PROJECT FINAL REPORT - PUBLIC

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Scientific representative of the project's coordinator:

Dr. Jessica THERY

Commissariat à l'Energie Atomique et aux Energies Alternatives

Tel: +33 438 78 19 40/+33 6 22 86 15 20

Fax: +33 438 78 51 57

E-mail: jessica.thery@cea.fr

Project website: www.smallinone.eu

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1. Content

2. Final publishable summary report

SMAllinOne
Smart Membrane for hydrogen energy conversion:
All fuel cell functionalities in One material

2.1 Executive summary

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 SMALLINONE project addresses an architecture that strongly differs from the classical approach. The catalysts and the membrane are deposited step by step on a porous substrate using vacuum techniques. This architecture can be compared to the "top down integration" approach that is common in microelectronic. With respect to classical PEM fuel cell, this modifies drastically the morphology of the fuel cell materials. This innovative architecture is associated with the development of the basic PEM fuel cell materials (catalyst and ionic membrane) using vacuum technologies.

Volatile precursors suitable for the deposition of proton conductive membranes with vacuum techniques were synthesized. Proton conductive membranes were successfully deposited via PECVD, iCVD and ASPD. Conductivities as high as 150-200mS/cm were reached. For the realization of a composite catalyst via vacuum techniques two approaches were 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 such as ATO nanoparticles. For these last composite catalysts systems, a quite innovative UV photo-reductive deposition method using covalently attached UV-asensitizing benzophenone (BPh) moieties onto the surface of inorganic conductive (WO_3, WC, & ATO NPs) was developed. This method was compared to an hydride-mediated chemical reductive process. Promising electrochemical outputs were measured (ATO support disclosed most promising results). The use of the UV-reactive benzophenone modification shell in the photochemical synthesis was shown to afford lower-sized deposited Pt nanoparticles.

These vacuum deposited catalysts have been associated with the plasma processes for the synthesis of an ion conductive catalyst composite. These materials have been assembled to build fuel cells. For a complete evaluation of the material potential, two fuel cell configurations were used: planar breathing fuel cells, without hot pressing the materials between bipolar plates: the various layers are deposited onto a porous substrate and tested in a self-breathing configuration. We also have deposited materials on commercial gas diffusion layers hot pressed between bipolar plates. In the planar breathing configuration, open circuit voltage of 900mV could be measured provided membranes thicknesses superior to 6µm are used. Coupling the vacuum catalysts with a Nafion® membrane power density of 120mW/cm^2 could be measured (platinum load 100µg/cm^2). When the MEA is sandwiched between bipolar plates, the result is quite close with a commercial Nafion® membrane as separator but when a vacuum deposited membrane is used as separator, no open circuit voltage could be measured. On the whole, one can see that the soft conditions of the planar breathing configuration are favorable to reach correct open circuit voltages: the thin vacuum membranes might be damaged by pressurization. Additionally, the deposition on rough gas diffusion layer is favorable to the formation a crossing defects. On the whole, the mechanical stability of these vacuum deposited membrane are below the one of Nafion® like membrane.

2.2 Project context and objectives

Today, there are many types of fuel cells in the industry. The structure of a fuel cell system can take the form of either a stack or a planar system. A fuel cell "stack" is formed when groups of cells are layered and combined in series via bipolar plates. Fuel cell stack generally require bipolar plates and thick end plates, as well as additional components such as pumps and fans. Planar fuel cell has a simpler design and is formed when the cells are placed on a flat surface, next to each other, in succession, with opposing electrodes connected. A planar passive fuel cell does not require anything else other than a fuel supply; the air needed for the reactions flow in automatically from the surroundings[1].

Fuel cell stack is the most common architecture. It is used for automotive and stationary applications but it can also be used for portable systems in the range 50W-500W. Planar breathing fuel cells are mainly used for micro-fuel cells (5-50W), for which the power density is not the limitation, but rather the ratio power/weight. Depending on 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, 5,000-hour durability and increased efficiency to 60%. The cost target is for production at manufacturing volumes of 500,000 systems per year[2] [3]. 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[4]. Of course, costs must also be competitive and costs of $10/W are targeted. Last year, the educational fuel cell sector has seen shipments of over 100,000 units over the past year – making 2009-2010 the year that mass commercialisation of the portable sector began. After a number of false starts and false promises, 2010 was the year that mass commercialisation began in a number of other portable fuel cell niches. The forecasts show that 40 million of portable fuel cells could be shipped annually by 2020, with small portable fuel cells (1-100 W) seeing the most shipments[5].

