

## 7- Multifunctional membranes for electrochemical systems

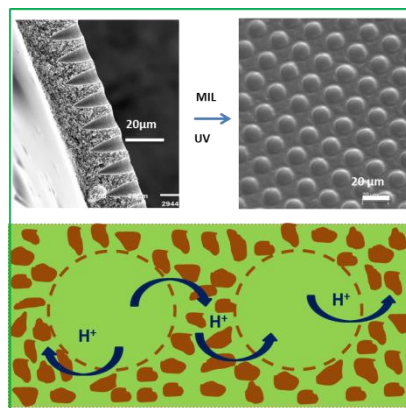
### **Hierarchical porous Polybenzimidazole microsieves: An efficient architecture for anhydrous proton transport via Poly-ionic Liquids**

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Collaboration: Univ. of Twente- The Netherlands, Univ. of Zaragoza- Spain

Involved MCP researchers: Anne Julbe, Martin Drobek

Liquid induced phase separation micromolding (LIPS $\mu$ M) has been successfully used for manufacturing hierarchical porous polybenzimidazole (HPBI) microsieves (42-46% porosity, 30-40  $\mu$ m thick) with specific pore architecture (pattern of macropores  $\sim$ 9  $\mu$ m in size perforated in a porous matrix with 50-100 nm pore sizes). Using these microsieves, proton exchange membranes were fabricated by infiltration of 1-H-3-vinyl imidazolium bis(trifluoromethanesulfonyl)imide liquid and divinylbenzene (as cross-linker) followed by in-situ UV polymerization. Our approach relies on the separation of the ion conducting function from the structural support function. Thus, the polymeric ionic liquid (PIL) moiety plays the role as a proton conductor, while the HPBI microsieve ensures the mechanical resistance of the system. The influence of the porous support architecture on both proton transport performance and mechanical strength has been specifically investigated by means of comparison with both straight macro-porous (36% porosity) and randomly nano-porous (68% porosity) PBI counterparts. The most outstanding results were obtained with poly[1-(3H-imidazolium)ethylene]bis(trifluoromethanesulfonyl)imide polymeric ionic liquid (PIL) cross-linked with 1 % divinylbenzene supported on HPBI membranes with 21  $\mu$ m thick skin layer, achieving conductivity values up to 85 mS $\cdot$ cm $^{-1}$  at 200  $^{\circ}$ C under anhydrous conditions and in the absence of mineral acids.

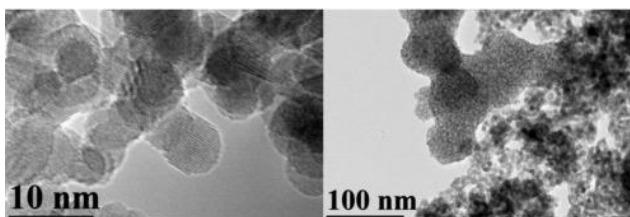


### **Sintering and conductivity of nano-sized yttria-doped ZrO $_2$ synthesized by a supercritical CO $_2$ -assisted sol-gel process, The Journal of Supercritical Fluids 115 (2016) 26–32**

Collaborations : LSFC-Saint-Gobain CREE- Cavailon-France, Univ. Lille- France, CEA Marcoule- France

Involved MCP researcher: Anne Julbe

This study reports on the electrical characterization of nano-sized zirconia powders doped with 3 and 8 mol% Yttria, referred to as 3Y-ZrO $_2$  and 8Y-ZrO $_2$ , respectively. Powders were synthesized using a super-critical CO $_2$  assisted sol-gel method to control the size and morphology of the powder particles. Spark plasma sintering (SPS) was used to sinter the



TEM micrographs of nanometric 8Y-ZrO $_2$  powders

powders and maintain a fine microstructure with small grain size. The microstructure and chemical composition of the resulting ceramics was evaluated by electron microscopy techniques, showing grain boundaries depleted of amorphous phase. Electric conductivity of the 8Y-ZrO $_2$  pellets was determined by electrochemical impedance spectroscopy techniques, between 200 and 800 $^{\circ}$ C, and correlated with the microstructure. The bulk electric response at 300 $^{\circ}$ C is comparable to commercially available Y-ZrO $_2$  compositions. Compared to conventionally prepared samples we obtain lower conductivity in the high temperature range, still values in this study are twice superior to 3Y-ZrO $_2$  samples similarly prepared by SPS.

