

## Application 2076



### **Hydrogen bond network distortion of water confined in Proton-Exchange Membrane (PEM) for fuel cells.**

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Nafion is probably the most famous PEM used in fuel cells these days [1]. However, because of its high cost and, although very good, limited performances, an intense search for new materials for PEM candidates is going on.

The Nafion system has been extensively studied, from applicative but also fundamental point of view. Its complex structure is the result of the organization of an amphiphilic polymer made of Teflon-like chains with terminating  $\text{SO}_3^-$  groups forming the hydrophilic part. The arrangement of the hydrophilic groups leads to the formation of interconnected channels and cavities in which water enters during the swelling process. This enables the presence of a network of interconnected water pores of nanometric (2-6 nm) dimensions where water has a diffusivity close to the one of the bulk phase although it is confined in the polymeric matrix. The structural organization of the material, as well as water dynamics which is closely related to the high proton conductivity, is still the subject of current research in order to address the origin of the performances of the material. Several unusual behaviors have been observed in Nafion, among which a sorption/desorption phenomenon at low temperatures [2]. Indeed, when slowly cooled below 273K, water progressively desorbs as long as the temperature decreases, forming ice on the surface. This phenomenon lasts until ~200 K. Upon heating, ice melts and reversibly reintegrates the membrane. Previous investigations [3] pointed out an entropic origin of the effect, due to the presence of hydronium ions in water released by the sulfonate groups, that decrease the freezing point of the solution inside the membrane upon increase of ion concentration (causing water sorption/desorption).

More subtle origin of the phenomenon was then searched in the structure of the solution, by means of Compton spectroscopy. The Compton profile, giving the momentum distribution of the electrons, indeed provides direct information on chemical bonding, more specifically in water on hydrogen-bonding. Compton profile was measured in hydrated Nafion membranes [4]. The profile of water confined inside the membrane was extracted, and exhibits a lower intensity at  $Q=0$  with respect to bulk water. The intensity increases and the profile tends to reach the one of bulk water when hydration increases. This behavior of the profile is interpreted as a distortion of the hydrogen bond network of water in the membrane with respect to bulk water, that may cause the variation of chemical potential explaining the sorption/desorption phenomenon and other properties like the proton conductivity. However, two effects are competing in this distortion: the proximity of ions (that can be slightly kosmotropes or 'structure-maker') and the nanoscale confinement. In order to disentangle the two effects, one needs to investigate further systems.

We propose in the following project to explore the geometry of the hydrogen bond network of water in other materials proposed as PEM, as for example [5]: (sulphonated) poly(etheretherketone) ((s)PEEK), (sulphonated) poly(etherketone) ((s)PEK), (sulphonated) poly(ethersulfone) ((s)PES), (sulphonated) poly(benzimidazole) ((s)PBI), sulphonated polyimide (sPI), sulphonated poly(phenyl quinoxaline) (sPPQ), or sulfonated polyphosphazenes (sPPZ).

These membranes are a promising alternative to Nafion for elevated temperature operation because of low cost, processability, wide latitude to tune the chemistry, and mechanical, thermal and oxidative stability. The hydration behavior and the transport of protonic charge carriers and water have been examined and compared to the corresponding properties of Nafion. It was found that the pathways for water in the ketones are narrower than in Nafion at full hydration. The distinct differences between both membranes are qualitatively explained by differences in the microstructures and the acidity of the sulfonic acid functional groups [6].

We will therefore be able to determine the characteristics of the hydrogen bond network of water surrounding acid groups of different strength. The hydration dependence will be investigated, and samples will be compared at similar values of the hydronium concentration and confinement radius. Because hydration is a swelling process, the water pore dimension is directly related to the water content and can be tuned to have comparable effects in the various systems. The experimental setup available at the University of Perugia [7] will be used in similar conditions as it was for the Nafion experiment. Base on previous experience, the time requested for the experiment is 2 weeks.

#### References

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