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# Anisotropy of Water Self-Diffusion in a Nafion Membrane under Traction

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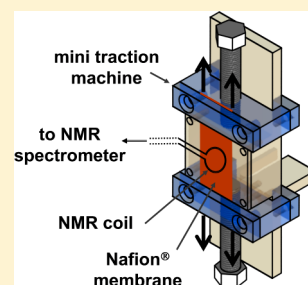
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## Supporting Information

**ABSTRACT:** Measuring water self-diffusion in the oriented structure of stretched Nafion represents an effective way of studying the correlations between the stress-induced order and the transport properties of the membrane. In this work, we performed pulsed-field gradient NMR experiments to investigate water self-diffusion in a single membrane under traction. The data were collected with a high signal-to-noise ratio and small draw ratio steps using a specially design NMR probe together with a mini traction apparatus. The results demonstrate that the anisotropy of diffusion is much larger in a membrane under traction than in a stack of membranes that were uniaxially stretched at high temperature before the measurements. Arguments based on the mechanical properties of Nafion can explain qualitatively the observed differences by highlighting the important role of both applied stress and temperature in the stress-induced order. We used a simple, but realistic, deformation model to analyze the experimental data by extracting the evolution of the diffusion anisotropy as a function of the orientational order parameter of the water conducting channels. Finally, we made analogies between the self-diffusion of water in the anisotropic structure of stretched Nafion and the Brownian dynamics of elongated particles.



## INTRODUCTION

**General.** Nafion (E.I. Dupont de Nemours and Co) is the most extensively studied ionomer as it represents the benchmark membrane material for applications such as proton exchange membrane fuel cells (PEMFC) or water electrolyzers. This copolymer contains small proportions of sulfonic ionic ( $-\text{RSO}_3^-$ ) groups attached at the extremity of side chains regularly spaced along its polytetrafluoroethylene (PTFE) backbone. Nafion membranes can be purchased in the form of thin films of different thicknesses ( $\sim 25$  to  $\sim 250 \mu\text{m}$ ) and different equivalent weights EW (EW, grams of dry polymer per equivalent of sulfonic functional groups). When sufficiently hydrated, Nafion membranes exhibit remarkable ion transport properties: a proton conductivity  $\sigma > 0.1 \text{ S/cm}$  is measured in Nafion N1100 (EW = 1100 g/equiv, e.g., N212, N115, N117, and N1110) at  $T > 80^\circ\text{C}$  and at a relative humidity RH  $> 80\%$ .<sup>1,2</sup> The high sorption capacity of the membrane, on the order of 25 wt %, is responsible to a large extent for its high proton conductivity and a fast increase of  $\sigma$  is observed when increasing the water content. The structure of the polymeric membrane represents also a key element and the understanding of the interplay between structure and transport is today the focus of a large number of studies. In this regard, the water self-diffusion coefficient,  $D_s$ , is an extremely useful parameter to characterize the membrane transport properties. As observed with the proton conductivity,  $D_s$  strongly increases with the water content.<sup>3</sup> Even if an unambiguous relationship between

these two quantities is still lacking, it is clear that water is the transport medium through which the protons are transported during the operation of a PEMFC. Numerous studies have focused on the characterization of water dynamics in Nafion using  $^1\text{H}$  NMR relaxometry<sup>4–8</sup> and water self-diffusion by  $^1\text{H}$ -pulsed-field gradient nuclear magnetic resonance (PFGNMR).<sup>2,3,9–17</sup> PFGNMR<sup>18</sup> is the most used technique in the literature to measure  $D_s$  in Nafion. Because the polymer backbone is only composed of PTFE and fluorocarbonated side chains, the NMR signal arises almost exclusively from the protons of the adsorbed water in the pores. Furthermore, this method is well established, relatively easy to implement, robust, fast and nonintrusive. Compared to proton conductivity measurements which require information on impedances at electrode–electrolyte interfaces and the knowledge of membrane thickness, PFGNMR is free of interfaces effects, thickness variations and is a noncontact method.

**Water Self-Diffusion as a Probe of Structural Order.** PFGNMR has been used in the literature for the determination of  $D_s$  as a function of water content<sup>2,3,16</sup> and temperature.<sup>9,11,16</sup> The results demonstrate that

- $D_s$  increases with increasing water content;<sup>2,3,16</sup>

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- in a fully hydrated membrane,  $D_s$  is only reduced by a factor  $\sim 4$  compared to bulk water at the same temperature<sup>3</sup> ( $\sim 6 \times 10^{-6}$  cm<sup>2</sup>/s in Nafion hydrated at  $\lambda = [\text{H}_2\text{O}]/[\text{SO}_3^-] = 14$  and  $T = 30$  °C compared to  $\sim 2.6 \times 10^{-5}$  cm<sup>2</sup>/s for bulk water<sup>19</sup>);
- $D_s$  strongly increases with temperature.<sup>9,11,16</sup>

Recently, other studies have used  $D_s$  as a probe of the membrane structure. Using <sup>2</sup>H NMR spectroscopy and <sup>1</sup>H-PFGNMR simultaneously, Li et al.<sup>13</sup> showed that water diffusion in extruded Nafion (Nafion N112, Nafion N117) was slightly faster in the direction of the lamination than in the directions perpendicular to it. A 18% diffusion anisotropy was detected in N112 at both high and low water contents due to the uniaxial in-plane order induced by the fabrication process. This small structural anisotropy is in agreement with the small birefringence observed by Van der Heijden and co-workers<sup>20</sup> in extruded N117. The situation in the dispersion cast N212 is somewhat different as the membrane presents a uniaxial through-plane order, but nearly isotropic diffusion behavior.<sup>13</sup> The authors reported furthermore that not all the extruded samples present such transport anisotropy and that this was due to a lower degree of ordering caused by different chemical and thermal treatments.

In order to artificially impose a structural order in the polymeric structure of Nafion and study the link between structure and water diffusion, the most recent studies have focused on the effect of a uniaxial stress in traction.<sup>12,14,15,17</sup> Lin et al. have measured  $D_s$  in a series of prestretched recast membranes (prepared from a Nafion solution) at different draw ratios.<sup>12</sup> The resulting films, which contained 10–15 wt % DMAc were stretched at high temperature (125 °C) to a variable draw ratio and annealed under tension at 150 °C for 2 h. The authors measured sorption, proton conductivity, water self-diffusion using PFGNMR and performed tests during DMFC operation.<sup>12,21–23</sup> The prestretched recast samples produced the higher power compared to both commercial N117 and recast undrawn film and presented a methanol permeability that decreased with elongation. The water content in the water-equilibrated samples was shown to be constant as a function of the draw ratio, with a varying partition between the freezable (bulk-like) water and the nonfreezable (strongly bond) water. The water-self-diffusion coefficient measured in the fully hydrated prestretched membranes was equal to that measured in the undrawn recast membrane, with no significant variation as a function of the draw ratio. The measurements, however, were performed on membranes that were rolled into long cylinders and placed in the NMR tube. As no indication of the direction of the diffusion measurement was given it is not possible to conclude about the presence of any diffusion anisotropy. Interestingly, the through-plane proton conductivity measured at 25 °C in the water equilibrated samples was also shown to be invariant with the draw ratio<sup>12,23</sup> while it was observed to slightly increase in the stretching direction at low temperature (–20 °C) as a result of the increase of the proportion of nonfreezable water during stretching.<sup>21</sup> Other studies have exploited complementary measurements (<sup>2</sup>H NMR,<sup>14,15,17</sup> <sup>1</sup>H-PFGNMR,<sup>14,15,17</sup> small angle X-ray scattering (SAXS),<sup>14,15</sup> and proton conductivity<sup>14,15,17</sup>) and simulations,<sup>24</sup> and the authors demonstrate unambiguously that the increase of the diffusion anisotropy is intimately linked to the degree of the imposed uniaxial order. The authors all agree on the fact that uniaxial deformation enhances water diffusion and proton