As explained, the majority of the PEM Fuel cells correspond to fuel cell "stacks". 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. The various components of a PEM fuel cell (proton exchange membrane, electrodes and bipolar plates) are built using vacuum techniques. 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 (Dupont), which displays a proton conductivity of around 80-90 mS/cm whilst fully hydrated at room temperature[6] [7] [8].

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[1] http://www.myfuelcell.se/technology/micro-fuel-cells/
[2] 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.
[3] Multi-Year Research, Development and Demonstration Plan, Hydrogen, Fuel Cells & InfrastructureTechnologies Program, October 2007, Table 3.4.2
[4] Mini-Micro Fuel Cells: Fundamentals and Applications Par S. Kakaç, A. Pramuanjaroenkij, L.Vasiliev
[5] Fuel Cell Today Portable Fuel Cell Analysis - 2010
[6] Mauritz, K. A.; Moore, R. B. *Chem. Rev.* 2004, *104*, 4535.

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 cross-linked polymers[9].

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	SO_2 + penta / tetra or per-	0.04 mS/cm
Ogumi et al., Chem. Lett. **953** (1990) Ogumi et al., J. Electrochem. Soc. **137**, 3319 (1990)	CF_3SO_3H CF_3CH_2Cl	0.025-0,05 mS/cm
Brumlik et al., J. Electrochem. Soc. **141**, 2273 (1994)	Trifluoroethylene and CF_3SO_3H	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_3SO_3H + 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. Previous plasma polymers have also often relied on copolymerization of an acid-containing monomer together with another 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.
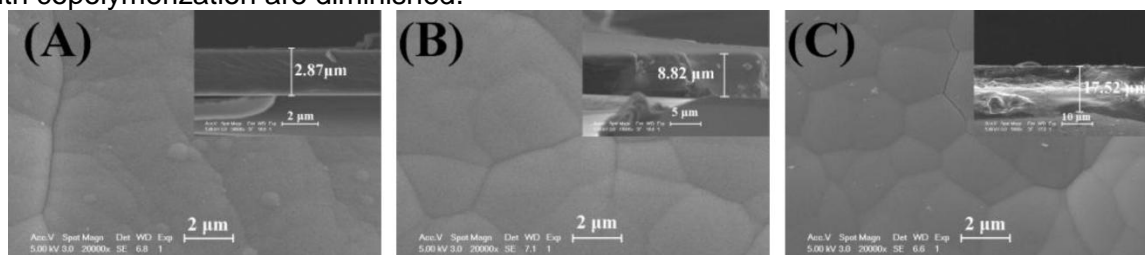

Figure 1: SEM images of trifluoromethanesulfonic acid/styrene copolymers produced by plasma polymerization. Taken from *Jiang et al. - Journal of Membrane Science 372 (2011) 303–313.*

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[7] Fontanella, J. J.; Wintersgill, M. C.; Chem, R. S.; Wu, Y.; Greenbaum, S. G. *Electrochim. Acta* 1995, *40*, 2321
[8] Mikhailenko, S. D.; Guiver, M. D.; Kaliaguine, S. *Solid State Ionics* 2008, *179*, 619
[9] Yasuda, H. Plasma Polymerization; Academic Press: New York, 1985

