

NMR investigation of water diffusion in a Nafion[®] membrane under tractionJ.-C. Perrin¹, M. Klein¹, S. Leclerc¹, L. Guendouz², J. Dillet¹, and O. Lottin¹¹LEMETA, Université de Lorraine, CNRS UMR7563²IJL, Université de Lorraine, CNRS UMR7198

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When hydrated the Nafion membrane presents remarkable transport properties that make it the benchmark material for applications such as low temperature fuel cells. The membrane structure and the dynamics of the adsorbed water represent fundamental parameters in the understanding of the mechanisms associated to proton transport. It is well known that water diffusion is faster when water is bulk-like in a fully hydrated membrane than in a drier sample. Furthermore, it has been shown recently [1, 2] that water self-diffusion is favored in stretched samples in the direction of the alignment of the polymer aggregates. This finding can be of importance in the objective of increasing fuel cell performances by controlling the structure of the polymer electrolyte. The application of a uniaxial extension provides also a very useful means of studying membrane morphology in relation with water transport. PFGNMR is an adapted tool to characterize water self-diffusion in Nafion because this method is water selective and relatively easy to implement. The lack of sensitivity of NMR techniques, however, represents a severe drawback that prevents any measurement on a single membrane using conventional hardware.

To address this problem we developed a specific NMR coil able to provide a strong magnetic radiofrequency field close to the membrane plane (Figure 1). Using a home-made stretching device incorporated inside the spectrometer and placed close to the NMR probe we were able to measure the water self-diffusion coefficient in a unique Nafion membrane under traction.

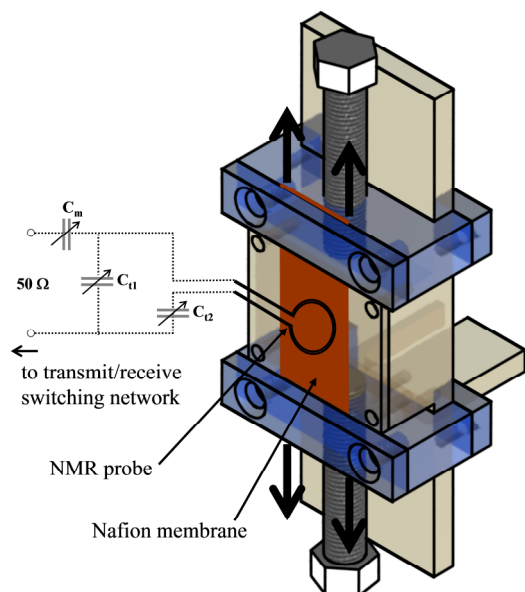


Figure 1. Home-made experimental setup developed for measuring water self-diffusion in a membrane under traction.

With this apparatus we performed PFGNMR measurements using a 3 axis magnetic field gradient unit. By combining 2 gradients of different strengths and directions we were able to determine the diffusion coefficient along any direction of the membrane plane or

through it. The fine control of the stretching allowed precise measurements at very small draw ratio steps (0.05 typically).

Figure 2 shows data measured on a Nafion membrane under traction (open circles) compared to data collected on a stack of 10 membranes stretched at high temperature in an oven, cut and placed in a NMR tube. The latter protocol corresponds to the “standard” used up to now in the literature [1, 2]. The figure presents the evolution of the diffusion anisotropy, defined as the ratio between the self-diffusion coefficient measured in a direction parallel to draw and the coefficient measured through the membrane, as a function of the draw ratio DR (DR = final length / initial length).

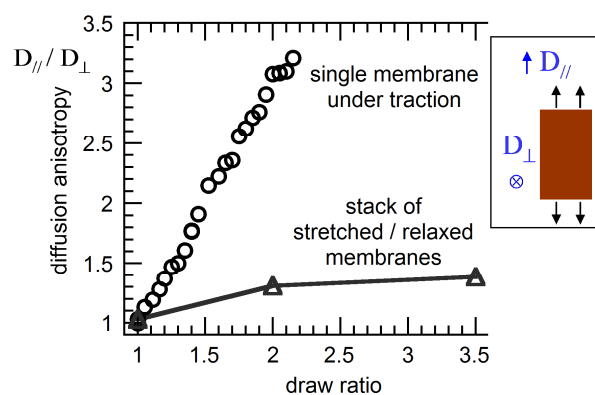


Figure 2. Diffusion anisotropy measured as a function of draw ratio in a Nafion membrane under traction compared to results obtained using the standard protocol (stack of several stretched/relaxed samples).

Our results demonstrate that:

- The diffusion anisotropy increases with the draw ratio. This is observed in both cases (stretched/relaxed membranes and single membrane under traction) in accordance with literature [1, 2].
- The diffusion anisotropy is much higher in a single membrane under traction than in a stack of stretched/relaxed samples equilibrated at a similar hydration state. This difference can be the result of mechanical relaxations occurring stretched/relaxed when the imposed stress is released. The ordering is thus different in the stack of membrane than in the sample under traction where, by definition, there is no relaxation. An averaging effect, coming from a misalignment of the membrane's director during stacking, is also probably affecting the overall order in the stack of membrane.
- At first approximation, diffusion anisotropy increases linearly with draw ratio until rupture. This finding, related to the progressive orientation of the polymer aggregates during stretching, needs to be understood in the framework of the different structural models for Nafion.

References:

- [1] Park J. K., Li J., Divoux G. M., Madsen L. A., and Moore R. B., *Macromolecules* (2011), Vol. 44, No. 14, pp. 5701–5710.
 [2] Klein M., Perrin J.-C., Leclerc S., Guendouz L., Dillet J. and Lottin O., *Diffusion-fundamentals* (2013), in press.