

NEW STRUCTURAL MODEL FOR NAFION® MEMBRANES

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Proton Exchange Membrane Fuel Cells are considered to be the most promising system for electric power generation. The heart of these cells is made of a polymeric solid electrolyte which has to satisfy several features: high ionic (protonic) conductivity (10^{-2} - 10^{-1} S.cm⁻¹), excellent chemical and electrochemical stability (>5000 h), low permeability to reactants ($p < 10^{-15}$ m²s⁻¹Pa⁻¹), and stable mechanical properties over a wide range of water content (0-30% wt) and temperature (0-100°C)

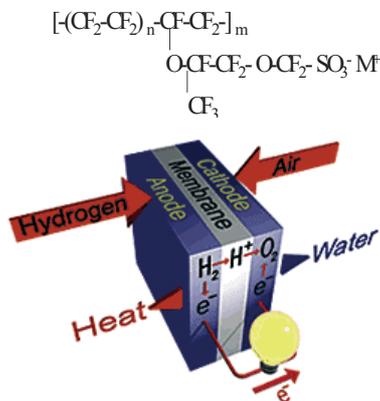


Figure 1. Schematic view of a Hydrogen fuel cell.

Nafion¹™, a perfluoro-sulfonated ionomer membrane is the benchmark material in terms of performance and stability, at least in stationary operation conditions. Although numerous studies are performed on alternative membranes, blends and composites (organic-inorganic system), all results are systematically compared to Nafion membranes. However the Nafion structural models are mainly based on the Eisenberg² description which considers ionic clusters dispersed in a hydrophobic polymeric matrix (in order to reduce the total free energy of the system). Based on the assumption that this cluster picture is correct, different models³ of aqueous membrane swelling were developed to explain data from structural studies, aqueous sorption and swelling, ionic conductivity, etc. A considerable effort has been made in the last few years in order to understand the underlying conduction processes, with the objective to ameliorate the membrane performances for industrial applications. However, few studies have been designed to explore the structural and transport evolution at different

length scales taking into account the complete hydration processes

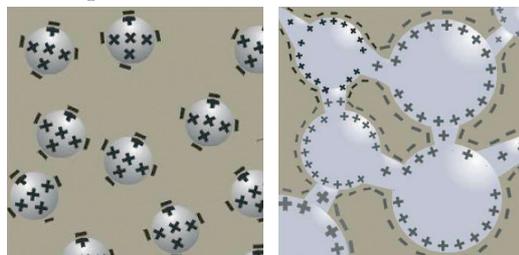


Figure 2. Representation of dry (left) and swollen (right) ionic clusters in an ionomer bulk system.

Recent developments in x-ray and neutron scattering techniques permit us to obtain high resolution data over an extended angular range and to define more accurate model. In parallel, the application of microscopy techniques such as the atomic force or electronic microscopies also reveal important information about the membrane structure. It is clear that both the microscopy and scattering data must be correlated to validate the proposed models. From this analysis, a new structural model of Nafion⁴ (applicable to other perfluorinated ionomer systems) has recently been developed in our laboratory. It describes Nafion membrane as an aggregation of polymeric chains forming elongated objects (simplified as cylinders), embedded in a continuous ionic medium. At larger scales, those aggregates form bundles, characterised by an orientation order between the aggregates. This new insight of a multi-scale structure can explain the membrane swelling process from dry state to the colloidal suspension, in a continuous way.

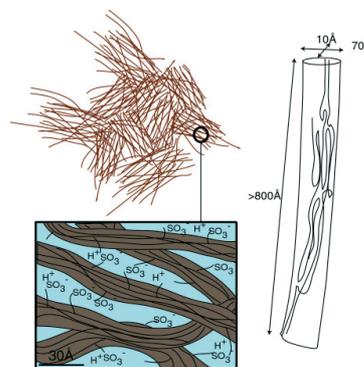


Figure 3. New insight of a Nafion membrane multi-scale structure.

Neutron scattering was chosen to take advantage of the contrast variation method and was a key experiment in our study. Using SANS a partially deuterated solvent and a highly protonated counter-ion such as TMA⁺ (non-transient contrast agent), it was previously demonstrated that the counter-ions condense at the polymer-solvent interface and that the highly swollen membrane spectra can be to some extent simulated by a core-shell cylindrical form factor (polymeric core surrounded by a counter-ions shell⁵).

Therefore, SANS combined with contrast variation is a suitable technique to determine the distribution of the counter-ions in NafionTM and to determine the shape of the polymeric aggregates. In this new model, the water medium is described as a 3D continuous media (as a function of water sorption) rather than confined water molecules in a channel and micelles network (Gierke's model).

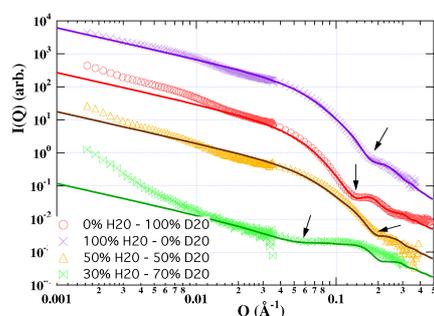


Figure 4. Scattering curves from an hyper-swollen Nafion membrane for different H₂O/D₂O ratios. Black curves correspond to theoretical form factors.

On the other hand, membrane drawing experiments have confirmed the “cylinder” model and the structure orientation effect on the protonic conductivity have been measured. SAXS and SANS studies on stretched Nafion films were analysed thanks to a basic deformation model taking into account randomly oriented set of bundles (assuming cubic shape) at the origin. Those results have been correlated with birefringence measurements⁶.

References

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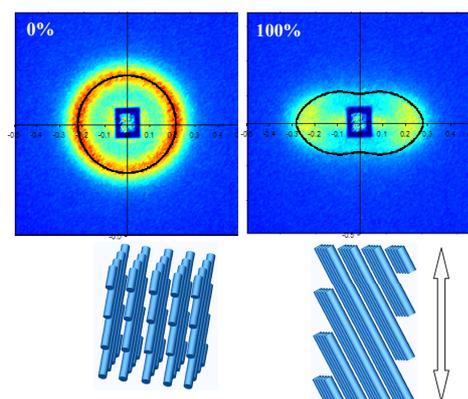


Figure 5. 2D scattering pattern from a Nafion membrane at rest (left) and under stretching (right). Taking into account a simple model of a distorted bundle of rod-like aggregates, the position of the ionomer peak as a function of the azimuthal angle (black lines) is simulated and superimposed to the experimental spectra.

The results of this study allow us to propose some modification of ionomer systems in order to improve performances in fuel cell. Moreover, the associated dynamical processes are expected to occur at different time scales: internal motion of protons along aggregates, motion from one aggregate to another, from one bundle to another, and through the whole membrane.

The relaxation times associated to the proton dynamics in these systems are consequently expected to range from the picosecond (local jump of a proton between two sulfonated groups) to few tenths of seconds (macroscopic conductivity through the whole membrane).

A complete study of the dynamics, using various complementary techniques, is necessary in order to verify that they correlate with what we know about the structure. Quasi-elastic neutron scattering, neutron spin echo, back scattering studies, gradient field-pulsed NMR and field cycling NMR relaxometry will be conducted to understand the multi-scale ionic and water transport in this kind of material. This understanding is crucial to be able to model the water management in fuel cells