Origin of α and β relaxations of Nafion

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Our experiments disentangle the low and high frequency dispersions in perfluorosulfonate ionomer solutions and membranes, providing a reasonable model for understanding these relaxations. Dielectric spectroscopy (DS) and small angle x-ray scattering (SAXS) measurements revealed that the dielectric relaxations observed at low (α relaxation) and high (β relaxation) frequencies show typical features of the longitudinal and radial polarization, respectively, of rodlike polymeric aggregates. Such relaxations were attributed to counterion fluctuations in the vicinity of sulfonic acid groups, in resemblance with polyelectrolytes. Characteristic correlation lengths calculated from both DS and SAXS data are in good agreement adding further evidence to the proposed model. Such description provides insights for the understanding of the crossover from polyelectrolytes, dominated by charge repulsion, to ionomers, dominated by dipolar attraction.

I. INTRODUCTION

Ionomers are high performance polymers in which the presence of a small fraction of ionic groups (<15 mol %) along the polymer chains gives rise to a nanophase-separated morphology consisting of clustered ionic reinforcements ubiquitously distributed in a hydrophobic matrix [1]. The distinction between ionomers and polyelectrolytes is evident. In polyelectrolytes each monomeric unit usually bears an ion pair giving rise to particular effects such as the counterion condensation [1,2]. In the framework of Oosawa-Manning (OM) theory, the counterion condensation in a polyelectrolyte takes place when the separation (h) of monovalent charges (z) along the polymer chain is less than the Bjerrum length (l_b) [3]. The Bjerrum length is given by

$$l_b = \frac{e^2}{4\pi \varepsilon_0 \varepsilon kT},\tag{1}$$

where e is the elementary charge, k is the Boltzmann constant, T is the absolute temperature, and ε *and* ε_0 are the dielectric constant of the medium and the vacuum permittivity, respectively. For polyelectrolytes in aqueous solution ($\varepsilon \sim 80$) the interionic distance along the polymer backbone can be less than the Bjerrum length ($l_b \sim 7$ Å) resulting in a high linear charge density, $n = zl_b/h > 1$ [2,3]. In this case, the thermal fluctuations are insufficient to reduce the Coulomb repulsion energy and a layer of condensed counterions is formed in the vicinity of the ionic group to such an extent that the charge density along the chain is reduced to unity [2,3]. In ionomers, due to the low dielectric constant of the ionomer matrix ($\varepsilon \sim 2$) the dipole-dipole interactions among neighboring ion pairs prevail, thereby forming a mesoscopic clustering of ionic groups (multiplets) [1]. Moreover, due to the large interionic distance in the polymer backbone the counterion condensation phenomenon in ionomer chains in solution is improbable to occur. Such features constitute some of the main differences between ionomers and polyelectrolytes [4].

Nonetheless, an important family of ionomers, namely, perfluorosulfonate ionomers, is produced by statistical copolymerization. In this ionomer long sequences of the neutral and ionic monomers coexist along the polymer backbone [5]. Such feature can give rise to polymer chains with ion-rich segments with the distance between sulfur atoms ranging from ∼22 to ∼5 Å, as revealed by molecular dynamic simulations [6,7]. Additional experimental evidences of relatively short distances between ionic species were obtained by extended x-ray absorption fine structure (EXAFS) and Mössbauer spectroscopy indicating that the Fe-Fe distance in hydrated Nafion membranes is ∼3.4 Å [8]. Such a low intrachain distance of sulfonic acid groups can result in polymer segments with the charge density higher than the Oosawa-Manning critical threshold, leading to the condensation of counterions in ionomer chains. Infrared and fluorescence spectroscopy studies of hydrated Nafion membranes revealed that ∼80% of the counterions are strongly linked to the sulfonic acid groups [9]. By using Donnan equilibrium experiments and small angle x-ray scattering (SAXS) analysis, the extent of counterion condensation in hydrated Nafion membranes was previously estimated to range within 72% to 98% [10]. In this context, the properties of perfluorosulfonate ionomer lie between those of polymers with low and high ion content, and the study of such ionomers may help establish the knowledge gap of the transition from charge repulsion in polyelectrolytes to ion clustering in ionomers [11].

