



## Interplay between $\alpha$ -relaxation and morphology transition of perfluorosulfonate ionomer membranes



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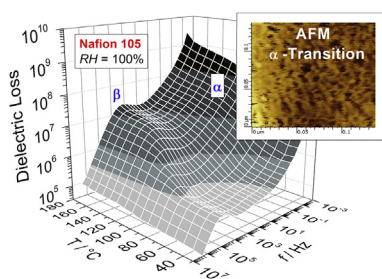
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### HIGHLIGHTS

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

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 10 April 2015

Received in revised form

29 May 2015

Accepted 30 May 2015

Available online 12 June 2015

#### Keywords:

Ionomers

Conformation transition

Morphology

Microstructure

Polymer electrolyte fuel cells

### ABSTRACT

Nafion  $\alpha$ -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  $\alpha$ -transition. The dielectric permittivity curves of Nafion membranes show that for relative humidity higher than ~60% and for temperatures higher than ~120 °C, the  $\alpha$ -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  $\alpha$ -relaxation, commonly observed at  $T_\alpha \sim 110^\circ\text{C}$  [7–9]. Several applications rely on the understanding of the nature of  $\alpha$ -relaxation. The  $\alpha$ -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  $\alpha$ -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  $\alpha$ -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  $\alpha$ -transition is missing.

Previous characterizations of the  $\alpha$ -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  $\alpha$ -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  $\alpha$ -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  $\alpha$  and  $\beta$  relaxations of Nafion: both relaxations shift to lower frequencies with increasing annealing temperature [17,19]. The proposed assignment of  $\alpha$ -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  $\alpha$ -relaxation in perfluorosulfonate ionomers does not exhibit the characteristic features of a glass transition and suggested that the  $\alpha$ -transition can be linked to a morphological transition of the ionomer [5,8]. Therefore, the relationship between the morphology and the dynamics of  $\alpha$  and  $\beta$  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  $\alpha$  and  $\beta$  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 ( $\Delta\epsilon \sim 10^2\text{--}10^4$ ) [12–14]. The high dielectric increment observed in Nafion dielectric spectrum has posed a challenge to the determination of the origin of Nafion  $\alpha$  and  $\beta$  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  $\alpha$  and  $\beta$  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  $\alpha$  and  $\beta$  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  $\alpha$ -relaxation with the polarization of the polymeric aggregates due to the diffusion of condensed protons, and the association of  $\alpha$ -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  $\alpha$  and  $\beta$  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:  $\text{HNO}_3$  ( $7 \text{ mol L}^{-1}$ ),  $\text{H}_2\text{O}_2$  (3 vol.%), and  $\text{H}_2\text{SO}_4$  ( $0.5 \text{ mol L}^{-1}$ ) at  $80^\circ\text{C}$  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  $\sim 3$  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]:

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

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

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