

Application 2012



Structural study of ionomeric composite membranes

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The user group of the Laboratory of Inorganic Chemistry of Perugia University has a consolidated experience on the preparation and characterisation of proton conducting composite membranes based on ionomers for applications as solid proton conductors in Polymer Electrolyte Membrane Fuel Cells (PEMFC). Polymer electrolyte membrane is a key component of a PEMFC and should fulfill several properties, such as high ionic conductivity, excellent physical, chemical and electrochemical stability, low permeability to reactants and stable mechanical properties over a wide range of water content and temperature. A well known strategy to improve the properties and, in turn the fuel cell performance of a ionomer is the incorporation, within the polymer matrix, of inorganic filler particles; the properties of the composite membrane are affected by the nature and extension of the interfacial surface between the two phases and, consequently, by their chemical, structural and morphological characteristics.

The composite membranes mainly studied in our laboratory are based on layered inorganic fillers, such as zirconium phosphates and phosphonates which turned out to be able to improve the mechanical stability of perfluorinated ionomers, without significantly reduce their proton transport properties and, in some cases, to reduce their permeability to methanol.

The properties of proton conducting membranes (PCMs) are significantly affected by their microstructure, which is very complex and multiscale, especially that of composite PCMs. Nevertheless, the optimization of their properties clearly depends on the knowledge of the structure-property relationship. X-ray scattering techniques (WAXS and SAXS) are well suited for the study of the structural properties of PCMs (determination of the degree of crystallinity and phase separation) [1] and the present project aims to study the microstructure of composite PCMs by x-ray diffraction experiments. In particular, it is of interest to investigate the effect of the chemical and morphological features of an inorganic filler on the structural characteristics of the ionomer matrix. With this aim, different kinds of composite membranes will be prepared, based on the following inorganic fillers:

- hydrophilic filler, specifically nanosized layered zirconium phosphate (ZrP);
- hydrophobic filler, specifically organic derivatives of ZrP functionalised with fluoro-alkyl, fluoro-aryl groups;
- mixed hydrophilic-hydrophobic fillers.

The different nature of the filler could promote specific interactions with the ionomer, which could rebound on the PCM properties.

[1] a)Yarusso, D. J., & Cooper, S. L. (1983). Microstructure of ionomers: interpretation of small-angle x-ray scattering data. *Macromolecules*, 16(12), 1871-1880; b)Gebel, G., & Diat, O. (2005). Neutron and X-ray Scattering: Suitable Tools for Studying Ionomer Membranes. *Fuel Cells*, 5(2), 261-276; c) Yang, C., Srinivasan, S., Bocarsly, A. B., Tulyani, S., & Benziger, J. B. (2004). A comparison of physical properties and fuel cell performance of Nafion and zirconium phosphate/Nafion composite membranes. *Journal of Membrane Science*, 237(1), 145-161; d) Arico, A. S., Baglio, V., Antonucci, V., Nicotera, I., Oliviero, C., Coppola, L., & Antonucci, P. L. (2006). An NMR and SAXS investigation of DMFC composite recast Nafion membranes containing ceramic fillers. *Journal of membrane science*, 270(1), 221-227; e) Arico, A. S., Baglio, V., Di Blasi, A., Creti, P., Antonucci, P. L., & Antonucci, V. (2003). Influence of the acid-base characteristics of inorganic fillers on the high temperature performance of composite membranes in direct methanol fuel cells. *Solid State Ionics*, 161(3), 251-265.