

Confinement, entropic effects and hydrogen bond network disorder of water in Nafion membrane

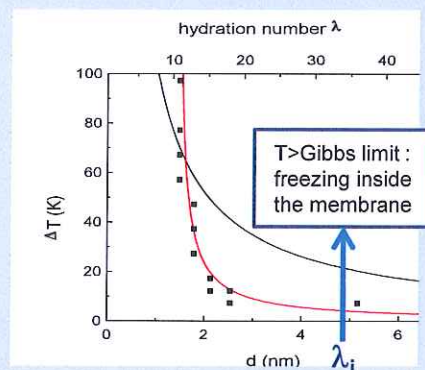
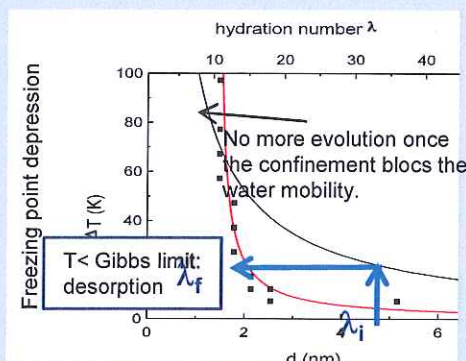
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Nafion is, to date, the most widely used polymeric material as Proton Exchange Membrane. The complex structural organization of this amphiphilic polymer leads to unique physical properties, especially the proton conductivity, which is related to the properties of water confined in the hydrophilic nanochannels, embedded in the hydrophobic matrix, that swell upon hydration. At subzero temperatures, the water remains mobile down to ~ 200 K, desorbing and re-sorbing reversibly in and out of the membrane depending on the temperature. We therefore investigated the structure of water by Compton spectroscopy in order to check if some unusual distortion of the hydrogen bond network was involved into this particular behavior.

Subzero Temperature: sorption/desorption phenomena

Below 0°C , the water desorbs out of the membrane progressively during cooling, down to ~ 200 K. It forms ice in the hexagonal Ih form on the surface of the membrane. As soon as the temperature raises up again, the ice melts and reintegrates the membrane. The hydration, which is directly related to the pore characteristic dimension, is determined by the equilibrium of the ideal solution of hydronium ions in water. The effect of confinements, according to the Gibbs-Thomson equation with adequate parameters taken from (J. Memb. Sci. 369,148), helps in keeping the solution unfrozen below 0°C .

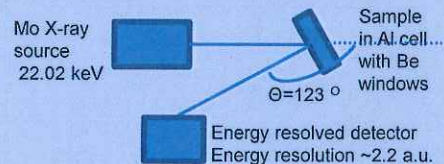


M. Plazanet et al., J. Phys. Chem. B 113 (2009), 10121.; M. Plazanet et al., J. Memb., Sci. (2014), 419-424

Compton Spectroscopy (CS)

CS is a direct probe of the momentum distribution of valence electrons, as the core electrons produce a fairly broad contribution to the Compton profile $J(q)$. $J(q)$ is sensitive to minor changes of the electrons which are involved in chemical bonds and provides a quantitative measurement of electronic density, therefore particularly suitable for the investigation of the geometry of hydrogen bonds. In particular $J(0)$ is a rough measurement of the wavefunction broadening and fluctuations. In the case of water, differences in Compton profiles with respect to bulk water are a direct probe of the disorder and/or structural differences of the hydrogen bond network.

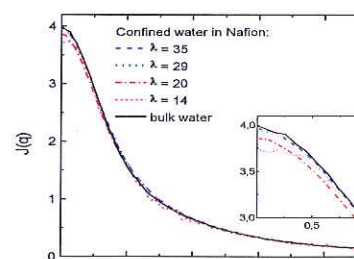
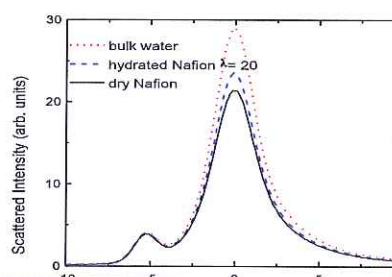
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The CP, measured at room temperature, follows a progressive variation from the lowest hydration to the highest one. For the highest hydration, the normalised profile $J(q)$ is almost identical to the one of pure water. This corresponds to $\lambda = 35$ water molecules per sulfonate group, corresponding to a characteristic confinement size of about 5 nm. At lower hydration, instead, differences in $J(q)$ can be observed between confined and bulk water. The strongest differences are observed for the lowest hydration $\lambda = 14$ in which the confinement radius is about 2 nm.

At this point, the origin of the variation in CP can either be assigned to distortions of the hydrogen bond network of water due to the presence of ions, or because of the confinement.

As the concentration increases while the confinement size decreases, both effects act together versus a larger distortion of the hydrogen bond network at lower hydration. Further studies such as temperature behavior or water confined in neutral systems are therefore needed to discriminate between the two possible origins.



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