Water transport in Nafion membranes under various conditions studied by NMR

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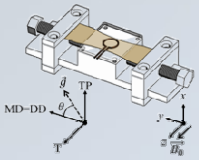
Objectives

In a Proton Exchanging Membrane Fuel Cell (PEMFC), the membrane is at the heart of the assembly and is the place where electrochemical reactions happen. As water mobility governs these reactions, the Nafion polymer has been studied extensively by NMR techniques (imaging, self diffusion…), but mostly outside a fuel cell. However, in an operating fuel cell, the membrane is exposed to multiple mechanicals constraints (hydration, swelling…). Therefore, we wanted to study the effect of such conditions on the water transport in the polymer. Three boundary conditions were investigated using various NMR techniques: stretching, compression and drying/hydrating.

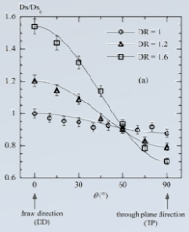
Stretching

Self diffusion experiments were performed on Nafion N1110 membranes stretched inside the NMR spectrometer using a specifically designed system. A one-loop surface coil was used for emission and detection in order to increase sensitivity.

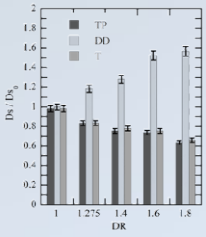
Self diffusion coefficients (Ds) were measured in the three spatial directions. Due to the manufacturing process, there is a small diffusion anisotropy in the y direction. This anisotropy augment with the stretching: diffusion coefficient increases in the stretch direction (DD) and decreases in the other directions (TP, T).



Mini-traction machine (made out of polycarbonate and PTFE) and 2D NMR coil developed for the measurement of *Ds* in a single membrane under traction. The experiments were performed on a Bruker Biospec 24/40 (^{1}H resonance frequency : 100 MHz) equipped with a 20cm diameter gradient coil.

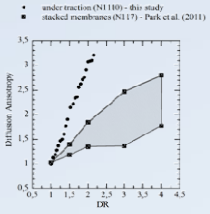


Angular evolution of the water self-diffusion coefficient measured in a N1110 membrane hydrated at $\lambda = 4 \pm 0.5$. The values are normalized by D_{s0}, the coefficient measured at $\theta = 0°$ in the unstretched sample. DR (Draw Ratio) is the ration between the final and the initial length of the membrane.



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)

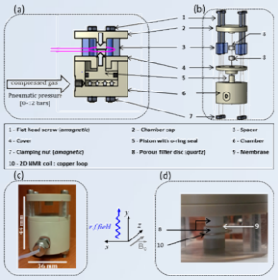
These results were compared with other studies in the literature which were performed on membranes stretched ex-situ at high temperature and then hydrated at similar water content. The anisotropy is higher with our methodology, showing that the ordering of the polymer aggregates (or, equivalently, the water channels) caused by stretching is thus more important when the membrane is under traction at ambient temperature than when stretching was imposed at high temperature and the stress was released.

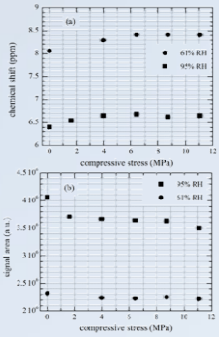


Comparison between water self-diffusion anisotropy in Nafion under traction (black dots) and in a stack of membranes (gray surface)

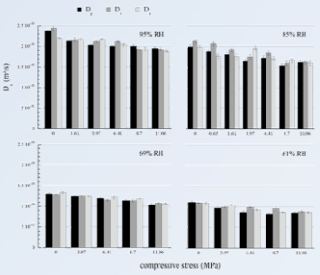
Compression

In a fuel cell, the membrane is exposed to high compression loads. This is caused by the clamping of the membrane-electrode assembly but also by the swelling of the membrane due to the production of water during operation. We designed a pressure cell compatible with NMR in order to investigate this effect and its consequences on water transport. This system allows us to apply a pressure on the membrane up to 120 bars.





(a) Chemical shift and (b) NMR signal area as a function of the applied stress in N1110 membranes equilibrated at 61% RH and 95% RH.



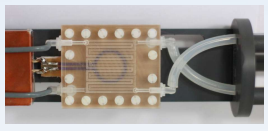
Evolution of water self-diffusion coefficient measured in Nafion® N1110 in the through-plane (y) and in-plane (x, z) directions. The measurements are performed at different RH as a function of the imposed stress.

Water content was measured under pressure using chemical shift and signal integral. In highly hydrated membranes, the water content decrease for low pressure (<3 Mpa). This shows that internal pressures (elastic and osmotic) are lower than the applied stress. On the contrary, in the [0-85% RH] range, internal pressures are much higher and water content does not decrease with applied stress.

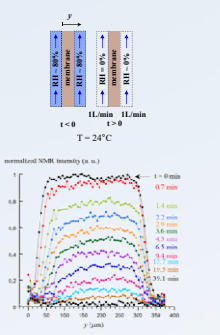
The diffusion measurements show that the water mobility is also affected in the stressed membrane: stress-induced structural modifications or reorganizations are seen at the micrometric scale through the decrease of the water self-diffusion coefficient. These effects likely impact the performances of the PEM in terms of proton conductivity. We did not detect any anisotropy in the diffusion, contrary to stretching experiments.

Hydration and Drying

Hydration of the membrane is a critical parameter a fuel cell. Water is produced during the operation of the PEMFC but the quantity can vary depending on the outside humidity. One of our goals was to quantify the effects of the interfacial resistance on the water distribution inside the membrane. We used Spin Echo Single Point Imaging (SE-SPI) in order to obtain water profile across membranes.



Hydration chamber designed for imaging the membrane. Air humidity can be varied separately for each face. The system is inserted in a 60 mm diameter gradient coil (1000 mT/m gradient strength)



Water profiles in a drying N1110 membrane. Before the experiment, the air relative humidity is 80%. At the start of the experiment, it is switched to dry air (RH<0.1%). One imaging profile is acquired every 45s.
Signal intensity decrease due to T2 is corrected, the relaxation times varying with the water content.

During drying experiments, the water profiles across the membrane stay roughly flat. It means diffusion is fast and the desorption is limited by the transfer at the membrane interface.

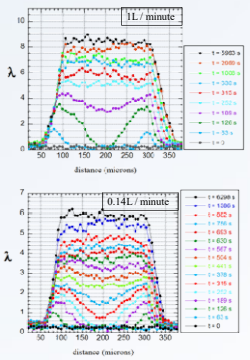
We also performed hydration experiments for different gas flow rates.

$Bi = R_{Diffusion} / R_{Boundary}$ (Biot number)

$Bi \ll 1$ Diffusion is not limiting during sorption and desorption

$Bi \geq 1$ Effects of diffusion are visible on the profiles

By decreasing the flow rates, $R_{boundary}$ also decrease and diffusion effects become more visible.



Water profiles across a N1110 membrane during humidification for two gas flow (1 and 0.14 L/min). The air relative humidity is 80% in both cases.

References :

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- Impact of a compressive stress on water sorption and diffusion in ionomer membranes for fuel cells. A 1H-NMR study in vapor-equilibrated Nafion®, A. El Kaddouri, J.-C. Perrin, T. Colinart, C. Moyne, S. Leclerc, L. Guendouz, O. Lottin, Macromolecules, *submitted* (2016)