conductivity in the direction parallel to draw while reducing it in the two orthogonal directions. A diffusion anisotropy varying between 2 and 3 (depending on water content) was measured in N117 stretched at a draw ratio of 4.<sup>14</sup> Finally, the same authors<sup>14,15</sup> showed that transport anisotropy scaled linearly with the degree of ordering. This result, in full agreement with earlier SAXS and SANS studies of Nafion under traction,<sup>25,26</sup> shows the orientation of the polymer bundles (rather than their deformation) during stretching.

**Limitations of “Standard” Protocols for PFGNMR Measurements in Oriented Membranes.** PFGNMR, although powerful to determine unambiguously water self-diffusion coefficients in Nafion exposed to constant  $T$  and RH conditions, suffer naturally from a lack of sensitivity inherent to all NMR methods. In order to increase the NMR signal—and thus reduce the experimental error made on  $D_s$ —one must increase the quantity of polymer present in the measurement volume. To achieve this, all the published measurements (to the best of our knowledge) have been performed either on a strip of membrane rolled at the bottom on the NMR tube (when the object of the study is to measure the isotropic value of  $D_s$ ) or on a stack of 6 to 14 samples oriented along the same averaged direction (when the objective is to detect anisotropy). In the latter case, and because the volume of the NMR coil is small, the lateral size of the stack of membranes must be very limited (typically  $5 \times 5$  mm<sup>2</sup>).<sup>14,15,17</sup> This limitation causes a number of experimental issues if one is interested in the characterization of diffusion anisotropy in stretched membranes:

- The studied membrane is not under traction when the  $D_s$  measurement is performed. To prepare the sample in a state as close as possible to the real “under traction” state, the stretching is usually made in an oven at a temperature above the  $\alpha$ -relaxation temperature of the H<sup>+</sup>-form.<sup>27</sup> The objective is to deform permanently the polymeric structure and, thanks to a fast quenching at room temperature, to prevent from relaxation phenomena. Even if the orientation is observed to persist after several months,<sup>13,27</sup> the imposed order in a stack of stretched-relaxed membranes is probably different from the order present in the polymer under traction.
- The studied membrane has experienced very high temperature conditions during stretching. After being exposed to very high temperatures (125–150 °C<sup>12,15,17</sup>), the membrane’s properties are different from those measured on the pristine material. It is known indeed that sorption, diffusion, conductivity, and mechanical properties strongly depend on the thermal history of the membrane.<sup>2,28–30</sup> This effect does not introduce errors if the anisotropic transport measurements are compared to results obtained on a reference membrane that was effectively exposed to the same temperature conditions for approximately the same time. The self-diffusion coefficients, however, will probably be different from those measured under traction on a membrane stretched at lower temperature (room temperature for instance). Also, since temperature has a strong influence on the morphology and the mechanical properties of Nafion, cold drawing will produce effects in the microstructure that will be distinct from those induced upon drawing at high temperature. These effects will be discussed in the Discussion part of this paper.

- The stack of membranes is made of several samples that are aligned in the same averaged direction. Stacking up multiple samples inevitably introduces averaging effects that artificially reduce the structural order. Again, the observed diffusion anisotropy is probably different from the one that would be measured on a single membrane under stretching.

Finally, we note that in order to measure anisotropy at least two measurements made in two orthogonal directions are necessary. If more intermediate positions are needed, the orientation of the stack of membranes with respect to the magnetic field gradient must be controlled, either by physically rotating the stack or by artificially rotating the field gradient. The latter solution is preferable since it minimizes the errors (if one has access to a three-axis gradient diffusion—or imaging—NMR probe).

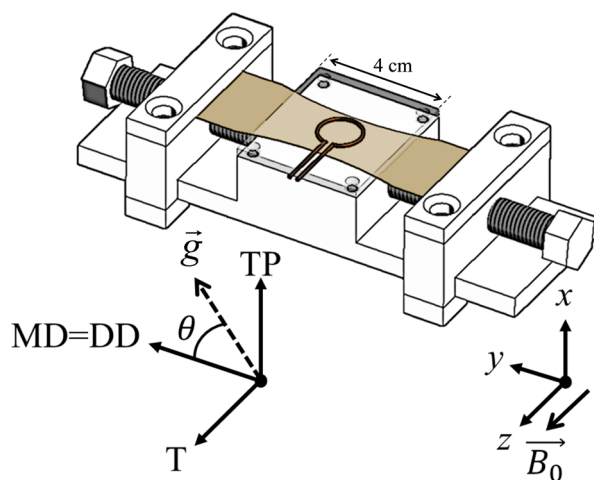
**Objectives of the Present Study.** The main objectives of this study are to overcome the previously described experimental limitations by developing a suitable methodology and to characterize the situation truly encountered in a Nafion membrane under stretching at room temperature. The method includes the development of a specific NMR hardware (2D single turn coil) coupled to a homemade mini traction machine. In this paper we present water self-diffusion coefficients measured on a single Nafion 1100 membrane under traction as a function of the draw ratio and the angle between the membrane plane and the diffusion direction. The last objective of this work is to analyze the data in the frame of a realistic deformation model, able to describe analytically the structural order induced by stretching while being compatible with the previous structural and transport characterizations of Nafion.

## EXPERIMENTAL SECTION

**Materials.** Extruded Nafion N1110 membranes (EW = 1100 g/equiv, acid form) were purchased from Ion Power, Inc. and prepared in a well-defined reference state using the following procedure (see ref 2 for details): the as-received membranes were first cleaned by boiling in 3 wt % oxygen peroxide ( $\text{H}_2\text{O}_2$ ) to eliminate organic residues. They were then rinsed with demineralized water at room temperature. To guarantee a complete acidification, the samples were soaked in aqueous 10 M nitric acid ( $\text{HNO}_3$ ) at room temperature during 30 min and rinsed with demineralized water. Finally, the membranes were boiled 1 h in aqueous 1 M sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and then 1 h in demineralized water. This pretreatment was followed by a 24 h long drying period in an oven at 60 °C.

