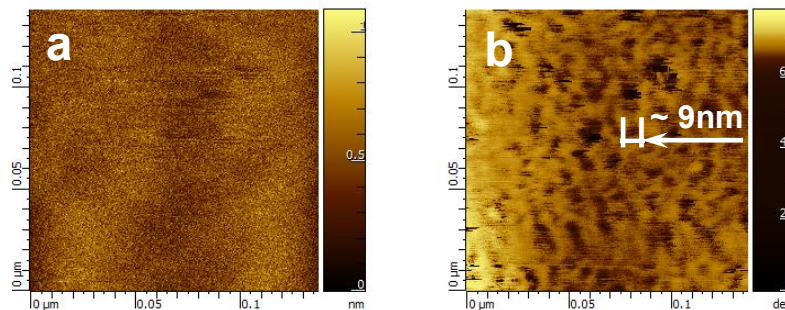


Figure 5. AFM images of Nafion annealed at 140°C. The scan range is 150 nm by 150 nm.

Images displayed in **Figs. 5** show the sample surface, which 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 [2]. The anisotropic orientation of the microstructure of Nafion is in accordance with **Fig. 5** that evidences the presence of vertical elongated structures. In order to compare the correlation distance among the elongated structures with the ones obtained by DS (**Fig. 5b**), the average distance was roughly estimated in **Fig. 5b**. The average distance between the elongated structures (~ 9 nm) is in accordance with the correlation distance for the annealed samples shown in **Fig. 3b**. Thus, the AFM images 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.

CONCLUSION

Careful dielectric spectroscopy analysis along with atomic force microscopy images provided valuable insights to advance the understanding of the properties of Nafion. The α -relaxation was related to the polarization of counterions distributed along the length of polymeric aggregates. At temperatures similar to the observed increase of water sorption, the α -relaxation displaces to lower frequencies indicating the elongation of polymer aggregates. Such a morphological transition was confirmed by atomic force microscopy, which revealed the presence of elongated structures in the Nafion samples annealed at temperatures higher than α -transition.

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