## CHEMICAL STABILIZATION OF POLYMER ELECTROLYTES USED IN PEMFC

Guillaume Monin<sup>a,b</sup>, <u>Laurent Gonon</u><sup>a</sup>, Vincent Mareau<sup>a</sup>, Catherine Marestin<sup>b</sup>,

<sup>a</sup>Structures et Propriétés d'Architectures Moléculaires, UMR 5819 (CEA-CNRS-UJF), INAC/SPrAM, CEA-Grenoble, 38054 Grenoble cedex 9, France

<sup>b</sup>LEPMI, UMR 5279 CNRS / INP Grenoble / UJF / Université de Savoie, chemin du Canal 69360 Solaize, France

(Laurent.gonon@cea.fr)

Proton exchange membranes (PEM) are key components in fuel cell (FC) systems as they allow proton transport between the two electrodes, without any gas mixing. However, the enhancement of the durability of the PEM lifetime is critical to viability for the FC. The aging of the membrane is due to a chemical / electrochemical and a mechanical degradation. Hydrogen peroxide and its products of decomposition (HO• and HO<sub>2</sub>•) generated during the fuel cell operation are considered as one of the important vectors of the membrane degradation<sup>1,2</sup>.

The first works devoted to a strategy of chemical stabilization of membranes appeared only very recently (2003). These works are based on a radical scavengers approach<sup>3, 4</sup>. Following a different strategy, our work intends to develop sacrificial stabilizers able to decompose hydrogen peroxide formed in fuel cell operation. Two stabilizers based on thiourea (THP) and tetrasulfide (TS) groups were synthetized. In order to avoid leaching of the stabilizer induced by membrane swelling in the fuel cell, the stabilizer were grafted onto SiO<sub>2</sub> nanoparticles (figure 1). Nanoparticles dispersion in the membrane is expected to have a strong impact on both conductivity and mechanical properties of the membrane, and was thus thoroughly studied.

AFM analyses performed on the cross section of cryo fractured membranes have shown an excellent dispersion of functionalized THP loads whereas the formation of aggregates was observed with functionalized TS. (figure 2a). The ability of stabilizers to limit the membrane degradation was evaluated with a sPAEK membrane, for different aging times in an  $H_2O_2$  environment. The most efficient stabilizer appears to be the one based on THP groups. However, this stabilizer cannot be used because strong acid base interaction with the sulfonic groups of the polymer reduced the proton conductivity of the membrane and as a consequence the performances of the FC. On the other hand, the oxidation of the TS stabilizer leads to the formation of sulfonic groups and consequently to an increase of the ionic conductivity of the membrane (figure 2b).

## References

- 1. Liu W., Zuckerboard D., J. Electrochem. Soc. 152 : A1165-A1170, 2005.
- 2. Scherer G.G., Bunsen-Ges Ber., Phys. Chem. 94: 1008–1014, 1990.
- 3. Zhao D. Yi B.L. et al., J. of Power Sources 190: 301-306, 2009.
- 4. Trogados P., Parrondo J. et al., Electrochem. and solid State Letters, 11: B113-B116, 2008



Figure 1: Synthons grafted on SiO<sub>2</sub> particles to produce stabilizing nanoparticles



Figure 2: a-AFM image of cryo-fractured membranes (tapping mode/phase contrast) and b-Ionic conductivity of the composite membranes versus aging time in  $H_2O_2$  vapor at 70°C