**NMR Hardware and Stretching Protocol.** The experimental setup was specifically designed to measure the water transport properties of a single membrane under traction. The combination of two homemade elements was necessary: a stretching device that can be incorporated in the NMR spectrometer, and a 2D NMR coil that produces an intense magnetic field close to the membrane and receives the NMR signal (Figure 1). The NMR coil is a single turn 10 mm diameter copper loop. Its dimensions are small enough compared to the wavelength at 100 MHz. When tuning and matching are achieved by a symmetrical capacitive circuit the coil exhibits a good quality factor of about 110. Thanks to the 2D geometry, the plane of the membrane was close to the coil (2.5 mm) and was consequently exposed to a strong magnetic rf field. In the conditions of the experiments described below the 90° pulse length was 8  $\mu\text{s}$ . The dimensions of the sample were chosen to ensure that the coil covered a uniformly stretched part of the sample (far from the ends).

The N1110 membrane sample (20 × 40 mm<sup>2</sup>, initially 275 ± 5  $\mu\text{m}$  thick) was first clamped to the two extremities of the stretching device. The diffusion measurements were performed before stretching (at DR =  $L_f/L_i = 1$ , where  $L_f$  and  $L_i$  are the final and the initial lengths, respectively) with a small stress applied to ensure a wrinkle-free



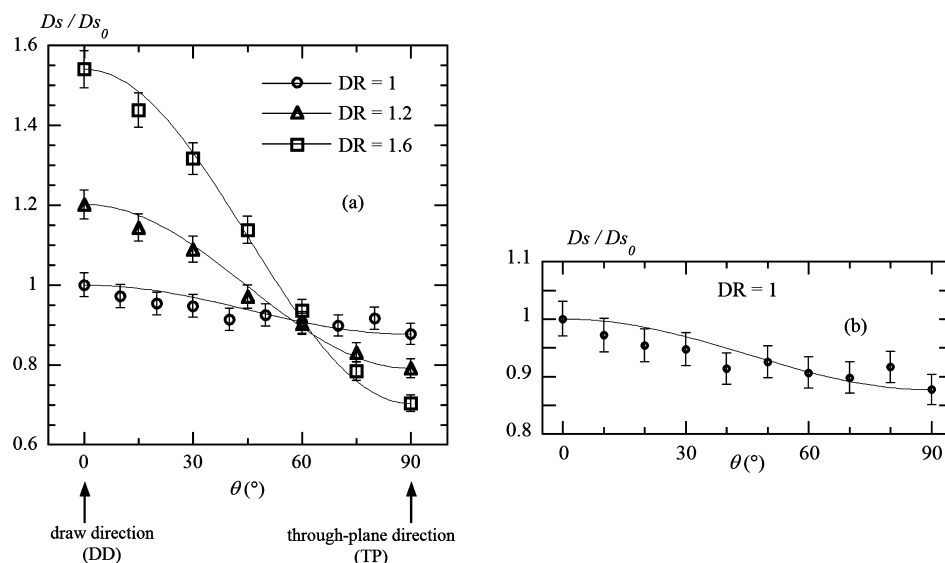
**Figure 1.** Mini-traction machine (made out of polycarbonate and PTFE) and 2D NMR coil developed for the measurement of  $D_s$  in a single membrane under traction.

membrane but not high enough to induce a measurable creep. The membrane was then stretched along the extruded direction (machine direction MD) with a draw step of 0.05. At each draw ratio the water self-diffusion coefficient  $D_s$  was measured in the draw direction (DD), the through-plane direction (TP), the transverse direction (T) and sometimes at intermediate positions  $\theta$  (Figure 1) so that the time between two consecutive draws was always longer than twice the time required for one diffusion measurement ( $\sim 2 \times 18$  min). The minimum time between the application of a draw increment and the first  $D_s$  measurement was about 15 min. We make the assumption that this duration is long enough so that the stress relaxation is always completed when the first  $D_s$  measurement is performed at a given strain. All the NMR experiments detailed in this paper were performed in the conditions of the air-conditioned experimental room. The averaged values of the temperature and the relative humidity over the total experimental time were  $T = 25 \pm 2$  °C and  $\text{RH} = 20 \pm 3\%$ .

The determination of the membrane water content was possible *in situ* at DR = 1 by measuring the NMR transversal relaxation time  $T_2$  using a conventional CPMG sequence.<sup>31,32</sup> As reported in the literature,<sup>33,34</sup>  $T_2$  is indeed strongly dependent on the membrane water content and can thus serve as a calibration parameter to precisely determine  $\lambda$ . We calibrated the evolution of  $T_2$  as a function of  $\lambda$  for the N1110 membrane and evaluated the water content at the beginning of the experiment (DR = 1) to  $\lambda = 4 \pm 0.5$ . The parameter  $\lambda$  represents the number of water molecules ( $\text{H}_2\text{O}$ ) per ionic group ( $\text{SO}_3^-$ ). Our calibration curve was valid for the unstretched membrane but since the NMR relaxation times  $T_1$  and  $T_2$  are dependent on the changes in the local structure experienced by the water molecules we were not able to link the transverse relaxation times determined under stretching (DR > 1) to the absolute membrane water content. As a consequence we cannot exclude a variation of  $\lambda$  during stretching. Experimental data and models predict in fact a decrease of  $\lambda$  in a membrane under mechanical compression<sup>35–38</sup> but we are not aware of an investigation of  $\lambda$  variations under traction.

**PFGNMR Experiments.** The water self-diffusion coefficients were determined using a horizontal Bruker Biospec 24/40 spectrometer operating at a proton Larmor frequency of 100 MHz. The inside diameter of the spectrometer (20 cm) was large enough to accommodate the whole system (2D coil, electronics and stretching device). The spectrometer was equipped with a 3-axis gradient unit delivering a maximum gradient strength  $g$  of 20 G/cm. We used a combination of two orthogonal field gradients in the ( $xy$ ) plane to change the orientation of the magnetic field gradient with respect to the plane of the membrane (Figure 1) and thus control the direction of the diffusion measurement. A stimulated spin-echo sequence (PGSTE) with unipolar gradients was used to performed the experiments with  $\delta = 12$ –15 ms and  $\Delta = \tau = 100$ –150 ms. 32





**Figure 2.** Angular evolution of the water self-diffusion coefficient measured in a N1110 membrane hydrated at  $\lambda = 4 \pm 0.5$ . The values are normalized by  $D_{s_0} = 1.099 \times 10^{-6} \text{ cm}^2/\text{s}$ , the coefficient measured at  $\theta = 0^\circ$  in the unstretched sample. The continuous lines are best fits using eq 2. (a) Unstretched (DR = 1) and stretched (DR = 1.2 and 1.6) membranes. (b) Zoom on the DR = 1 curve.

