

H1. QENS STUDY OF WATER DYNAMICS IN THE NAFION MEMBRANE

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Proton Exchange Membrane Fuel Cells are electrochemical devices developed for energy systems able to offer a competitive and clean alternative to standard oil based power suppliers. The key element of the cells is the ionomer membrane that must allow for proton transport from the anode to the cathode. The ionic conductivity insured by the acidic functionalities (SO_3^- groups) strongly depends on the hydration state of the membrane. Since the swelling state of the membrane can vary under operative conditions in a fuel cell, the hydration level appears as a crucial parameter for optimizing the performances. Moreover, proton conductivity and water dynamics are strongly coupled. In this work, we focused on the confinement effects on water mobility at the molecular level, as a function of the water loading in the Nafion. For this purpose, we have used QuasiElastic Neutron Scattering (QENS) to investigate the nano to picosecond molecular dynamical behaviour of the water adsorbed in the membrane.

Experiments. The QENS experiment were performed at 25°C on the time of flight (TOF) spectrometer Mibemol of the LLB with incident wavelengths $\lambda_i = 5.2 \text{ \AA}$ and 8 \AA corresponding to an elastic resolution of $\Delta E = 140 \text{ \mu eV}$ and 40 \mu eV FWHM respectively. The time scale has been extended to the nanosecond range by a complementary backscattering (BS) experiment performed on IN16 of ILL ($\lambda_i = 6.27 \text{ \AA}$; $\Delta E = 1 \text{ \mu eV}$).

Sample preparation. The membrane samples have been prepared from almost dry to fully hydrated. The combination of sorption measurements and SANS experiments allowed us to know with precision the quantity of water in each sample. We characterize this quantity by the parameter λ , which corresponds to the number of water molecules per ionic SO_3^- group.

Data analysis. In this work, local diffusion in confined geometry, long-range diffusion and atomic granularity are accounted for in a single model in the full Q -range ($0.34 < Q < 2.25 \text{ \AA}^{-1}$). The raw data analysis shows that the spectra needs to be analysed in terms of the superposition of two kinds of dynamics in the water-swelled Nafion that necessarily corresponds to the existence of two types of protons that are not exchangeable within the longer time-scale of the experiments ($\sim 600 \text{ ps}$). As a consequence, the experimental intermediate scattering function has been written as the sum of two components witch correspond respectively to “fast” (few ps) and “slow” ($> 100 \text{ ps}$) motions⁽¹⁾:

$$I_{\text{exp}}(Q, t) = \text{Amp} \times [N_{\text{fast}} \times I_{\text{fast}}(Q, t) +$$

$$N_{\text{slow}} \times I_{\text{slow}}(Q, t) + I_{\text{el}}(Q)] \times R(t) \quad (*)$$

N_{fast} and N_{slow} correspond to the number of mobile protons involved in the corresponding dynamics, $I_{\text{el}}(Q)$ is the elastic contribution of the polymer matrix, $R(t)$ is the temporal resolution function and $I_{\text{fast}}(Q, t)$ and $I_{\text{slow}}(Q, t)$ are the intermediate scattering functions written as:

- $I_{\text{fast}}(Q, t) = I_{\text{loc}}(Q, t) \times I_{\text{lr}}(Q, t)$, where

$$I_{\text{loc}}(Q, t) = \exp \left[-Q^2 \sigma^2 \left(1 - \exp \left[\frac{-(D_l / \sigma^2) t}{(1 + 2D_l Q^2 \tau_{\text{mi}})} \right] \right) \right]$$

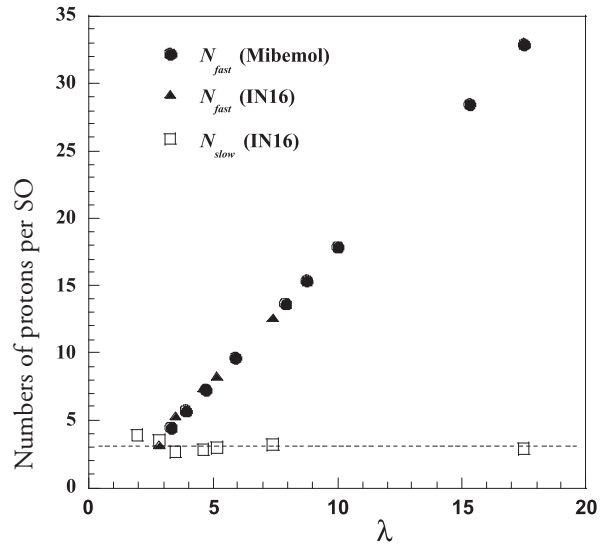
accounts for localized translational diffusion (with a diffusion coefficient D_l and a microscopic jump time τ_{mi}) inside a volume of typical size 2σ and $I_{\text{lr}}(Q, t) = \exp(-D_l Q^2 t)$ accounts for long range diffusion⁽²⁾.

- $I_{\text{slow}}(Q, t) = (1 - a(Q)) + a(Q) \times \exp(-t / \tau_{\text{slow}})$,

where $a(Q) = \exp(-Q^2 \sigma_{\text{slow}}^2)$ is the EISF of the slow motion (characteristic time τ_{slow} and characteristic distance $2\sigma_{\text{slow}}$). The quasielastic spectra have been calculated by numerical Fourier transform calculations of expression (*).