Regarding the vacuum deposited catalysts, it is known that vacuum deposition might favour platinum nanoparticles dispersion for a reduction of the platinum amount in fuel cell. Regarding vacuum deposited catalysts for PEM fuel cells, it has already been demonstrated that plasma technologies are suitable for obtaining an efficient use of the catalyst[10]. Nanostructured catalytic films have been grown on silicon wafer and carbon-cloth using a combination of evaporation, microwave plasma enhanced chemical vapour deposition (PECVD), and sputtering methods. Most of the studies are related to ultra-fine particles production and direct metal catalyst deposition on a support[11]. Sun et al.[12] tried to deposit Pt nano-particles on nitrogen containing CNTs (CNx NTs) for micro-fuel-cell application. The CNx NTs were grown on Si substrate through microwave-plasma-enhanced chemical vapour deposition (MPECVD). For Pt deposition, a DC sputtering technique was employed. Some well separated Pt nano-particles were formed with an average diameter of 2 nm on CNx NTs while a continuous Pt thin film was observed on the bare Si substrate. These results suggest that the sputter-deposition technique is a good way to deposit small and uniform Pt layer that could give a higher fuel cell cathode performance and, at the same time, reduce the Pt loading considerably. Recently, improved performances were showed for the co-deposition via sputtering of C/Pt catalyst layer[13]. The highest utilization of platinum at ultra-low loadings has been achieved with electrodes prepared by sputtering methods with power density of 20kW/g Pt (pure H_2 and O_2 gases). This result is attributed to the improved dispersion of the platinum clusters which are distributed on the 300nm of the gas diffusion layer and to the fact that co-depositing carbon may favour both the efficiency and the utilization of platinum.

With the objective to produce an innovative membrane electrode assembly using vacuum technologies, the SmallinOne project proposes an innovative architecture corresponding to a thin film protonic conductive membrane with two catalytically functionalized sides. The idea is to keep a same proton conductive backbone for each layer, and to functionalise it with embedded conductive catalyst particles for the electrodes. The electronic conduction is allowed by the platinum cluster percolation.

The project is divided into three parts. In a first time, the objectives were to develop the basic materials, that is to say the catalysts and the ionic membrane via vacuum technologies. This happened in two steps: first, chemical precursors were developed, and second, these precursors were used to build the ionic membrane. Commercial precursors were utilized for the development of the vacuum deposited catalysts. In a second part of the project, these materials are assembled together for the fabrication of fuel cells via incorporation of the catalysts in a proton conductive matrix. Finally, the project focused on enhancing the performances via improving the electronic conductivities for example. The project is highly ambitious. The final targets are very high taking into account the various challenges we had to face: First, even if interesting chemical structure can quite easily be drawn, it is not easy to predict the physical properties of these materials, and especially to predict if these molecules can be used for vacuum deposition. Another issue is the synthesis of performing ionic membrane via vacuum techniques. Indeed, the literature already reports various paths for the synthesis of proton conductive membranes via vacuum techniques, however, these materials present ion conductivities far below from the actual target of 100 mS/cm. Another challenge comes from the fact that both the catalyst and the proton conductive membrane should be made in the same vacuum tool, with is not obvious, from a technical point of view.

[10] C.J. Liu, G.P. Vissokov and B.W.L. Lang, Cat. Today, 2002, 72, 173

[11] S. Mahima, R. Kannan, I. Komath, A. Aslam and V. Pillai, Chem. Mater., 2008, 20, 601

[12] Sun CL, Chen LC, Su MC, Hong LS, Chyan O, Hsu CY, et al. Chem Mater 2005;17:3749e53

[13] Cavarroc et al. Electrochemistry communication – Volume 11, issue 4 – April 2009

To address these challenges, the consortium is composed of industrial partners and research centers or universities. For the material development, three partners worked in parallel, CEA, UNIBA, and an industrial partner, SIL (which was recently sold to the company P2I). CEA is involved in the characterization of the materials and fuel cells. UNIBA is involved in the synthesis and characterization of the chemical precursors. BIU developed liquid precursors for the synthesis of ionic membrane and prepared catalyst nanoparticles. The materials were evaluated and tested by IRD, which has a strong knowledge in PEM fuel cell for stationary application, and by CEA for the portable (small power range) applications. FMSP advised the consortium with its background in roll-to-roll production tools.

2.3 Main S&T results/foregrounds

2.3.1 Membranes development

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Plasma and chemical vapour deposition processes have been optimized to synthesise thin protonic membrane. Both commercially available precursors and ad hoc synthesized ones have been tested in the deposition of such coatings. The precursors consisted in organic acid and ester derivatives with a high vapour pressure in order to make easier the admission in the vacuum reactor. In any case, major attention has been devoted to monomer structure retention in the membrane by limiting monomer fragmentation and loss of the relevant acid functional group during the deposition process. Furthermore in the case of precursor in ester or other derivatives form, the deposited film have been treated in a wet hydrolysis step to convert the functional groups in acid moieties.