scans were accumulated with a recycle delay of 1.5 s (the recycle delay was superior to  $5 \times T_1$  in all cases). The experimental time required to measure a  $D_s$  value was 18 min. Estimated errors resulting from data acquisition and treatment were estimated to 3% of each  $D_s$  value. For all the measurements, the water self-diffusion coefficient  $D_s$  was calculated from a plot of the signal attenuation  $E/E_0$  against the magnitude of the gradient  $g$  and using the Stejskal–Tanner equation<sup>39</sup>

$$E = E_0 \exp \left[ -D_s \gamma^2 g^2 \delta^2 \left( \Delta - \frac{\delta}{3} \right) \right] \quad (1)$$

where  $E$  and  $E_0$  are the signal intensity at  $g$  and  $g = 0$ , respectively,  $\gamma$  ( $\text{rad}\cdot\text{s}^{-1}\cdot\text{T}^{-1}$ ) is the gyromagnetic ratio of the hydrogen nucleus,  $\delta$  (s) is the duration of the field gradient pulse of magnitude  $g$  ( $\text{T}\cdot\text{m}^{-1}$ ) and  $\Delta$  (s) is the delay (diffusion time) between the two gradient pulses. The length-scale probed by the water molecules confined in the “porous” structure of Nafion during a PGSTE experiment is given by  $l = (2D_s\Delta)^{1/2}$ . In our experimental conditions, and taken into account all the  $D_s$  values presented in this paper, we have  $3.8 < l < 5.7 \mu\text{m}$ . The length scale over which diffusion takes place during our measurements is thus much larger than all the known structural elements of Nafion so that the diffusion coefficient effectively reflects the tortuosity of the hydrophilic network. Potential effects of water confinement under traction leading to a dependence of  $D_s$  with the diffusion time have been checked by Park et al.<sup>15</sup> The authors varied  $\Delta$  between 7 and 70 ms and found that the diffusion coefficients along the three orthogonal directions were not significantly dependent on  $\Delta$ .

## RESULTS

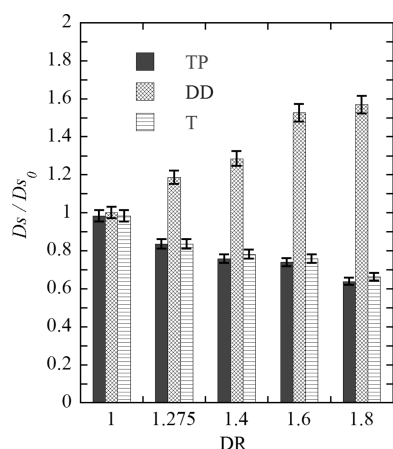
**Angular Evolution of  $D_s$  in a Membrane under Traction.** Figure 2a presents the evolution of the water self-diffusion coefficient  $D_s$  measured in the N1110 membrane equilibrated at  $\lambda = 4 \pm 0.5$  as a function of the angle  $\theta$  between the plane of the membrane and the measurement direction. The results are shown for different draw ratios: 1 (unstretched sample), 1.2 and 1.6. In the unstretched sample (Figure 2b), the water self-diffusion coefficient is maximum when measured in the machine direction ( $D_s^{\text{MD}} = D_{s_0} = 1.099 \times 10^{-6} \text{ cm}^2/\text{s}$  at  $\theta = 0^\circ$ ) and minimum in the through-plane (TP) direction ( $D_s^{\text{TP}} = 0.964 \times 10^{-6} \text{ cm}^2/\text{s}$  at  $\theta = 90^\circ$ ). The diffusion anisotropy, defined as  $D_s^{\text{MD}}/D_s^{\text{TP}}$  by reference to the value measured in the TP direction, is 1.123, a value close to published results

obtained in similar conditions (1.10 in N115 at  $\lambda = 3.8$ ,<sup>17</sup> 1.18 in N112 equilibrated at 22 wt %<sup>13</sup>). The absolute values of the diffusion coefficients also match literature data measured on Nafion 1100 at similar water content and temperature.<sup>2,9,15,16</sup> The continuous lines drawn in Figure 2 represent the best fits to the experimental points using eq 2, which corresponds to the expression expected when the diffusion coefficients are measured in the directions of the principal axes of the diffusion tensor. In the present study we use this relation as a basic indicator of the uniaxial character of the order.

$$\frac{D_s}{D_{s_0}}(\theta) = \frac{D_s^{\text{DD}}}{D_{s_0}} \cos^2(\theta) + \frac{D_s^{\text{TP}}}{D_{s_0}} \sin^2(\theta) \quad (2)$$

The fit to the data of Figure 2b is not satisfactory, showing that the order is not purely uniaxial, although being preferentially along the extrusion direction. This result is in agreement with the results of Van der Heijden et al. who showed that commercial Nafion presents a biaxial behavior.<sup>20</sup> As stretching goes on, the self-diffusion coefficient strongly increases in the draw direction and decreases concurrently in the through-plane direction (Figure 2a). The series of data follows a coherent order as the draw ratio is incremented: the diffusion is enhanced along the stretching direction while it is noticeably reduced through the plane of the membrane. The diffusion anisotropy increases to reach 1.42 at DR = 1.2 and 2.22 at DR = 1.6.

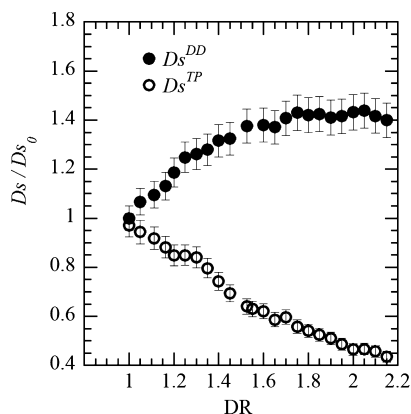
**Symmetry of the Diffusion Tensor and Orientation of the Structure During Stretching.** The fitting curves shown in Figure 2a for DR = 1.2 and 1.6 are satisfactory as they fall within the experimental error bars. According to eq 2 this demonstrates that the DD and TP directions are two principal axis of the diffusion tensor in the stretched sample. The full symmetry of the diffusion anisotropy can be resolved by measuring the diffusion coefficient in the third orthogonal direction, namely the transverse (T) direction (Figure 3). The transverse direction lies in the plane of the membrane and is perpendicular to the stretching direction. Before stretching (DR = 1) a small anisotropy is detected, although it is smaller than



**Figure 3.** Water self-diffusion coefficient measured along the three principal axes of the diffusion tensor: draw direction (DD), through-plane direction (TP) and transverse direction (T). The values are normalized by  $D_{s_0}$ , the coefficient measured at  $\theta = 0^\circ$  in the unstretched sample.

the one shown in Figure 2. Since two distinct membranes were used for the measurements of Figure 2 and Figure 3 this difference shows the variability in the anisotropy value from one sample to another. As the draw ratio increases,  $D_s^T$  decreases and stays equal to  $D_s^{TP}$  thus proving the cylindrical symmetry of the diffusion tensor around the stretching direction. The induced uniaxial symmetry traduces the progressive orientation of the polymer aggregates along the stretching direction and is in agreement with previous structural studies of stretched Nafion.<sup>15,20,26</sup>

The continuous evolution of  $D_s^{DD}$  and  $D_s^{TP}$  during stretching is displayed in Figure 4 for small draw steps. After several



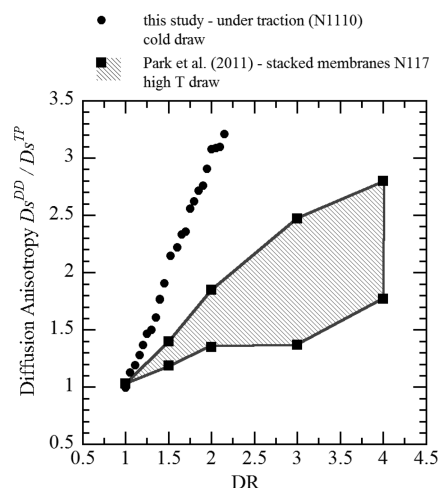
**Figure 4.** Diffusion coefficients in the draw (DD) and in the through-plane (TP) directions as a function of draw ratio.