Nevertheless, the understanding of the role of free and condensed counterions on the electric and dielectric properties of perfluorosulfonate ionomers is hampered due to the difficulty in determining the origin of Nafion α and β relaxations by dielectric spectroscopy (DS) [12]. The dielectric spectroscopy study of Nafion membranes, in particular, the α ($f \sim 10^{-1}$ Hz) and β ($f \sim 10^5$ Hz) relaxations, were previously attributed to segmental polymer relaxations [12–15], interfacial polarization [16,17], and electrode polarization [18]; however, no consensus about the origin of Nafion dielectric dispersions has been reached yet [19]. The understanding of the mechanism involved in the α and Nafion β relaxations is considered crucial for determining

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morphology–electrical properties relations, which can be a guideline to the development of novel high performance ionomers and ionomer-based materials for electromechanical applications.

Herein, by combining SAXS and DS data of both Nafion membranes and solutions, it is demonstrated that the low and high frequency dispersions have the same underlying mechanisms of polyelectrolytes: the longitudinal and radial polarization of the rodlike polymeric aggregates due to counterion fluctuations.

II. EXPERIMENT

Nafion 5 wt % solution in water-alcohol mixture (DuPont) was evaporated at 50 °C until a polymer residue was obtained. The residue was redissolved with de-ionized water under stirring for 24 h to obtain Nafion precursor solution (5 wt %) in water. Solutions with final concentration of 0.08, 1.25, 2.50, 5.00, 10.0, 15.0, 20.0, 25.0, and 30.0 wt% of Nafion were prepared by evaporation (50 °C) and dilution of the precursor solution. All solutions were kept in closed vessels at 25 °C for 24 h, after which high concentration solutions (25 and 30 wt %) became gels. Nafion 0.08 wt % solutions were prepared with different molarities ($0.06M$, $0.12M$, $0.25M$, $0.50M$, and $1.00M$) by adding sulfuric acid (95%–98%, Aldrich). A Nafion membrane was obtained from DuPont and by the solution casting using the procedure reported elsewhere [13].

The sample holder for dielectric spectroscopy ($\varepsilon^* = e' - i\varepsilon''$) measurements of Nafion solution is a cylindrical chamber (∼15 mm diameter) with the configuration of a parallel plate capacitor (stainless steel) with lead terminals insulated with Teflon. The sample holder is filled with the Nafion solution covering the fixed electrode placed at the bottom of the chamber. Subsequently, the movable (top) electrode is partially immersed in the solution keeping ∼2-mm gap between the capacitor plates. The sample holder for the measurements of Nafion membranes consists of a parallel plate capacitor inserted in a stainless steel chamber able to keep the relative humidity constant (RH = 100%) [13]. A Solartron 1260 frequency response analyzer was used in the 4 mHz to 3 MHz frequency (f) range with 100 mV ac amplitude. The measurements of Nafion solutions were performed at $T = 25$ °C. Further details of DS measurement are described elsewhere [13]. The Kramers-Kronig (KK) transform semianalytical formula, $\varepsilon''(\omega) = -\pi/2[d\varepsilon'(\omega)/dln\omega]$, was used for Nafion membranes to calculate the imaginary part of the permittivity from the real one, which is exempt of the dc contribution [19]. Due to the high degree of superposition of the dielectric relaxations of Nafion solutions, the relaxation frequency was obtained by plotting the imaginary component of the conductivity ($\sigma'' = 2\pi f \varepsilon_0 \varepsilon'$) as a function of frequency. The relaxation peaks of Nafion membranes were obtained by using Havriliak-Negami fits [14]. The dc proton conductivity was calculated at $f \sim 10^6$ Hz and $f \sim 10^{-3}$ Hz using the relation: $\sigma' = 2\pi f \varepsilon_0 \varepsilon''$.

