

NMR study of the anisotropic transport properties of uniaxially stretched membranes for fuel cells

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Abstract

We used NMR techniques to probe the anisotropic properties of stretched Nafion[®] 115 membranes. The alignment of the polymeric structure under a uniaxial load is at the origin of a strong anisotropy of both the water self-diffusion coefficient and the proton conductivity. The determination of these two important membrane properties may lead to new fundamental information on the nature of the proton transport mechanisms in such oriented weakly-charged systems.

Keywords

Proton exchange membranes, NMR, diffusion anisotropy, proton conductivity, fuel cells.

1. Introduction

Perfluorosulfonic acid (PFSA) membranes are the most used electrolytes in proton exchange membrane fuel cells (PEMFCs). Despite the large number of attempts to synthesize a better, more durable and cheaper polymer, Nafion[®], a PFSA-based membrane commercialized by DuPont de Nemours & Co, remains the standard for this application. The transport properties of this polymer film are essential to the performance of the system: it must be an excellent proton conductor to transfer the charges efficiently from the anode to the cathode. The mobility of the water adsorbed in its structure also represents a key property as the proton transport mechanisms are all coupled to water dynamics and diffusion.

The anisotropy of the transport properties in Nafion have been measured in several studies [1] [2] and attempts have been made to orient the structure of the membrane during the manufacturing process in order to enhance its conductivity [3]. Here, we first characterize by NMR the local order in the structure of uniaxially stretched Nafion membranes. Then, using PFG techniques, we measure the impact of the orientation of the structure on the water self-diffusion and the ionic conductivity.

2. Methods and Materials

The Nafion N115 (thickness = 125 μm) membranes were purchased from Ion Power, Inc. They were pre-treated following the protocol described in ref. [4], dried 24 hours at 60°C and stretched at 80°C using a home-made device at different draw ratios DR ($DR = \text{final length} / \text{initial length}$). The samples were then cut with a cutting die into 5.6×6.1 mm² pieces, hydrated with D₂O or H₂O at different water contents and stacked to enhance the signal-to-noise ratio of the NMR measurements. The stack of membranes was sandwiched between two PTFE half-cylinders and placed in a cylindrical PTFE support. The assembly was inserted in a 10 mm diameter NMR tube (see the schematic in fig. 2) and could rotate around a direction perpendicular to the main magnetic field \vec{B}_0 which allowed the precise control of the angle θ between \vec{B}_0 and the plane of the membranes. All the NMR experiments have been performed at 298 K on a Bruker Avance III 600 MHz spectrometer equipped with a broad band 10 mm H-X probe, the X channel being tuned to the ²H NMR frequency. The diffusion experiments have been carried out using a stimulated spin-echo sequence with bipolar gradients [5]. The maximum strength of the magnetic field gradient was 20 G/cm, the gradient duration δ varied between 14 and 18 ms and the diffusion time was fixed to $\Delta = 125$ ms. The proton conductivity was measured at 303 K using a home-made 4-probe conductivity cell [4]. In this study, the water content is parameterized by the quantity $\lambda = [\text{H}_2\text{O}]/[\text{SO}_3^-]$, which represents the number of water molecules per ionic SO_3^- site.

3. Results

3.1. Local order induced by the uniaxial stretching

The ²H-NMR spectrum of the almost dry N115 membrane ($\lambda = 3.8$) presents a small quadrupolar splitting (fig. 1) typical of a slightly oriented medium [6]. The order parameter S , extracted from the fit of the curve $\Delta\nu_Q(\theta)$ with eq. 1 is 6.3×10^{-4} . The experiment also shows that the main direction of the ordering, marked by the θ direction in eq. 1, is located in the plane of the membrane. As noted by Li *et al.* [7], this moderate in-plane ordering is caused by the extrusion process of the N115 membrane.

$$\Delta\nu_Q(\theta) = \frac{1}{2} \Delta\nu_Q^0 (3\cos^2\theta - 1 - \eta\sin^2\theta) \quad ; \quad \Delta\nu_Q^0 = S \times 360 \text{ kHz} \quad \text{eq. 1}$$

