Water transport in Nafion membranes under various conditions studied by NMR

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To cite this version:
Jean-Christophe Perrin, Assma El Kaddouri, Mathieu Klein, Sébastien Leclerc, Jérôme Dillet, et al.. Water transport in Nafion membranes under various conditions studied by NMR. MRPM 13, Sep 2016, Bologna, Italy. hal-01704321

HAL Id: hal-01704321
https://hal.univ-lorraine.fr/hal-01704321
Submitted on 8 Feb 2018

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Water transport in Nafion membranes under various conditions studied by NMR

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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 mechanical 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/hydration.

**Objectives**

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.

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**

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 << 1** Diffusion is not limiting during sorption and desorption
- **Bi ≥ 1** Effects of diffusion are visible on the profiles

By decreasing the flow rates, R_boundary also decreases and diffusion effects become more visible.

**References**


**Stripping**

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 augments with the stretching: diffusion coefficient increases in the stretch direction (DD) and decreases in the other directions (TP, 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.

**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.

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