SAXS measurements of Nafion solutions were performed using Nanostar equipment (Bruker) and the Nafion membranes were measured in the Brazilian synchrotron facility LNLS. The dispersions were placed in cylindrical glass capillaries with an internal diameter of 1.0 mm. The scattering curve of a

single water filled capillary was used as blank scattering, which was removed from the sample intensities after transmission correction. The acquisition time of each scattering curve was 1 h. The SAXS curve of hydrated membrane samples was obtained by placing the Nafion cast film inside a glass reservoir filled with water. The diffraction figure was integrated to generate an intensity file of the scattering vector (q) as a function of the scattering angle (2θ): q = $(4\pi \sin \theta)/\lambda$ (Cu $K\alpha$ radiation, $\lambda = 0.1540$ nm). The correlation length of the interference scattering was obtained by d = $2\pi/q$. The SAXS patterns were fitted with the SASFIT free software package.

III. RESULTS AND DISCUSSION

In order to understand the origin of the relaxations of Nafion, detailed dielectric spectroscopy measurements were carried out. Figure 1 shows the dielectric spectra of Nafion membrane [Fig. 1(a)] and solution [Fig. 1(b)].

In the dielectric spectrum of hydrated membranes [Fig. 1(a)] the β relaxation can be identified at high frequencies ($f \sim 10^5$ Hz) whereas the α relaxation usually is superposed by the dc conduction at $f < 10^{-1}$ Hz [19]. The contribution of the dc conduction is eliminated in the dielectric loss obtained by KK transform, revealing the α relaxation at lower frequencies ($f \sim 10^{-2}$ Hz). The huge dielectric increment, $\Delta\varepsilon \sim 10^8$ and $\Delta\varepsilon \sim 10^6$ of both α and β relaxations, respectively, indicates a high degree of polarizability occurring in Nafion membranes, which can be an outcome of the high ionization constant of sulfonic acid groups. The dielectric spectrum of Nafion 5 wt % solution [Fig. 1(b)] shows two dielectric
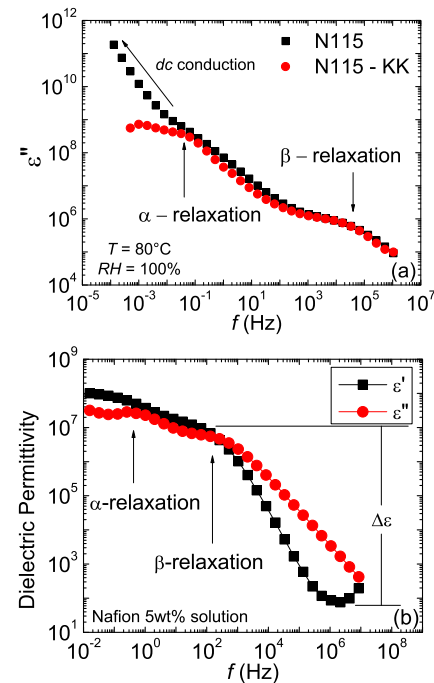

FIG. 1. (Color online) (a) Imaginary part of dielectric permittivity of Nafion membrane at $T = 80$ °C and RH = 100% and the corresponding Kramers-Kronig transform. (b) Real and imaginary parts of dielectric permittivity as a function of frequency of Nafion 5 wt % solution $T = 25$ °C.
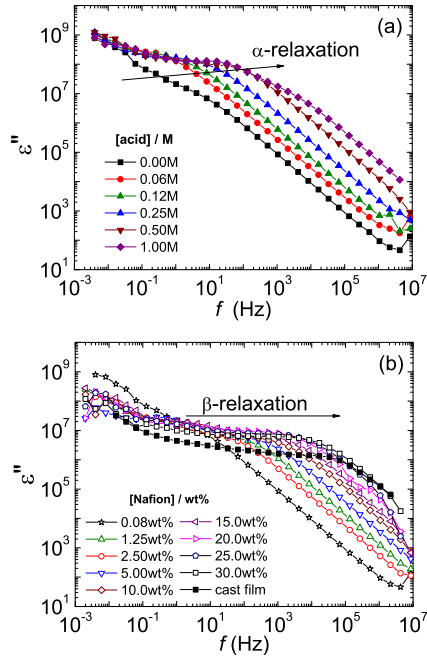
FIG. 2. (Color online) (a) Dielectric loss for Nafion 0.08 wt % solutions with increasing acid molarity. (b) Dielectric loss for Nafion (acid free) solutions with increasing polymer concentration. The arrows point to increasing acid molarity (a) and concentration (b).