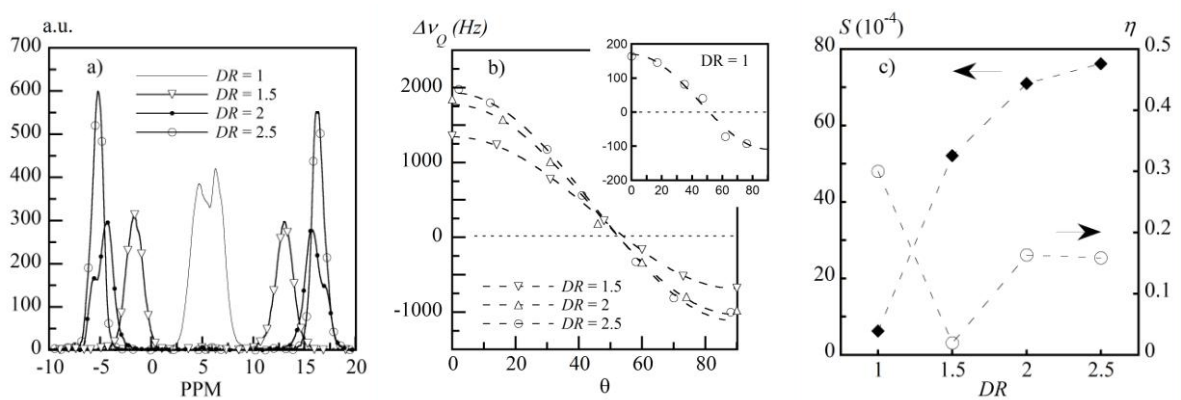


Fig. 1: **a)** ²H-NMR spectra of unstretched ($DR = 1$) and stretched ($DR = 1.5, 2$ and 2.5) N115 membranes equilibrated at small D₂O contents ($\lambda = 3.8, 2.5, 2.5$ and 3.1 respectively). Spectra recorded at $\theta = 0^\circ$. θ is the angle between the stretching direction and the magnetic field. **b)** Evolution of the quadrupolar splitting as a function of θ for the three stretched membranes and the unstretched ($DR = 1$) membrane (inset). The dashed lines are fitting curves (eq. 1). **c)** Evolution of the order parameter S and of the biaxiality parameter η extracted from fig. 1b).

When the hydration of the membrane increases the residual quadrupolar interaction vanishes and the splitting is no longer observable. (Data not shown here because of space limitations. See reference [7] for supporting data.) In stretched membranes, the residual interaction increases first very strongly between $DR = 1$ and $DR = 1.5$ then more moderately at higher stretching. The increase of the order parameter with DR demonstrates the progressive orientation of the structure of the polymer around the stretching direction. The biaxiality parameter, however, does not exhibit monotonic behaviour. This quantity is in fact very sensitive to the number and the level of noise of the data points in the $\Delta\nu_Q = f(\theta)$ curve and is thus not very relevant in our case.

3.2. Influence of the structural order on the transport properties

The structural organization of the Nafion membrane strongly influences its transport properties in terms of water diffusion and proton conductivity. In order to better understand the structure-transport relationships in this material, we performed water self-diffusion coefficient (D_s) measurements in stretched samples as a function of the angle (θ) between the direction of the magnetic field gradient (\vec{g}) and the stretching direction (fig. 2a). In the unstretched membrane, θ corresponds to the angle between the gradient and the direction of the lamination (*i.e.* machine direction). We observe in fig. 2a) that the water self-diffusion coefficient is strongly dependent on the direction of the measurement. Moreover, D_s is higher in the stretching (para) direction than in the transverse (perp) direction. The diffusion anisotropy, defined as the ratio $D_s(\text{para}) / D_s(\text{perp})$, increases with DR , which shows the influence of the structural anisotropy on the diffusion of the adsorbed water: the diffusion is faster along the oriented polymer aggregates than it is perpendicular to them. This phenomenon is amplified when the structural uniaxial order increases.