attempts the maximum value of DR reachable by cold drawing was inevitably about  $DR = 2.2$  because of membrane rupture. This prevented us from collecting data at higher draw ratios. The data shown here correspond to the average over two sets of measurements (two different membrane samples). They are normalized by  $D_{s_0} = 1.015 \times 10^{-6} \text{ cm}^2/\text{s}$ , the water self-diffusion coefficient measured at  $DR = 1$  in the machine direction. As already observed in Figure 3, the diffusion coefficient decreases continuously in the through-plane direction while it increases in the draw direction. At  $DR \sim 1.75$ ,  $D_s^{DD}/D_{s_0}$  reaches a plateau

value of  $\sim 1.40$  and stays constant afterward. This result can be the consequence of the maximum degree of structural ordering that is reached at this value in the direction parallel to stretching. At the same time, the diffusion coefficient  $D_s^{TP}/D_{s_0}$  in the through-plane direction continues to decrease above  $DR = 1.75$ , although we observe a slight change in the slope of the curve at this point. These observations will be briefly addressed in the Discussion.

## DISCUSSION

**Comparison with Literature Data.** The diffusion anisotropy  $D_s^{DD}/D_s^{TP}$ , calculated from the data of Figure 4, is plotted in Figure 5 (black dots) and compared to literature data

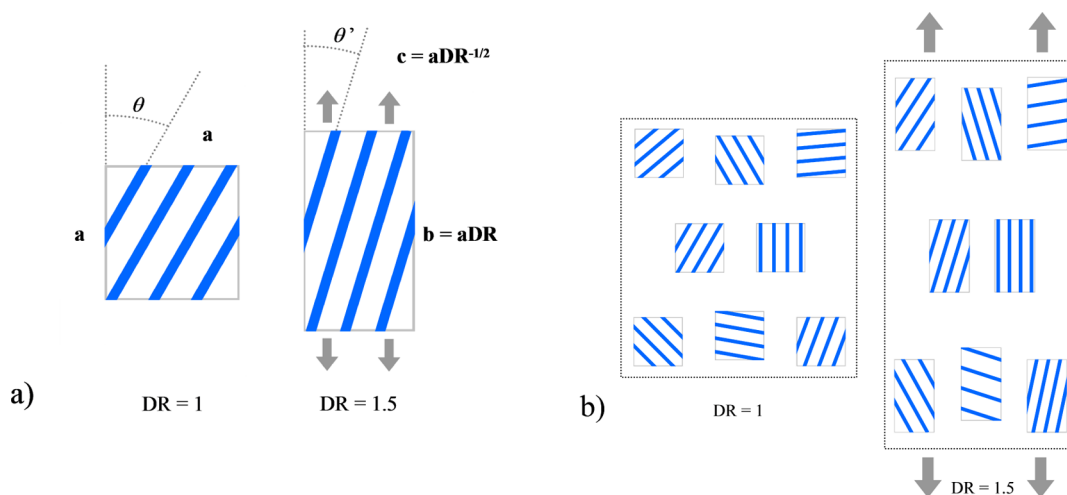


**Figure 5.** Comparison between water self-diffusion anisotropy in Nafion under traction (black dots) and in a stack of membranes (gray surface, data extracted from ref 15).

measured on a stack of N117. The gray surface delimits the regions of minimum and maximum anisotropy extracted from the figure in the “Abstract” of reference.<sup>15</sup> As the anisotropy decreases when swelling the membrane, and because the N1110 membrane was equilibrated at low RH, the measured anisotropy is probably close to the highest possible values, in our temperature conditions. We observe that the anisotropy is much higher in the membrane under traction than in the stack of membranes stretched at identical draw ratios and hydrated at similar water content. For example, the highest anisotropy ( $\sim 2.8$ ) measured in the stack of N117 at  $DR = 4$  and  $\lambda = 4$  corresponds here to a draw ratio of  $DR = 1.9$ .

In order to understand this observation, we need to consider the viscoelastic properties of Nafion and their dependence on temperature and compare the effects that the two very different stretching conditions may have on the polymer microstructure.

In general, temperature and relative humidity strongly affect the mechanical properties of Nafion.<sup>40,41</sup> It is known that the elastic modulus decreases and that the creep strain increases with temperature. These combined effects explain why the rupture of the membrane is reached a lower draw ratio during cold drawing than during high temperature stretching. In Figure 5, the gray surface extends to high DR values ( $DR = 4$  at maximum) because the elongation at rupture was maximized by the high temperature imposed during stretching. Conversely, in the present study, cold drawing induced early rupture which precluded measurements at draw ratios higher than  $\sim 2.2$ .



**Figure 6.** (a) Left: basic structural element composed of oriented parallel water channels fixed to a squared frame before deformation (DR = 1). Right: the same element, under traction. The channels are fixed to the frame so that they rotate during stretching. (b) Left: a meridian plane, containing a set of structural elements oriented at different angles before deformation. The medium is isotropic on average ( $S = 0$ ). Right: the same set of elements during deformation (DR = 1.5). The medium is anisotropic ( $0 < S < 1$ ) and the orientation function of the frames is given by eq 3

The stretching temperature also influences the way the microstructure deforms upon stretching. During cold drawing, the glassy polymer and the ionic aggregates are coupled to each other by cross-links so that the deformation of the glassy and the ionic phases are interdependent and large diffusion anisotropy can be induced by a relatively small deformation.<sup>42</sup> In contrast, at a temperature higher than the glass transition temperature ( $T_g$ ), the glassy polymer is melted and the cross-links are no longer connecting the deformation of the two phases. Nevertheless, a high ordering of the structure is also induced by stretching in this case as revealed by the SAXS experiments of ref 15. Although the ordering of the membrane structure represents a key factor for the understanding of its diffusion behavior these results demonstrate that it cannot explain solely the differences observed in the water diffusion anisotropy of Figure 5. As discussed later in this paper, it may be also required to consider changes in the organization and/or the dimensions of the water channels during cold drawing.

The changes induced in the mechanical properties of Nafion through the modification of its microstructure by both the temperature and the applied stress give qualitative arguments that can explain for the most part the differences observed in Figure 5. Averaging effects, coming from an imperfect alignment of the individual membrane samples during staking, may also contribute to the decrease in the observed anisotropy measured in ref 15. This effect, however, is certainly negligible as measurable changes would only be produced by a substantial misalignment, which was probably not the case. This is supported by the resonance lines of the  $^2\text{H}$  NMR spectra presented in refs 14 and 15, which would be broader if the misalignment was important.