relaxations centered at $f \sim 10^{-1}$ Hz $(\Delta\varepsilon \sim 10^8)$ and at $f \sim 10^2$ Hz $(\Delta\varepsilon \sim 10^7)$, which will be labeled, in analogy with the relaxations observed in membranes, as α and β relaxations, respectively. As the dielectric increment in ion-containing polymers is proportional to the counterion polarizability, the large $\Delta\varepsilon$ measured is an indication that the polarization of Nafion aqueous solutions and hydrated membranes share common mechanisms [2,20]. The similarity between solution and membranes is in accordance with previous dielectric spectroscopy measurements of ion-containing polymers that showed that both solutions and the corresponding cross-linked gels exhibit the same dielectric relaxations [20]. Nonetheless, the different relaxation frequencies observed in membrane and solutions have to be addressed.

To further understand the dependence of the relaxation frequencies on the morphology of Nafion, detailed dielectric spectroscopy measurements were carried out by controlling both the polymer concentration and acid molarity of Nafion solutions. Figure 2 shows the dielectric loss spectra of Nafion solutions as a function of both the acid concentration [Fig. 2(a)] and the polymer concentration [Fig. 2(b)].

It is interesting to note that the dielectric spectra of Nafion solutions with increasing acid molarity and polymer concentration are very similar to the ones observed for polyelectrolyte solutions [2]. The dielectric spectra of polyelectrolyte solutions display two characteristic relaxations with high dielectric increment $(\Delta\varepsilon \sim 10^2$–$10^4)$. Such relaxations usually occur at low f, $\sim 10^0$–10^2 Hz and high f, $\sim 10^2$–10^6 Hz and are attributed to the polarization of the polyelectrolyte chain along the longitudinal and radial directions, respectively [21]. The polarization is due to free (high-f relaxation) and condensed counterions (low-f relaxation) surrounding the ionic groups distributed along the polymer backbone [2,21].

In Fig. 2(a) the dielectric curve of Nafion dilute solution (0.08 wt %) without added acid displays the α and β relaxations at $f < 10^{-1}$ Hz $(\Delta\varepsilon \sim 10^8)$ and $f \sim 10^1$ Hz $(\Delta\varepsilon \sim 10^7)$, respectively. With increasing acid concentration from $0M$ to $1M$, the α relaxation displaces from 10^{-1} Hz to 10^2 Hz. Such an effect can be compared with the shift to high frequencies observed in the dielectric spectra of polyelectrolyte solutions with added acid or salt. In polyelectrolytes, the shift to high frequencies is attributed to the reduction of the length (end-to-end distance) of the polymer backbone [21]. The electrostatic screening, due to added acid, reduces the repulsive forces along the polyelectrolyte chain thereby promoting the rod-to-coil conformation transition [2,21]. Nafion chains in solution exhibit a rodlike conformation stabilized by strong electrostatic repulsions among sulfonic acid groups at the end of side chains [22,23]. Thus, the electrostatic screening due to increasing acid concentration changes the polymer backbone conformation from an extended rodlike conformation to a more coiled one. Similarly to polyelectrolytes, the shift to higher f of the α relaxation with increasing acid molarity results from the reduction of the length of the polymer backbone in Nafion solution.

The dielectric increment $\Delta\varepsilon$ of the longitudinal polarization was shown to increase with increasing fraction of condensed counterions $(1 - \theta)$, the counterion concentration (c), and the length of the polymer backbone (L) according to the relation [2]

