

Publishable summary

Context and project objectives

A breakthrough of Proton Exchange Membrane Fuel Cells (PEMFC) requires a radical performances improvement of the key fuel cell material components (catalysts and protonic membrane) as well as highly innovative solutions to overcome the membrane assembly and integration limitations. The proton exchange membrane of the fuel cell is required to have good proton conductivity, a lack of electronic conductivity (in order to prevent short circuit), physical/chemical stability under hydrated conditions, and low cost. The current benchmark is Nafion (Dupont¹), which displays a proton conductivity of around 80-90 mS/cm whilst fully hydrated at room temperature.^{ii,iii,iv} Plasma polymerization offers a potentially attractive solution to the problem of manufacturing films with high acid contents (i.e. high density of proton conducting moieties) conjoined with low water solubility. The reason for this is that, unlike many conventional polymerization techniques, plasma polymerization produces thin films of insoluble crosslinked polymers.^v Problems unaddressed so far have included low stability and cracking of films when hydrated^{vi,vii}.

Table 1 : literature survey on the main results regarding the vacuum deposited proton conductive membranes for PEM fuel cells

References	Precursors	Conductivity
N. Inagaki et al, Polym. Bull. 26 , 187 (1991)	SO ₂ + penta / tetra ou per-fluorobenzene	0,04 mS/cm
Ogumi et al., Chem. Lett. 953 (1990)	CF ₃ SO ₃ H	0.025-0,05 mS/cm
Ogumi et al., J. Electrochem. Soc. 137 , 3319 (1990)	CF ₃ CH ₂ Cl	
Brumlik et al., J. Electrochem. Soc. 141 , 2273 (1994)	trifluoroethylene and CF ₃ SO ₃ H	0.58 mS/cm
Uchimoto et al. J. Electrochem. Soc. 147 , 111 (2000)	Methylbenzene sulfonate+1,3 butadiene	0,2 mS/cm
Roualdes et al. – J.Power Sources 158 (2006) 1270–1281	CF ₃ SO ₃ H + styrène	0,1 mS/cm
Durand et al. – J. Power Sources 195 (2010) 232–238	styrene and trifluoromethane sulfonic acid	1,7mS/cm
Jiang et al. - Journal of Membrane Science 372 (2011) 303–313	styrene and trifluoromethane sulfonic acid monomers after glow discharge	180 mS/cm

The most recent of the plasma polymers in Table 1 is that of Jiang *et al's* triflic acid/ styrene copolymer. A very high value for the proton conductivity (measured at room temperature, fully hydrated) is quoted. However, the SEM pictures of the films after deposition (before hydration) show large cracks, Figure 1.

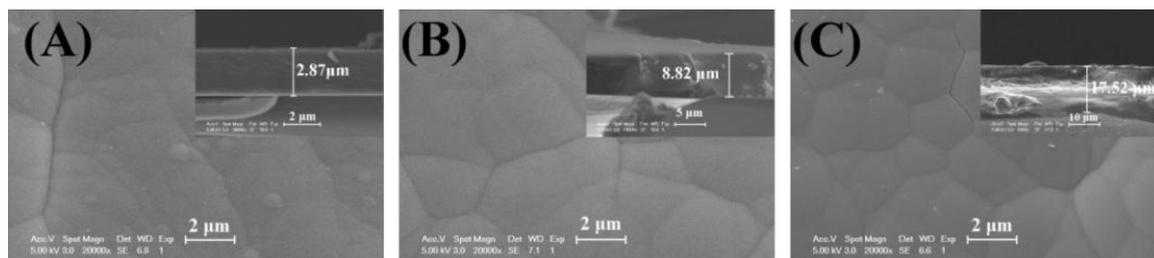


Figure 1: SEM images of trifluoromethanesulfonic acid/styrene copolymers produced by plasma polymerization. Taken from Jiang et al. - *Journal of Membrane Science* 372 (2011) 303–313

Previous plasma polymers have also often relied on copolymerization of an acid-containing monomer together with a monomer to provide a stable polymeric backbone, Table 1. The use of a single monomer to provide both polymeric backbone and acid functionalities would be preferable since reproducibility issues associated with copolymerization are diminished.