**Deformation Model of the Microstructure of Nafion and Evolution of the Order Parameter during Stretching.** In the following analysis, we derive the expression of the orientational order parameter as a function of the draw ratio DR in the framework of a deformation model applied to the microstructure of Nafion. The proposed model is similar to the so-called “pseudoaffine” model initially developed by Kratky<sup>43</sup> and successfully applied to describe the behavior of crystalline polymers under traction.<sup>44</sup> The validation of this model and the knowledge of the relation  $S = f(\text{DR})$  will then allow us to make

several analogies between the water diffusion anisotropy measured in Nafion under traction and situations encountered in the nematic phase of liquid crystals and of micellar aggregates of amphiphile molecules.

**Deformation Model.** The degree of orientation of a medium is generally described by parameters that represent orientation averages over its orientation distribution function. In the case of an oriented polymer the system possesses uniaxial symmetry and there is no preferred orientation in the plane perpendicular to the draw direction. This corresponds to what is observed on Nafion (Figure 3). The orientation function describing this situation is thus a function of a unique angle  $\theta$  between the draw direction and the orientation of the polymer aggregates. X-ray diffraction, SAXS and other spectroscopic techniques such as optical birefringence and NMR allow the determination of some orientation averages.<sup>45</sup> The knowledge of the second moment of the orientation function (noted  $S$ ) is usually sufficient to provide a clear understanding of the mechanisms of deformation. The order parameter  $S$  is calculated by averaging the second-order Legendre polynomial  $P_2(\cos(\theta))$  over the orientation distribution function.

The deformation scheme adopted here is described in details in the Supporting Information. Before deformation the basic structural element is composed of parallel water channels, fixed to a square frame, and oriented at an angle  $\theta$  with respect to the draw (vertical) direction (Figure 6a). During deformation, the dimensions of the frame vary according to an affine transformation and the water channels rotate because they are fixed to the frame. The initial orientation function of all the frames contained in the planes parallel to the deformation axis is uniform as the medium is isotropic (we neglect the small initial anisotropy induced by the lamination process). Given these hypothesis, the distribution function of the frames' orientation during deformation ( $\theta'$ ) can be calculated (see Supporting Information for the derivation of this expression):

$$N(\theta', \text{DR}) = \frac{\text{DR}^3}{[1 + \sin^2(\theta')(\text{DR}^3 - 1)]^{3/2}} \quad (3)$$

Equation 3 is plotted in Figure S.2 for different DR. As expected,  $N(\theta' = \theta, 1) = 1$  (uniform distribution) and the mean

value of  $\theta'$  decreases as DR increases, which traduces the progressive orientation of the water channels toward the draw direction.

**Order Parameter.** The order parameter is calculated by averaging  $P_2(\cos(\theta))$  over all the solid angles  $2\pi \sin(\theta') d\theta'$  (see eqs S.13 and S.14 in the Supporting Information). The analytical result is given by:

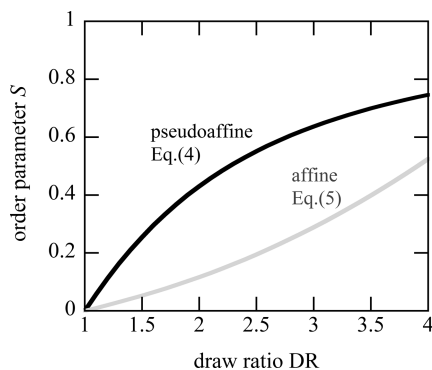
$$S = 1 - \frac{3}{2} \frac{DR^{-3}[DR^{-3} - 1 + \sqrt{DR^3 - 1} \times \arccos(DR^{-3/2})]}{(DR^{-3} - 1)^2} \quad (4)$$

**Validation of the Deformation Model.** The structure of stretched Nafion films has been studied by means of small-angle X-ray and neutrons scattering and birefringence experiments.<sup>15,20,26</sup> The results of these investigations demonstrate that the polymer aggregates (or ionic domains) rotate during stretching. This picture is fundamentally different from that of stretched elastomers or amorphous polymer above the glass transition where there is a change of the bond angles and lengths during stretching. A rubber, for example, is composed of an assembly of long chain molecules linked together at a small number of points. During deformation, the affine theory gives the evolution of the orientational order parameter  $S$  as a function of DR in a first order approximation:<sup>44</sup>

$$S = \frac{1}{5N} \left( DR^2 - \frac{1}{DR} \right) \quad (5)$$

where  $N$  is the number of random links ( $N = 6$  in polyethylene<sup>44</sup>). This theory was applied successfully to describe the nematic-like order probed by deuterated molecules in strained elastomers.<sup>46</sup>

The evolution of  $S$  as a function of DR is plotted in Figure 7 in the case of the pseudoaffine and the affine deformation



**Figure 7.** Evolution of the order parameter predicted from the pseudoaffine model and the affine model (with  $N = 6$ ) as a function of draw ratio.

models. As discussed by Ward<sup>45,44,47</sup> the increase of  $S$  is faster for small DR for the pseudoaffine model than in the affine model used to describe the behavior of rubber. We observe furthermore that the shapes of the curves are different (convex versus concave).

The theoretical treatment of strain-birefringence ( $\Delta n$ ) in rubbers has been worked out by Kuhn and Grün<sup>48</sup> and shows that  $\Delta n$  is proportional to the order parameter  $S$ . The evolution of the birefringence measured in Nafion (Figures 10 and 14 of

ref 20) clearly disqualifies the affine model for the description of Nafion's deformation as the evolution of  $\Delta n$  follows the shape of the pseudoaffine model of Figure 7. Similarly, the evolution of the orientational order parameter  $S$  measured by SAXS (Table 1 of ref 15) is in good agreement with the pseudoaffine scheme, although the order measured by the authors is higher than the values predicted by the model for small draw ratios. This difference may be explained by the fact that the pseudoaffine model is generally adapted to describe the behavior of polymers stretched below  $T_g$ , which was not the case in ref 15. Finally, a version of the pseudoaffine model based on the fibrillar Nafion morphology has been used by Rubatat and co-workers<sup>26</sup> to fit their scattering data obtained on membranes under traction and, more specifically, to treat the evolution of the ionomer peak. The ionomer peak is a correlation peak that appears in the scattering curve of Nafion and whose position is correlated to the mean distance between the polymer aggregates. The simulation of the data using the pseudoaffine deformation model was successful and the evolution of the interaggregate distance paralleled the one predicted by the model.

**Water Diffusion Anisotropy in Deformed Nafion Compared to Self-Diffusion of Elongated Particles in the Nematic Phase.** Theoretical expressions have been derived in the literature to predict the evolution of self-diffusion anisotropy of elongated particles in the isotropic and nematic phases.<sup>49,50</sup> These relationships take the order parameter of the nematic phase as the central parameter. In the following we use an analogy between the self-diffusion of such particles and water diffusion in stretched Nafion in the framework of our deformation model. Finally we use a comparison between our data and water diffusion anisotropy in the nematic phase of anisotropic micelles to clarify the direction that future studies should follow to get a clearer picture of water diffusion in the anisotropic structure of strained or compressed membranes.