$$\Delta\varepsilon \approx l_b\varepsilon\,(1 - \theta)\,cL^2, \qquad (2)$$

where l_b is the Bjerrum length and ε is the dielectric constant of the medium. Such a relation was used to roughly estimate $\delta\varepsilon$ in Nafion solutions. Light scattering studies of Nafion solutions showed that the hydrodynamic radius of the polymeric aggregates ranges within $R_H = 400$–$10\,000$ nm [23]. By assuming this R_H range as the length L of Nafion rodlike polymeric aggregates in solution, and the fraction of condensed counterions of $\sim 80\%$, as estimated by fluorescence spectroscopy [9], the calculated $\Delta\varepsilon$ is $\sim 10^4$–10^7, in reasonable agreement with experimental data [Fig. 1(a)]. Such high dielectric permittivity was previously attributed to macroscopic polarization of the counterions at the electrodes' surface (electrode polarization) [18]. However, the calculated dielectric permittivity values of Nafion in solution as well as previous dielectric spectroscopy studies of Nafion membranes indicate that the electrode polarization processes is out of the frequency range measured [13,14,16]. An important evidence for the absence of electrode polarization in the studied frequency range can be inferred from Fig. 1(a). As the electrode polarization occurs due to the pileup of charges across the electrode's surface at frequencies lower than the long range displacement of the ionic charges (dc conduction) [2], the presence of dc conductivity at $f < 10^{-3}$ Hz indicates that the electrode polarization takes place at much lower frequencies [2].

In Fig. 2(b), it can be observed that with increasing polymer concentration the β relaxation shifts pronouncedly to higher frequencies, while the dielectric increment remains essentially constant. Such an effect has been observed in polyelectrolytes further evidencing common features in the dielectric spectra of Nafion solutions and polyelectrolytes [21,24]. The increase in the polyelectrolyte concentration in the semidilute regime is followed by a displacement of

the high frequency β peak to higher frequencies as a result of the reduction of the distance between polymer chains in solution [24]. Figure 2(b) shows the dielectric spectrum of cast Nafion membrane at $T = 40\,^{\circ}\mathrm{C}$ for comparison. The β relaxation frequency of highly concentrated Nafion solutions approaches the one observed for cast membrane ($f \sim 10^5$ Hz). This behavior shows a progressive transition of the relaxation from low concentration solutions to the cast membrane and can be regarded as the result of an increased degree of packing and entanglement of the ionomer chains with increasing polymer concentration.

It is well accepted that the dielectric relaxations of polyelectrolyte solutions arise from free counterions in solution and condensed counterions in the regularly spaced ionic groups along the polymer backbone [2]. In the case of Nafion ionomer chains in solution, previous studies have pointed out that segments of the polymer backbone can have a high density of side chains with low intrachain spacing between sulfur atoms ($h \sim 5$ Å) while other segments of the polymer can contain a reduced number of side chains with larger spacing ($h \sim 5$–22 Å) [10,22]. Based on these findings, the linear charge density (n) in the side-chain-rich segments of Nafion backbone in aqueous solution is above the critical threshold as given in Oosawa-Manning theory ($n = z l_b / h > 1$) and a general description of counterions of perfluorosulfonate ionomers in aqueous solutions must consider two possible states: (i) a fraction of free counterions dissolved by water ($h > l_b$) and (ii) a fraction of condensed counterions in sulfonic acid groups ($h < l_b$) [9]. In this context, it is reasonable to assume that the motion of free and condensed counterions along the rodlike ionomer chains may have polarization mechanisms related to α and β relaxations analogous to polyelectrolytes.

The discussed similarities between Nafion solutions and polyelectrolytes extracted from the DS data were further investigated by SAXS measurements. Figure 3(a) shows the SAXS curves of Nafion solutions (acid free) with increasing polymer concentration. The SAXS pattern of a cast membrane sample is shown for comparison.

The SAXS patterns of Nafion solution display a scattering maximum at $q \sim 0.35$ nm^{-1} (10 wt %) attributed to the interparticle interference (ionomer peak) of the rodlike aggregates in solution [22]. As the polymer concentration increases the ionomer peak shifts to higher q and the peak width at half height decreases. These features were attributed to a reduction of the distance between adjacent rodlike aggregates with increasing polymer concentration [22].

