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Role of hydrogen bounding in proton conductivity of Nafion membranes.

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Several examples of soft confinement media, in which water is trapped, exhibit a similar behavior: under cooling, the water continuously desorbs from the sample and crystallises. Upon heating, the phase separation is fully reversible, the ice melts and readsorbs in the system, again continuously with temperature. This phenomenon occurs down to 20 to 50 degrees below 273K. Such an effect has been observed in purple membranes [1] for instance. Beside many other systems behaving in a similar way, Nafion membranes also exhibit a similar behavior. Nafion is the most widely used proton-exchange membrane in H2/O2 fuel cells. This membrane is a perfluorinated polymer, made of a Teflon-like hydrophobic backbone with hydrophylic ionic side groups SO3-. Although it has been studied for several decades, the structure of the hydrated polymer is still the subject of controversy and interest. Indeed, the knowledge of the structure could explain the fast diffusion of water and high proton conductivity. The original model was proposed by Gierke in 1981 [3], and proposed the formation of water cavities of ~60 diameters into the polymer matrix, connected by channels of about 10 Ł? diameters. More structural features were later emphasized, like the presence small crystallites and other elongated polymeric elements [4], and eventually, a recent model proposed the formation of nanochannels of water [5]. All these models are mainly based on the interpretation of the most prominent peak, arising from this self-organised structure in which water is trapped. This so-called « ionomer peak » varies shape and position during hydration, and gives rise, in the structure factor, to the peak around 0.1 -1.

The low temperature behaviour of this system has been little investigated. Volino et al. first reported the desorption and readsorption of water upon cooling observed by calorimetry [6], and recent studies by the same group indicate the formation of crystalline ice during cooling

of the sample [7]. More recently we investigated quantitatively the process of phase separation (dimension of ice crystallites), crystalline structure of ice, proportion of desorbing water as a function of temperature. The aim of the experiment was to provide the answer on the crystalline structure of ice. An hexagonal ice diffraction pattern was observed in all cases and a careful analysis provided an estimation of the quantity of ice formed during the process [8].

In the present experiment we propose the use of the Compton peak line shape (Compton profile) as a probe of the water arrangement inside the membrane to understand the possible role of electron distribution. The use of the Compton profile to derive some information about the local bonding in water date back to the seventies[9] and more recently such a technique has been successfully employed to enhance quantum effects and covalency in water[10] and ice[11].

According to the investigations performed in pure water or in ice, we plan to make an accurate measurement of the Compton profile using the apparatus available at the Dipartimento di Fisica dell Università di Perugia to determine the Compton profile of water in Nafion at room temperature as a function of the water content. To extract the water contribution to the Compton profile the data of the dry membrane will be measured first. The contribution of the membrane will be then subtracted by taking into account the increased attenuation due to the added water. The data shown in the H2FC site in a test experiment[12] on the present membrane are of adequate quality to perform a meaningful comparison of the data as a function of the water content.

To get meaningful data several samples must be measured from the dry membrane up to 50% by weight water content. A proper sample holder with thin Be windows will be designed and produced in order to preserve the water content during the experiment. Accordingly also the empty container will be measured, so that the total number of samples will be about 20. A reasonable estimate is that about 15 days will be necessary to complete the experiment.

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