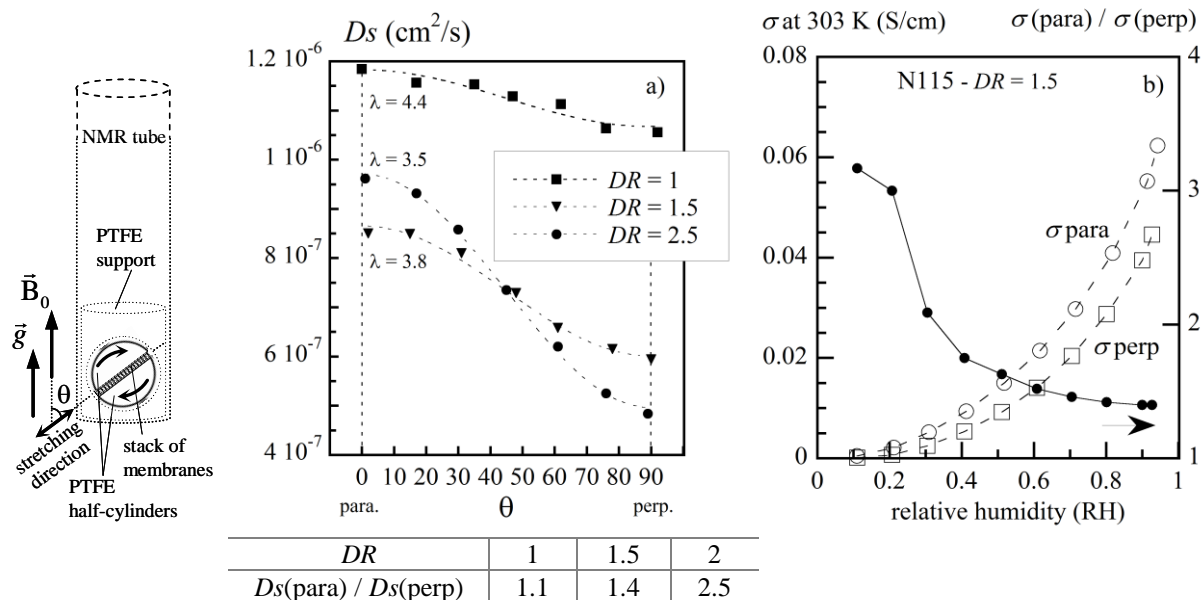


Fig. 2: Left Schematics of the device allowing the rotation of the stack of stretched membranes around an axis orthogonal to the NMR tube. **a)** Evolution of the water self-diffusion coefficient as a function of θ . In the parallel direction, $\theta = 0$ and the gradient direction lies in the plane of the membrane. The values of the diffusion anisotropy $D_s(\text{para}) / D_s(\text{perp})$ are indicated in the table. **b)** Evolution of the ionic conductivity, measured in the two orthogonal directions of the plane of the membrane, as a function of the relative humidity. The parallel direction corresponds to the stretching direction. The ionic conductivity anisotropy $\sigma(\text{para}) / \sigma(\text{perp})$ is indicated for each RH in plain symbols.

The ionic conductivity, which represents the most pertinent property of the membrane regarding the fuel cell application, is also impacted by the stretching-induced orientation of the structure. We observe in fig. 2b) that the conductivity anisotropy ($\sigma(\text{para}) / \sigma(\text{perp})$), where the two directions are the two in-plane orthogonal directions, para corresponding to the stretching direction) is significant in the stretched $DR = 1.5$ N115 membrane. We remark furthermore that $\sigma(\text{para}) / \sigma(\text{perp})$ strongly increases when the relative humidity RH (and thus the water content λ) decreases. Interestingly, $\sigma(\text{para}) / \sigma(\text{perp})$ is much higher than $Ds(\text{para}) / Ds(\text{perp})$ at the same water content (at $\lambda \sim 4$, $Ds(\text{para}) / Ds(\text{perp}) \sim 1.4$ and at $\text{RH} \sim 0.25$, $\sigma(\text{para}) / \sigma(\text{perp}) \sim 2.5$). This observation is to be linked to the different mechanisms of proton transport: in the so-called “vehicular mechanism”, where H^+ charges are electrically attached to water molecules, the diffusion of water is the factor limiting the proton transfer. Here, we observe that, at low hydration, the proton transport is faster than the diffusion of water, which indicates that at least one other transport mechanism is involved. This additional mechanism, which can involve proton hopping between adjacent water molecules, could be linked to the dimensionality of the anisotropic transport. As the membrane is stretched, the water diffusion is favoured in the aligned direction and the proton hopping might be enhanced. This hypothesis, of course, must be checked against additional experimental data.

4. Conclusions

We probed the local order in uniaxially-stretched Nafion 115 membranes. The ^2H NMR spectra reveal that the order is increasing as a function of the draw ratio and that the progressive orientation of the polymer aggregates during stretching results in a marked anisotropy of the water self-diffusion. Because the dynamics of water is strongly coupled to the rate of proton transfer, the parallel determination of the proton conductivity in the stretched samples allows us to compare the two phenomena and gain an original insight into the nature of the proton transport in the aligned systems.

References

- [1] Kidena, K., Anisotropic diffusion of water in perfluorosulfonic acid membrane and hydrocarbon membranes, *J. Membr. Sci.*, Vol. 323, 2008, pp. 201–206.
- [2] Park, J. K., Li, J., Divoux, G. M., Madsen, L. A., and Moore, R. B., Oriented Morphology and Anisotropic Transport in Uniaxially Stretched Perfluorosulfonate Ionomer Membranes, *Macromolecules*, Vol. 44, No. 14, pp. 5701–5710.
- [3] Lin, H.-L., Yu, T., and Han, F.-H., A method for improving ionic conductivity of Nafion membranes and its application to PEMFC, *J. Polym. Res.*, Vol. 13, No. 5, 2006, pp. 379–385.
- [4] Maldonado, L., Perrin, J.-C., Dillet, J., and Lottin, O., Characterization of polymer electrolyte Nafion membranes: Influence of temperature, heat treatment and drying protocol on sorption and transport properties, *J. Membr. Sci.*, Vol. 389, pp. 43–56.
- [5] Cotts, R., Hoch, M., Sun, T., and Markert, J., Pulsed field gradient stimulated echo methods for improved NMR diffusion measurements in heterogeneous systems, *J. Magn. Reson.*, Vol. 83, No. 2, 1989, pp. 252 – 266.
- [6] Deloche, B. and Samulski, E., Short-range nematic-like orientational order in strained elastomers: A deuterium magnetic resonance study, *Macromolecules*, Vol. 14, No. 3, 1981, pp. 575–581.
- [7] Li, J., Wilmsmeyer, K., and Madsen, L., Anisotropic diffusion and morphology in perfluorosulfonate ionomers investigated by NMR, *Macromolecules*, Vol. 42, No. 1, 2009, pp. 255–262.