# Project Report

**Application No.** 2011
**Short title** Role of hydrogen bounding in proton conductivity of Nafion membranes.

**Objectives: short, medium and long term (<250 words)**

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-. The polymer adopts a complex structural organisation resulting from the microsegregation between hydrophobic backbones and hydrophilic sulfonic acid groups. Upon hydration, water-filled channels and cavities appear, in which the acidic protons are released to form a solution of hydronium ions in water embedded in the polymer matrix. The performance of the membrane in terms of proton conductivity is related to the structure and dynamics of the solution, although the microscopic mechanisms responsible for the high conductivity are still debated and controversial. The long term objective of the study is to characterize the structure and dynamics of water inside the membrane and their role in the proton conductivity. With the present experiment, i.e. analysis of the Compton profile of the solution confined into the polymer, we aim at obtaining new information about the structure of water and hydronium ions with respect to bulk water.

**Brief summary of work carried out:**

Experiment 2011- X-rays /MCLab Role of hydrogen bounding in proton conductivity of Nafion membranes. This experiment was first one dedicated to the best way of extracting the contribution coming from water alone and make a comparison with bulk water measured in the same condition. Even if a previous test was performed before by the group in Perugia, a large part of the time was devoted to the production of the best container adequate for a liquid and tight enough to avoid any sample loss. The original sample container was modified to optimize the seal system. A good sealing is important also to perform the measurement on dry nafion to avoid water contamination during the experiment. After preliminary tests, a modification was made to allow for a simple use in the case of liquid systems or in the case of a sample which must be charged under controlled atmosphere. The new cell was built according to drawing below, with thin (0.2 mm) Be windows used for maximum transparency. This cell was quite good as it was very simple for the use with liquids and wet nafion. No water loss was observed after several days. Several measurements of Compton scattering have been performed, each one lasting several hours to have a good enough statistics. The incoming X-ray energy was fixed at 22.1 keV, the best one available at Perugia, and the scattered beam was measured at 140 degs scattering angle with an energy resolution of 250 eV. A typical result for bulk water at room temperature is reported in the following figure where it is visible the small elastic peak at about 22 keV and the inelastic Compton peak at about 20.5 keV which is much broader than the elastic peak. The red line is a guide to eye made by fitting the elastic peak with a Gaussian function and the Compton peak with two rather broader Gaussian functions which roughly describe the valence and core contributions of the water molecules. The contribution from the cell Be windows has been subtracted taking into account the water transmission, while no correction for multiple scattering has been considered. This point is a complex one and it was decided to neglect it because the different tests implied too much time and it was decided to confine this experiment to the comparison of wet nafion and bulk water. Other measurements have been devoted to the characterisation of the 50% water in nafion to confirm that the differences between various samples are visible within the experimental accuracy. The comparison of the Compton profile in bulk water and wet nafion is reported in the following figure. The normalization of the data has been obtained from the integral which must be equal to the total electron number. This point must be considered in more detail because this normalization procedure is affected by the energy width of the measurement and should be tested in the case of a mixture like the nafion sample. From the simple fit to the data it is seen that the spectra of water and nafion have different shapes well outside the experimental errors.

**Main achievements intended for publication <250 words**

The experiment has demonstrated that differences between the Compton profiles of pure water and Nafion-embedded water can be observed. Further measurements in different experimental conditions (membrane hydration content, temperature) will be performed. The result will then be linked to the water structure inside the membrane.

**Difficulties encountered <250 words**

Difficulties have been encountered with the sample container, as previously explained.

**Further comments:** No