**Brownian Dynamics of Liquid Crystal Molecules in the Nematic Phase.** Hess and co-workers<sup>49</sup> described the evolution of the diffusion tensor anisotropy of partially oriented ellipsoidal particles as a function of the order parameter in the nematic phase. The authors derived expressions for the variation of  $D_{para}$  and  $D_{perp}$  as a function of  $S$  and  $Q$ ,  $Q$  being the axis ratio of the ellipsoidal particles and *para.* and *perp.* the directions parallel and perpendicular to the director of the nematic phase, respectively.

The expressions are, in our notations

$$\frac{D_s^{DD}}{(D_s^{DD})^{1/3}(D_s^{TP})^{2/3}} = \alpha [Q^{4/3} - 2/3 Q^{-2/3} (Q^2 - 1)(1 - S)] \quad (6)$$

$$\frac{D_s^{TP}}{(D_s^{DD})^{1/3}(D_s^{TP})^{2/3}} = \alpha [Q^{-2/3} + 1/3 Q^{-2/3} (Q^2 - 1)(1 - S)] \quad (7)$$

with  $\alpha$  given by



$$\alpha = \frac{3Q^{2/3}}{(2+Q^2)} \left[ 1 + 2 \frac{(Q^2-1)}{(Q^2+2)} S \right]^{-1/3} \left[ 1 - \frac{(Q^2-2)}{(Q^2+2)} S \right]^{-2/3} \quad (8)$$

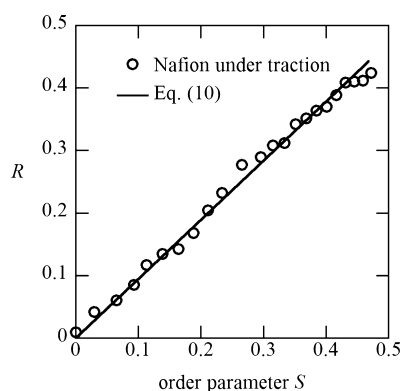
As expected, the ratio  $D_s^{DD}/D_s^{TP}$  is close to 1 when  $S = 0$  (isotropic phase):

$$\frac{D_s^{DD}}{D_s^{TP}} = Q^2 \frac{1 + 2/3(Q^2-1)(1-S)}{1 + 1/3(Q^2-1)(1-S)} \quad (9)$$

The theory predicts that the anisotropy of diffusion, defined here as the parameter  $R$ , is a linear function of  $S$ :

$$R = \frac{D_s^{DD} - D_s^{TP}}{D_s^{DD} + 2D_s^{TP}} = S \left( \frac{(Q^2-1)}{(Q^2+2)} \right) \quad (10)$$

Figure 8 shows the evolution of the experimental  $R$  values, calculated from the data of Figure 4 as a function of  $S$ ,

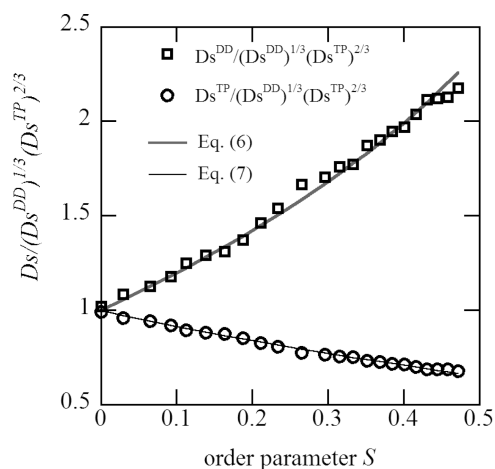


**Figure 8.** Plot of the diffusion anisotropy  $R$  measured in Nafion 1110 under traction as a function of the order parameter predicted by the pseudoaffine deformation model. Continuous line: fitting curve using eq 10

calculated from the deformation model (eq 4). A fit of the curve using eq 10 gives  $Q = 6.93$ . The fit is good which shows that water self-diffusion in the anisotropic structure of Nafion is analogous to the self-diffusion of very elongated ( $Q \sim 7$ ) ellipsoidal particles in the nematic phase. Figure 9 presents the predictions of the model given by eqs 6 and 7 with  $Q = 6.93$  and compared to our experimental data. The agreement is excellent for both the diffusion in the stretching direction and perpendicular to it.

The model of Hess et al. was first used in the literature on Nafion by Li and co-workers.<sup>14</sup> From a single value of  $S$  obtained by SAXS and PFGNMR diffusion data (at DR = 4 and  $\lambda = 5.5$ ), the author extracted the value  $Q = 1.8$ . This value was interpreted as the effective aspect ratio of the diffusing water molecules. In the present study the data were obtained step by step using cold drawing and the  $Q$  parameter is seen to be much higher than in membranes stretched at high temperature. The value of the aspect ratio is difficult to interpret here as the aspect ratio of the diffusing particles. Instead, it may reflect the changes in the microstructure that happen upon cold drawing.

Contrarily to stretching at high temperature where the glassy polymer is melted, cold drawing produces effects of the microstructure that affect both the fluoropolymer matrix and the ionic channels. This is due to the fact that, at low



**Figure 9.** Plot of  $D_s^{DD}/(D_s^{DD})^{1/3}(D_s^{TP})^{2/3}$  (squares) and  $D_s^{TP}/(D_s^{DD})^{1/3}(D_s^{TP})^{2/3}$  (circles) as a function of the order parameter predicted by the pseudoaffine orientation model. The continuous lines correspond to eqs 6 and 7 with  $Q = 6.93$ .

temperature, the cross-links between the ionic aggregates and the hydrophobic matrix are strong and the deformation of the glassy matrix is coupled with the deformation of the water channels. This situation is probably different from the one observed at high temperature where the tensile stress can stretch and deform the melted glassy fluoropolymer while leaving the dimensions of the water channels intact.<sup>14</sup> In both cases (high and low temperature), the amount of crystalline phase in the polymer matrix is probably not changing significantly with drawing as shown by SAXS results<sup>26</sup> and NMR. Clearly, more experimental data obtained at variable water contents are needed to elucidate the physical meaning of the parameter  $Q$  and give insights into the structural modifications of the water channels upon cold drawing. Such experiments would be possible using our experimental apparatus in a controlled climatic environment.

**Brownian Dynamics Simulations of Colloidal Particles.** The situation in Nafion can also be compared to Brownian dynamics simulations of colloidal particles. In the study of Lowen,<sup>50</sup> the author calculated the anisotropic translational long-time self-diffusion coefficient of hard spherocylinders in the nematic phase. Using a model with excluded volume interactions the author showed that, in the nematic phase, the long-time mean-square displacement (and thus the diffusion coefficient) becomes anisotropic and can be split into parts parallel and perpendicular to the nematic director. Simulations for aspect ratios between 4.8 and 16 show that the ratio  $D_L^{para.}/D_L^{perp.}$  depends essentially on the nematic order parameter alone. Assuming that there is only motion in the direction parallel to the rod orientations a simple theoretical estimate leads to the following relation (in our notations):

$$\frac{D_L^{para.}}{D_L^{perp.}} = \frac{D_s^{DD}}{D_s^{TP}} \approx \frac{2S+1}{1-S} \quad (11)$$

This formula, which contains no fitting parameter, is compared to our data in Figure S3 (Supporting Information) together with the predictions of the model of Hess et al. (eq 9 with  $Q = 6.93$ ). The agreement with both models is good, the predictions of eq 9 being closer to the data points than the simple estimate of eq 11.