The approach followed in the case of plasma deposition processing was that of working at low RF power with eventual addition of a fluorocarbon monomer to the functionalised precursor. Changing the ratio of the two monomers could help in tuning the acidity of the functional groups (which depends both on the content of the acid groups and on the presence of electronegative groups that withdraw electrons – CFx) and the wettability/water management of the membrane (increasing the content of fluorocarbons groups the hydrophobic character increases).

In Figure 2 the effect of RF power on the chemical coating composition in terms of infrared absorption is reported, for a typical system studied in SMALLINONE at a constant feed composition (acrylic acid, AA / exafluoropropene, C_3F_6). It can be observed that the acid groups (3000-3600 cm^{-1}) drastically decrease when the power is increased as a matter of boosted fragmentation in the gas phase. On the other hand coatings deposited at low power are more susceptible to water dissolution.
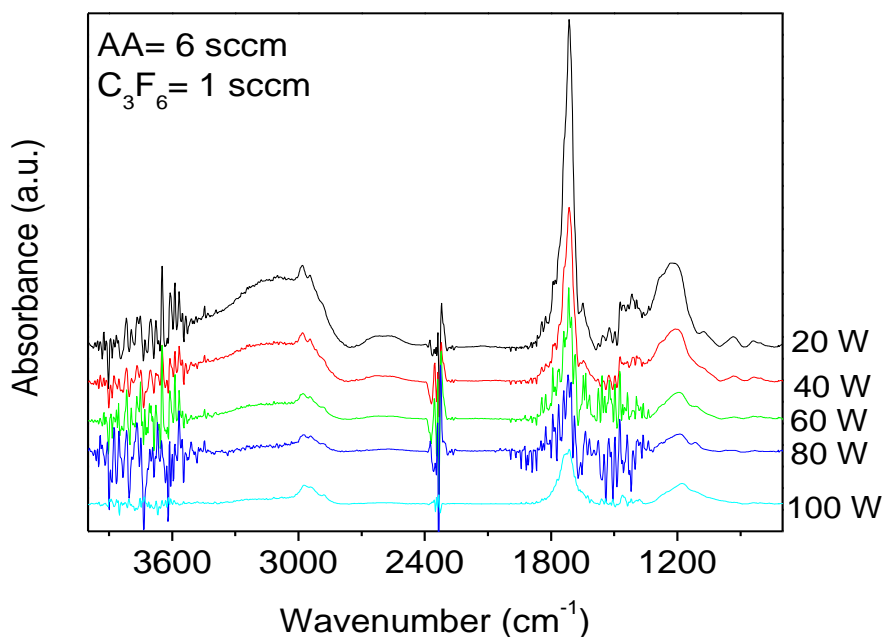

Figure 2 – FTIR spectrum for membrane coatings deposited by plasma processing

However, with this approach membranes with protonic conductivity as high as 70mS/cm can be obtained.