Results. The proton population of the “slow” motion is found to be constant over all the swelling range at the value $N_{\text{slow}} \sim 3$ (Figure 1), whereas the “fast” population N_{fast} increases almost linearly with the total number of water molecules λ .

Figure 1



This result pleads in favour of the existence of the hydronium ion as a long life-time entity in the Nafion. This picture is supported by the evolutions of the residence times τ_{mi} and τ_{slow} (Figure 2) and the characteristic confinement domains (2σ and $2\sigma_{slow}$) (Figure 3) which show that the 3 “slow” protons are diffusing ~ 50 times slower than the “fast” protons, in a confinement domain of almost identical size.

Figure 2

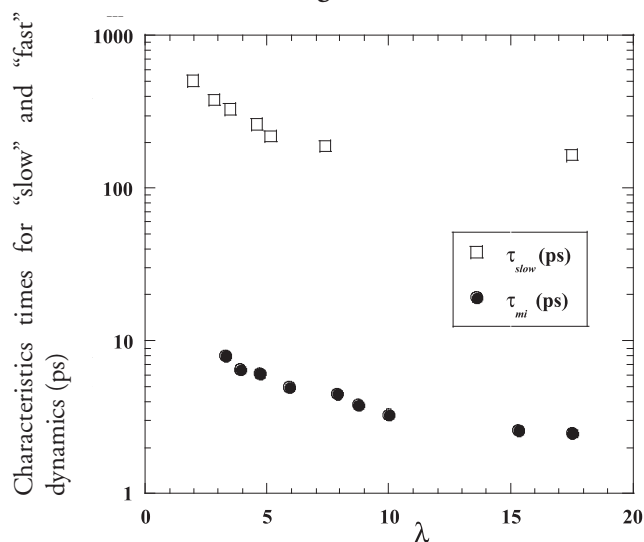
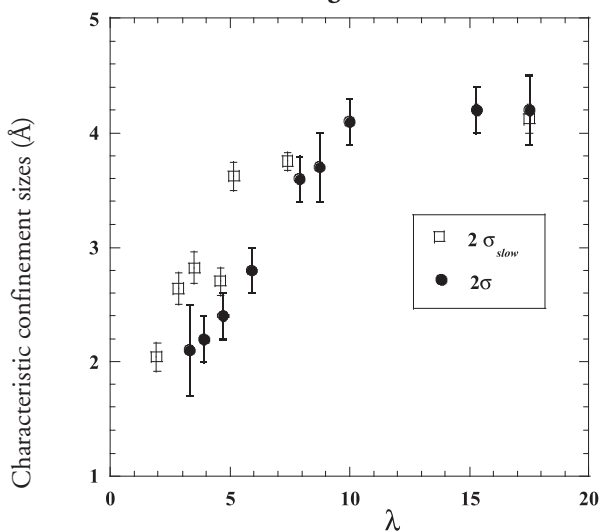
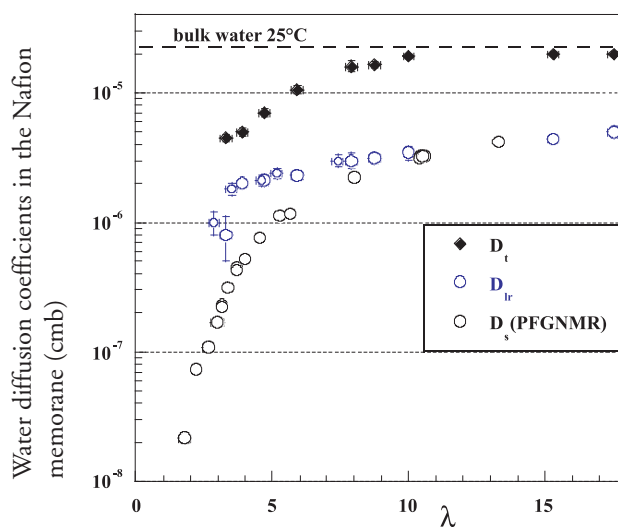


Figure 3



The evolution of these parameters, together with that of the local and the long-range diffusion coefficients (Figure 4) illustrates the progressive acceleration of the water dynamics when hydrating the membrane. For the highest hydration states, the local behaviour is very close the one observed in bulk water. Moreover, as soon as $\lambda \sim 3$, a long-range diffusion coefficient must be introduced in order to fit the quasielastic spectra in both experiments. The water can thus diffuse at larger distances than 2σ for very small amount of water.

Figure 4



Above $\lambda \sim 10$ the long-range diffusion coefficient is equal to the self-diffusion coefficient measured by pulsed field gradient NMR at the micrometer scale. This remarkable property of the membrane tells us that there is no slowing down of the diffusion between the nanometric and the micrometric scales when the membrane is sufficiently hydrated. At low hydration, the difference between the two diffusion coefficients can be attributed to the lamellar structure of the Nafion at the nanometric scale as revealed by NMR relaxometry experiments⁽³⁾.

(1) Perrin, J.-C.; Lyonnard, S.; Volino, F. *J. Phys. Chem B*, accepted for publication.

(2) Volino, F.; Perrin, J.-C.; Lyonnard, S. *J. Phys. Chem B* **2006**, *110*, 11217.

(3) Perrin, J.-C.; Lyonnard, S.; Guillermo, A.; Levitz, P. *J. Phys. Chem B* **2006**, *110*, 5439.