Since our experiments were performed at a unique water content  $\lambda$  we are not able to discuss the water diffusion properties when changing the polymer volume fraction. Following the analogy with the Brownian dynamics of the hard spherocylinders, we should expect two opposite effects to compete in the determination of  $D_s^{DD}$  as a function of DR and  $\lambda$ : first, a stronger alignment, manifested by an increase of the order parameter, should favor diffusion when  $\lambda$  decreases since there are less obstacles to cross when moving along the draw direction; second, with decreasing  $\lambda$ , there is less free space available between the polymer aggregates, which hampers diffusion in general.

**Directions for Future Studies.** Although the previous analogies between the situation in Nafion and those encountered in the nematic phases of elongated particles are enriching, a full understanding of the anisotropy of diffusion as a function of the membrane water content may require a more detailed model. Such a model should be able to describe obstruction effects that occur inevitably when increasing the draw ratio and/or the polymer volume fraction. On the basis of more experimental data, collected on membranes equilibrated at different water contents, a model close to the one proposed by Jóhannesson and co-workers<sup>51</sup> could probably be applied. The authors have used the PGSE NMR technique to probe the water diffusion anisotropy in the nematic phase of the cesium perfluorooctanoate (CsPFO) water system. Defining the diffusion anisotropy as

$$\alpha = \frac{D_{\text{perp.}} - D_{\text{para.}}}{D_{\text{iso}}}, \quad \text{with } D_{\text{iso}} = (D_{\text{perp.}} + 2D_{\text{para.}})/3 \quad (12)$$

the authors demonstrated that  $\alpha$  is proportional to the order parameter  $S$  in the case of a micro structural model of monodisperse oblate spheroidal micelles. This model takes the obstruction effects into consideration through the constant of proportionality  $f$ ,  $f$  being a function of the micelle volume fraction  $\phi$  and the aspect ratio  $\rho$  of the micelles:

$$\alpha = S \times f(\phi, \rho) \quad (13)$$

A plot of  $\alpha$  versus  $S$  is shown in the Supporting Information (Figure S2.). The linear dependence of  $\alpha$  with  $S$  is good for small  $S$  values but the data deviate from the model for  $S > 0.3$  which corresponds to the “transition point” at DR  $\sim 1.75$  where  $D_s^{DD}/D_{s_0}$  reaches a plateau (Figure 4). This model thus fails to describe our data in the full range of  $S$  values. However, since it describes a situation very close to the one met in Nafion, we believe that a modified version that takes into accounts the known structural features of the polymer could be developed and applied successfully to data measured on stretched samples hydrated at different water contents. To reach this goal and explain the diffusion behavior observed at high draw ratios it might also be required to adapt the basic deformation model adopted in this study. The model, in the present version, considers a basic structural element that contains parallel water channels and rotates during stretching. This vision is probably too simple and a more elaborate version that considers a progressive evolution of the water channel order (alignment) inside the basic elements would be more realistic. The total orientational order would then be the result of the progressive rotation of the bundles containing the water channels followed by the alignment of the water channels inside the bundles. This two-stage mechanism, adopted to interpret

the SAXS data of N117 under traction,<sup>26</sup> could explain the trends observed in the diffusion data (the plateau reached by  $D_s^{DD}$  while  $D_s^{TP}$  still decreases and the constant increase of the anisotropy). The effect of stretching in the “structure” of water represents another parameter that could also be considered. As in the study of Lin et al.<sup>12</sup> we measured a drop in the longitudinal ( $T_1$ ) and transversal ( $T_2$ ) NMR relaxation times of water as DR increases. Since the NMR relaxation times are sensitive to the interactions between water and its immediate surroundings this evolution reflects the average decrease of water mobility during stretching and may be related to a variation of the relative amount of free versus bound water measured by the authors (change in the water viscosity). This information would indicate that the observed variations of  $D_s$  during traction are not entirely due to modifications of the polymer structure but also, to some extent, to changes in the water mobility as a consequence of morphology changes. This of course would require a detailed study of the  $T_1$  and  $T_2$  variations as a function of the draw ratio and the water content.

We plan in the near future to apply our experimental protocol to the measurement of water diffusion in membranes under a compressive uniaxial stress. Although compression is close to traction from a mechanical point of view, the effects of compression on water diffusion and membrane performance in terms of proton conductivity are of greater importance for the PEMFC application. The measurement of the water self-diffusion coefficient in a membrane subjected to a compressive stress would then help the understanding of the structure/transport relationship in Nafion. The deformation model used (or a modified version, as discussed above) and the analogies made in the present study should in principle hold to describe compression. For simplicity, and because experimental data are lacking in the literature, we have assumed in this study that the membrane hydration stayed constant during our cold drawing experiments. As it is known that compression modifies the swelling pressure of the polymer backbone and results in changes in the water-uptake behavior of the membrane it will probably be required to add hydration effects in the modeling.

## CONCLUSION

The determination of the self-diffusion coefficient of water adsorbed in the polymeric structure of Nafion represents a convenient way of probing its internal organization. When the polymer is under traction, the diffusion becomes anisotropic because the polymer aggregates (or, equivalently, the water channels) align along the stretching direction. The diffusion is faster along the draw direction while it is reduced in the directions perpendicular to it. Using a specially designed NMR coil and a mini traction machine we measured for the first time the self-diffusion coefficient of water adsorbed in a single Nafion membrane under traction. Thanks to this experimental improvement we determined the precise evolution of the diffusion coefficient along the stretching direction and in the through-plane direction with very small draw ratio steps. The comparison between our method and the protocol previously used in the literature reveals that the induced diffusion anisotropy is much higher when the membrane is under traction at room temperature than when the membrane is first deformed at high temperature and then cut and stacked in the NMR tube. This deference can be explained qualitatively by the combined effects of temperature and applied stress on the microstructure of Nafion.

Using a simple deformation model, we exploited the experimental results by analyzing the evolution of the diffusion anisotropy as a function of the orientational order parameter of the water channels. The use of the pseudoaffine deformation model is adapted to the description of Nafion microstructure under traction and is in agreement with the literature results on optical birefringence and small angle scattering experiments. By comparison with the diffusion of liquid crystal molecules we further verified that the water diffusion in ordered Nafion is analogous to the self-diffusion of elongated particles with a high aspect ratio. We discussed the meaning of this parameter and compared our results to literature data obtained on membranes stretched at high temperature. The comparison reveals that, contrarily to what is observed upon drawing above  $T_g$ , cold drawing probably leads to changes in the dimensions of the water channels and in their organization within a bundle of polymer aggregates.

Using this experimental approach, we plan to collect more data on stretched membranes at different water contents and on compressed samples. As the sorption properties of the membrane vary in some circumstances under compression the interpretation of the diffusion anisotropy under a compressive stress will require a more physical model that will probably need to take hydration and obstruction effects into consideration.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Details on the deformation model adapted to the description on Nafion membrane under traction and comparison of our diffusion data with the model predictions of Lowen<sup>50</sup> and Jóhannesson et al.<sup>51</sup> This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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