Another approach followed at UNIBA consisted in the use of initiated Chemical Vapor Deposition (iCVD). In this case in a vacuum reactor a hot wire (about 300°C) breaks a radical initiator forming reactive species that diffuse towards a chilled substrate at T=10-50°C where it can react via a conventional radical polymerization, with vinyl precursors (Figure 3). Different precursors have been tested, similar to the ones tested in plasma processing, with and without the addition of crosslinkers, such as ethyleneglycoldimethacrylate.
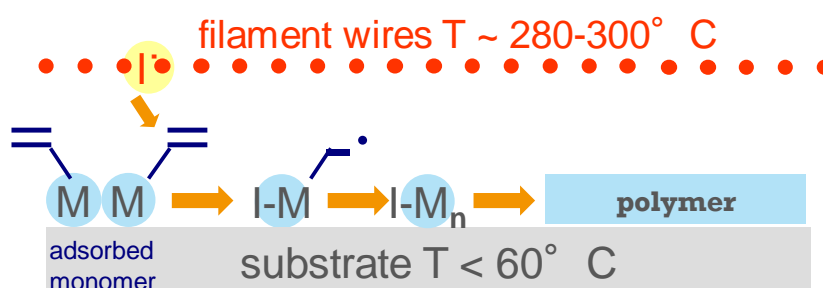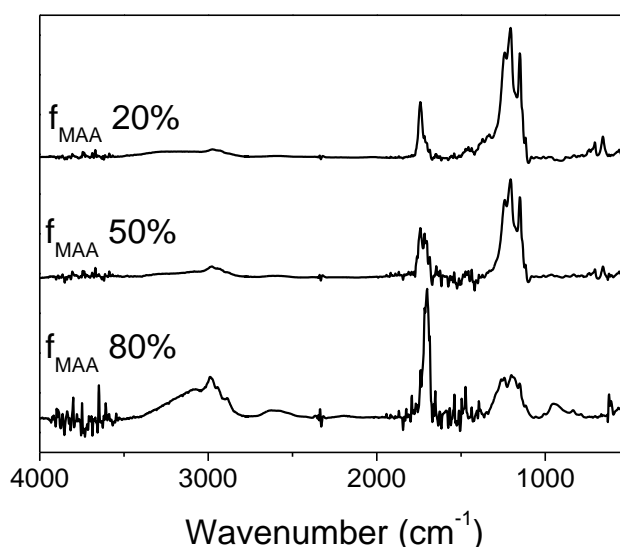

Figure 3 – scheme of iCVD process

Figure 4 – FTIR spectra of PFDA/methacrylic acid iCVD deposition

Also with this process the relative abundance of fluorocarbon and acid groups bearing precursors has been evaluated. In Figure 4 it can be observed how playing with the flow rate of the two precursors and their partial pressure in the vacuum chamber the composition of the coatings can be nicely tuned. This method can allow deposition rates as high as 500nm/min and the best proton conductivity attained was 70mS/cm.

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CFS and CFO membranes were realized by using a capacitive-coupled reactor with a RF power supply of 13.56 MHz. The radio frequency (RF) power is delivered by a Dressler Cesar 1310 generator to the showerhead-type upper electrode. Vacuum is made by a dry two-stage Alcatel ADS601 pumping system. Pressure is measured via MKS Baratron® gauges and controlled by a VAT throttle valve system. A base pressure of 10^{-3} mbar was reached before each deposition. The precursor is vaporized at room temperature and vapours are carried by inert Helium from a thermostatic bubbler to the chamber.