In order to perform a more quantitative analysis, the length scales probed by DS are compared with the ones obtained by SAXS. Figure 3(b) shows the correlation length obtained by SAXS (d) and DS (ξ) as a function of the polymer concentration. The dielectric correlation length (ξ) of polyelectrolyte solutions can be estimated using the frequency of the radial polarization (β relaxation) and counterion diffusion coefficient (D) by the following relation [2]:

$$\xi \approx \left(\frac{6D}{f} \right)^{1/2}. \qquad (3)$$

Since the counterion diffusion coefficient for Nafion solutions is not available, the correlation length dependence on
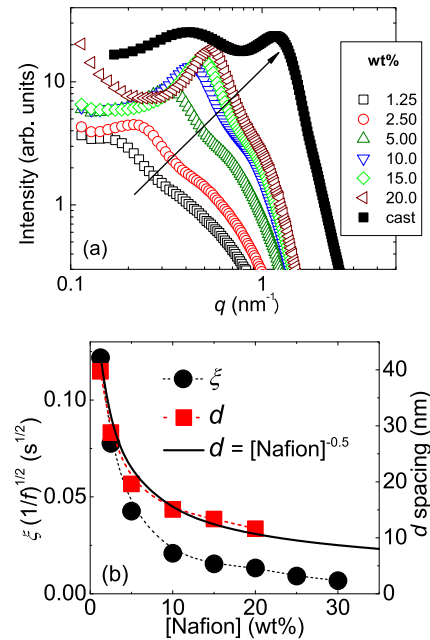

FIG. 3. (Color online) (a) SAXS patterns of Nafion solutions with increasing polymer concentration. The solid symbols represent the curves of a cast membrane from Nafion solution. The arrow points towards increasing concentration. (b) SAXS d spacing and dielectric correlation length ξ as a function of polymer concentration. The continuous line represents the characteristic dependence of the d spacing with polyelectrolyte concentration (–0.5 power law).

concentration was obtained by plotting $(1/f)^{1/2}$ as a function of polymer concentration, as shown in Fig. 3(b). In the semidilute regime the correlation length of polyelectrolytes scales with concentration with a characteristic power law of -0.5 [25]. The log-log plot of the SAXS d spacing of Nafion with concentration shows that the fitted power law -0.47 is in good agreement with the values observed for polyelectrolytes. Moreover, the similar dependence of both correlation lengths, obtained by SAXS and DS, on the polymer concentration adds further evidence that the β relaxation is associated with the correlation length of the Nafion rodlike aggregates in solution. By using the SAXS d spacing of Nafion 1.25 wt % solution as the dielectric correlation length ξ in Eq. (3) the counterion diffusion coefficient was estimated to be $D \sim 1.1 \times 10^{-10}$ cm^2 s^{-1}. The calculated D is in good agreement with the diffusion coefficient of condensed counterions in polyelectrolytes [2,21]. However, the high frequency mode of polyelectrolytes has been related to free counterions in solutions [2].

Thus, in order to correlate the SAXS and DS measurements of Nafion membranes and solutions the estimatives of the diffusion coefficient (D) of condensed and free counterions are required. The counterion diffusion coefficient can be obtained by using the proton conductivity of free and condensed counterions [26], which were extracted from the dc conductivity observed at high ($f \sim 10^6$ Hz) [27] and at low frequencies ($f \sim 10^{-3}$ Hz) in Fig. 1(a), respectively. The presence of two frequency independent conductivities at $f \sim 10^6$ Hz and $f \sim 10^{-3}$ Hz and two dielectric relaxations at $f \sim 10^5$ Hz and $f \sim 10^{-2}$ Hz in Nafion dielectric plots must give rise to

four plateaus in plots of the real component of conductivity (σ') in the investigated frequency range [2]. Such a feature is in accordance with the σ' vs f plots of Nafion previously reported [13,14].

The calculated proton conductivity (σ) corresponding to high frequency ($f \sim 10^6$ Hz) is $\sigma = 0.05$ S cm^{-1}. This value is comparable to the conductivity obtained in polymer electrolyte fuel cells tests and can be attributed to the conduction of free ions [28]. The proton conductivity calculated in the low frequency is $\sigma = 3.6 \times 10^{-7}$ S cm^{-1}, which is similar to the conductivity of dry Nafion membranes and reflects the transport of condensed counterions along the side chains [29]. Some additional features support the presence of two frequency independent conductivities in hydrated Nafion membranes: (i) the conduction pathway of condensed protons along the polymer side chains have a higher resistance compared to the free counterions [9]; (ii) the transport of free counterions in the absorbed aqueous medium and the transport of condensed counterions along the polymer structure have distinct conduction pathways and characteristic relaxation times.