Work performed

Volatile precursors suitable for the deposition of proton conductive membranes with vacuum techniques were synthesized (mainly persilylated precursors and perfluorinated esters precursors). The potential of these precursors as well as of some commercial precursors was evaluated via PECVD, iCVD and ASPD. The incorporation of carboxylic and sulfonic acid function into a fluorinated matrix via vacuum techniques (iCVD, PECVD, ASPD) was developed. In order to synthesize catalytic layers with a growth process compatible with the deposition process of the proton conductive membrane various techniques were screened by the consortium (MOCVD, Co-deposition PECVD-PVD) and associated with the plasma processes for the synthesis of a ion conductive catalyst composite. These materials have been assembled to build fuel cells.

Results achieved, intentions for use and impact

Sulfonic and carboxylic membrane with proton conductivities as high as 200mS/cm were deposited using various vacuum techniques. For the realization of a composite catalyst via vacuum techniques two approaches are developed, direct synthesis of the composite material in vacuum and injection of catalyst nano-particles. In this frame, composite materials were successfully developed via photodeposition of platinum cluster on various conductive supports and the first composite catalysts were successfully deposited. These materials are currently being evaluated via electrochemical analysis / realization of fuel cells.

Expected end results, intentions for use and impact

PEM fuel cells present a huge potential for automotive and stationary applications and can also be used for portable systems in the range 50W-500W and for micro-fuel cells (5-50W), for which the power density is not the limitation, but rather the ratio power/weight. Depending from the application, the targets for success in the marketplace differ. For example, the targets for automotive fuel cells include a cost target of \$30/kW by 2015 (\$45/kW by 2010), 5,000-hour durability and increased efficiency to 60%. The cost target is for production at manufacturing volumes of 500,000 systems per year^{viii,ix}. In other potential applications for fuel cells, such as stationary power generation (distributed power), backup power, portable power, material handling, and other specialty applications, the life-cycle cost of the competing technology allows for a higher fuel cell cost. These applications are

considered early markets for fuel cells. For example, for stationary power generation key targets include a fuel cell cost of \$750/kW and a durability of 40,000 hours. For Micro fuel cells, the challenges are mainly focused on the miniaturization of the systems and judicious coupling with the hydrogen sources^x. Of course, costs must also be competitive and costs of \$10/W are targeted. The SmallinOne project proposes a top down integration via realization of the membrane electrode assembly using vacuum techniques. The proposed architecture uses the techniques coming from micro-electronics, for the deposition of the various layers composing the active parts of the cell. This modifies drastically the morphology of the catalytic layer since the structure of both the substrate and the ionic membrane is totally different from the one of the anodic and cathodic GDLs. This integration is particularly suitable for miniaturization of the fuel cells interconnections but could also be interesting for high power application. These techniques can be useful for large scale production like roll to roll. In addition, they can facilitate the monolithic integration of fuel cell directly for a reduction in the assembly time and costs.

Consortium

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- Federal Mogul Systems Protection – France
- IRD Fuel Cells A/S – Denmark
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- ^{vii} Jiang, Z.; Jiang, Z.; Meng, Y. *J. Membr. Sci.* **2011**, *372*, 303.
- ^{viii} 2010 American Chemical Society Publication Date (Web): April 30, 2010 | doi: 10.1021/bk-2010-1040.ch001 In Fuel Cell Chemistry and Operation; Herring, A., et al.; ACS Symposium Series; American Chemical Society: Washington, DC, 2010.
- ^{ix} Multi-Year Research, Development and Demonstration Plan, Hydrogen, Fuel Cells & Infrastructure Technologies Program, October 2007, Table 3.4.2.
- ^x Mini-Micro Fuel Cells: Fundamentals and Applications Par S. Kakaç, A. Pramuanjaroenkij, L. Vasiliev