The CFS membranes results from the plasma polymerization of PSEVPE with C_4F_8. The plasma power was fixed at 10W, the deposition pressure was fixed at 0.25mbar and the sample holder temperature was varied between 35°C and 200°C. The graph from the Figure 5 shows the impact of the deposition temperature on the chemical composition of the CFS films (FT-IR spectra). For all deposition temperatures, one notices the presence of CF_2 stretches (at 1150 and 1210 cm^{-1}) and of the CF stretch (at 1260 cm^{-1}). The shoulder at 1470cm^{-1} can be attributed to the SO_2 bonds and the peak at 990cm^{-1} is characteristic from the C-O-C bonds. The CF_2 stretches are clearly resolved. This denotes a quite ordered nature in the CF_2 chains. This order is strongly correlated to the plasma power. As shown in the Figure 6, the lack of any distinction between the two CF_2 stretches suggests an amorphous and disordered film matrix which is deposited for the high power films. The large peak between 1100cm^{-1} and 1400cm^{-1} is related to an overlap of the CF_2 stretches (1150 and 1210 cm^{-1}) and the CF stretch (1260 cm^{-1}). From a deposition temperature between 150 and 200°C, one can see on the Figure 5 a decrease of the SO_2 peak intensity. We assume that this is related to the plasma assisted thermal degradation of the C-S bonds of the per fluorinated PSPVE molecule. This is mainly correlated to the thermal decomposition of the SO_2 bonds and this prevents us from working at temperatures superior to 150°C for the realization of the AllinOne material with the sulfonic bonds.
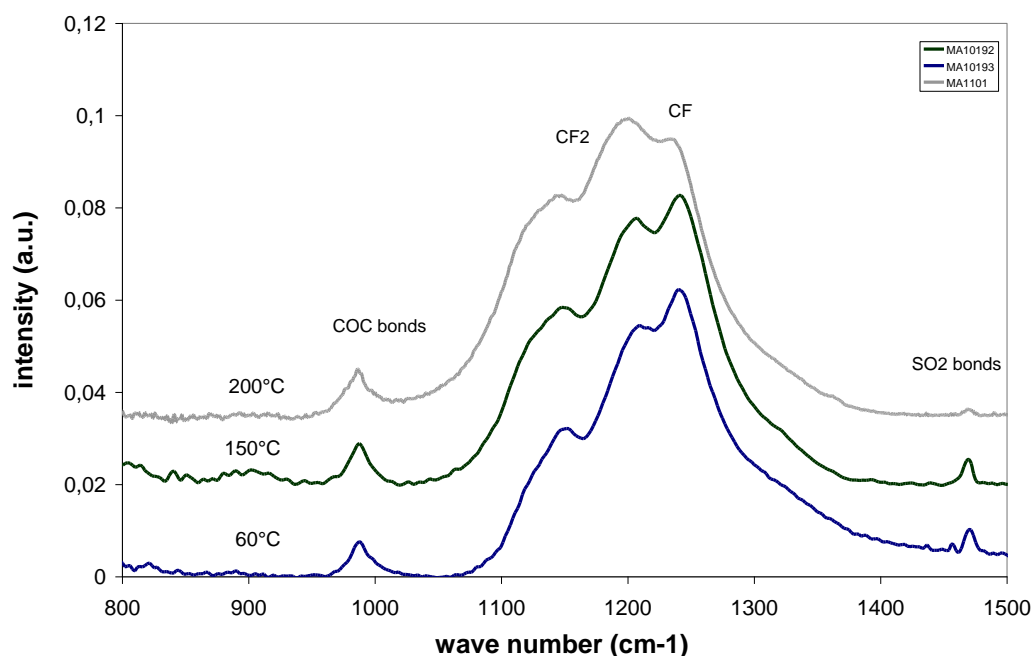

Figure 5 : FTIR spectra for CFS membrane deposited according the following conditions : He_b 100sccm, C_4F_8 80sccm, P 10Watt, Die 20mm, deposition temperature from 60°C to 200°C.
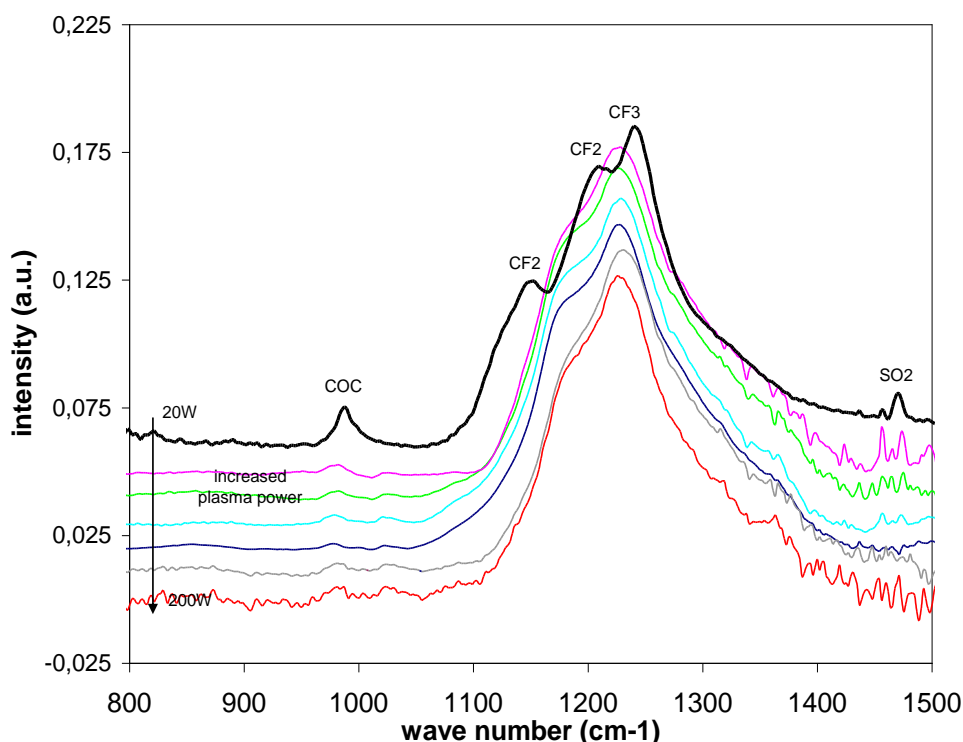
Figure 6 : Impact of the plasma power on the FTIR spectra for CFS membrane deposited according to the following deposition conditions: He_b 100sccm, C_4F_8 80sccm, P 20-200Watt, Die 20mm, deposition temperature 35°C.