By using the proton conductivities measured at low and high frequency the counterion diffusion coefficient can be calculated with the Nernst-Einstein relation [30]:

$$D = \frac{\sigma k_b T}{n e^2},$$ (4)

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. (4) takes into account the fraction of free (20%) and condensed counterions (80%) previously estimated [9]. The diffusion coefficients calculated using the conductivities of both free and condensed counterions are $D_f = 8.7 \times 10^{-5}$ cm^2 s^{-1} and $D_c = 2.2 \times 10^{-10}$ cm^2 s^{-1}, respectively. The D_f is in excellent agreement with the diffusion coefficient of hydrated Nafion membranes [30] and D_c is in agreement with both the diffusion coefficient of condensed counterions in polyelectrolytes and the diffusion coefficient estimated by SAXS (Fig. 3). Thus, it is possible to use D_c inferred from impedance data to estimate the correlation length of the rodlike aggregates in the hydrated Nafion membrane using Eq. (3). The calculated correlation length, using the β relaxation frequency [$f = 1.2 \times 10^4$ Hz, obtained from Fig. 1(a)] for hydrated Nafion membranes is $\xi = 3.3$ nm, which is in reasonable agreement with the d spacing ($d = 2\pi/q$) calculated from the ionomer peak of the Nafion membrane SAXS pattern ($d = 5.1$ nm). The length (L) of the rodlike aggregates can be calculated using the following equation [2]:

$$L \approx \left(\frac{6D}{f} \right)^{1/2}.$$ (5)

By using the α relaxation frequency ($f = 0.01$ Hz) and the D_c, the estimated value is $L = 3600$ nm, in good agreement with the L estimated from light scattering [23]. Both the correlation lengths ξ and L calculated from the diffusion coefficient D_c are in good accordance with the characteristic lengths of Nafion chains [22,23], therefore suggesting that the diffusion of condensed counterions is the effective process involved in the polarization of the Nafion ionomer.
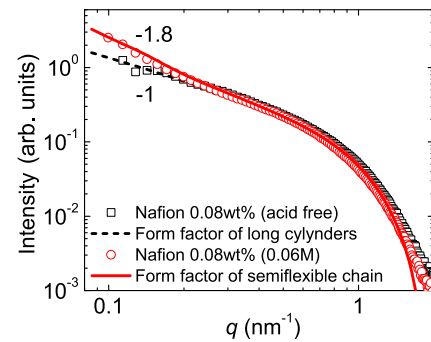

FIG. 4. (Color online) SAXS patterns of Nafion dilute solution free of acid and with the addition of 0.06M of sulfuric acid. The dotted and continuous lines are the fitting of the experimental curves with the form factor of cylinders and semiflexible chains, respectively.

Figure 4 shows the SAXS curves for acid free Nafion dilute solutions (0.08 wt%) and with added acid (0.06M). The scattering curves of Nafion 0.08 wt% solution containing different amounts of acid (0.06M–0.5M) are very similar and for this reason only the scattering curve of Nafion 0.06M solution is shown in Fig. 4.

The SAXS pattern of Nafion dilute solution (acid free) is typical of cylinders with characteristic slope -1 at lower q [31]. The scattering curve was fitted with the scattering function of randomly oriented cylinders, S_{cs}, using the equation [31]

$$S_{cs}(q) = \left[2 \frac{J_1(qR)}{qR} \right]^2,$$ (6)

where J_1 is a first-order Bessel function, and R is the cylinder radius. The adjusted cylinder radius ($R = 1.9$ nm) is in good agreement with the previous SAXS modeling of Nafion solutions [22]. The absence of a scattering intensity plateau at low q evidences the long length (>100 nm) of the rodlike aggregates [22]. On the other hand, the scattering curve of Nafion solutions with added acid (0.06M) displayed an increase in the scattering intensity for $q < 0.3$ nm^{-1} with a slope of -1.8. Such a slope is similar to the one observed for electrostatic screened polyelectrolytes in solution (–1.7), which is characteristic of a random walk configuration of the polymer chain [31,32]. The electrostatic screening of the interionic repulsive forces changes the rodlike shape of polyelectrolytes to a more coiled conformation similar to that observed in uncharged polymers [32]. Thus, in the case of the 0.06M solution the SAXS pattern of polyelectrolytes can be adjusted with the scattering function of a semiflexible wormlike chain [31]:

$$S(q) = S_{wc}(q, L_c, b) S_{cs}(q, R),$$ (7)

in which the S_{wc} is the scattering function representing the polymer chain flexibility at different length scales. Equation (7) is composed of the scattering functions of an infinitely thin Gaussian chain with excluded volume interactions predominant at low q (contour length, L_c) and an infinitely thin rod predominant at high q (Kuhn length, b), in which the finite radius of the chain is given by the scattering function of a cylindrical shape (S_{cs}) [Eq. (6)] [31].

The cylinder radius used for the fitted SAXS curve of Nafion $0.06M$ solution is $R = 2.0$ nm. The fitted apparent Kuhn length of Nafion $0.06M$ and $0.50M$ solutions are $b \sim 25$ nm and ~ 22 nm, respectively. The Kuhn length is a measure of the chain flexibility and can be defined as the ratio of the polymer chain mean square end-to-end distance to the chain length at its fully stretched position ($b = \langle L^2 \rangle / L_c$) [31]. The lower b of Nafion with higher concentration of acid is in good accordance with the higher chain flexibility due to the acid screening. By using the diffusion coefficient of condensed counterions [$D_c = 1.1 \times 10^{-10}$ cm^2 s^{-1}, calculated from Fig. 3(b)] and the α relaxation frequency [$f = 100$ Hz, obtained from Fig. 2(a)] of Nafion $0.5M$ solution in Eq. (5), the resulting length is ~ 25 nm, which agrees with the SAXS Kuhn length (Fig. 4). This result is in accordance with the dielectric spectroscopy studies of electrostatically screened polyelectrolyte in aqueous solutions, which revealed that the length associated with the low frequency relaxation is comparable to the persistence length of the polyelectrolyte [21]. The SAXS analysis of Nafion solutions with increasing acid molarity evidenced that the characteristic lengths fitted from SAXS data, such as cylinder radius and Kuhn length, are in good accordance with the length scales obtained by dielectric spectroscopy analysis.

In previous studies the investigation of Nafion dielectric relaxations was based on study of the behavior of Nafion relaxations upon heating or membrane water sorption [12,13,14,16,18]. Based on these studies the Nafion relaxations were mainly attributed either to segmental polymer relaxation or electrode polarization [13,14,18]. However, more recent studies showed that the relaxations display uncommon properties such as the displacement of α and β relaxations to lower frequencies at $T > 100\,°C$, a feature that could not be accounted for by the usual interpretations [13,16]. The

originality and the main advantage of our approach was the investigation of the origin of Nafion relaxations based on the study of dilute Nafion solutions that significantly simplifies the interpretation of the dielectric spectrum [2]. The high dielectric permittivity of ion-containing polymers in dilute solutions is due to the stronger polarizability of the counterions in aqueous media with respect to segmental polymer relaxations ($\Delta\varepsilon < 10$), which allowed a more precise assignment of the observed relaxation processes in Nafion membranes.

IV. CONCLUSION

In summary, we showed that α and β relaxations of Nafion membranes and solutions correspond to the counterion motion along the longitudinal and radial direction of rodlike polymeric aggregates. The dielectric spectroscopy measurements of Nafion solutions and membranes revealed that the dynamics of the observed relaxations corresponded to changes of length scales of the ionomer chains that were promoted by varying the distance and length of the Nafion rodlike aggregates in solution as inferred from SAXS analysis. The combined experimental data of SAXS and DS allowed the study of the dynamics of Nafion ionomers, which revealed important features to advance the understanding of the crossover from the intense electrostatic repulsion in polyelectrolytes to the ion clustering in ionomer matrices.

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