The CFO membranes results from the plasma polymerization of C_4F_8 with H_2O vapours. The Table 2 recapitulates the compared results for a PECVD CxFyCOOH film and a commercial membrane. One observes a stronger dispersion of the results for the PECVD membrane. For both membranes, we checked that the substrate had no influence on the measured value. The residual depth is weak for both membranes, which is characteristic of elastic materials. Creep is huge for both membranes. PECVD CxFyCOOH membranes are four times harder than the commercial membranes. To decrease the hardness of the CxFyCOOH membranes, pulsed plasma deposition was tried. These last are expected to impact the reticulation of the CxFyCOOH membranes and thus the mechanical behaviour. The duty cycle was fixed at 50 and the pulsed frequency was varied between 1Hz and 5Hz. No impact was seen on the FT-IR spectra, meaning that the kind of chemical bonds stay unchanged.

Table 2. Results for PECVD and commercial membranes. **Sample**	**Commercial membrane**	**CxFyCOOH**
Thickness (µm)	20	8
Indentation depth (µm)	2	2
Maximal strenght (mN)	3,1	15,1
Creep (µm)*	0,2	0,1
Residual depth (µm)*	1,2	1,3
Young modulus at 10% (GPa)**	0,78	3,45
Hardness at 10% (GPa)**	0,06	0,24

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One main objective was to screen further a range of existing SIL precursors previously used for plasma deposition of proton conducting membranes. Out of these, plasma-enhanced deposition of anhydride-containing precursors was found to display high proton conductivity values. Effectively this provides a single-step process for preparing proton exchange membranes at ambient temperatures.
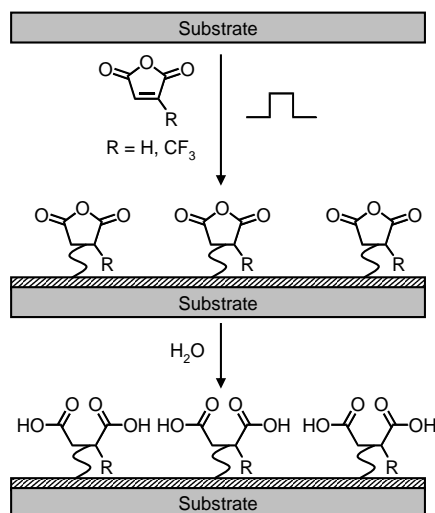

Figure 7 : Hydrolysed membrane layers

The resultant hydrolysed membrane layers contain a high density of carboxylic acid functionalities, which underpin proton conductivity (Figure 7). Carboxylic acids are weaker acids compared to the more popular sulfonic acid groups (as used in the current benchmark perfluorosulfonic acid containing polymer membranes (Nafion ®) and therefore have in the past been reported to yield low proton conductivities. However, the present study demonstrates that hydrolysis of anhydride functionalities can lead to a high density of proton conducting carboxylic acid centres.

Table 2: Water Uptake, Proton Conductivity, Water Contact Angle, and Stability in Water at 20 °C of Plasma Deposited Films.

Hydrated Plasma Deposited Film	Mass Increase Upon Hydration / wt %	Proton Conductivity (fully hydrated, 20° C) / mS cm^{-1}	Water Contact Angle / °	Optical Appearance
Poly(maleic anhydride)	167 ± 7	50 ± 5	38 ± 1	Cracking
Poly(trifluoromethyl-maleic anhydride)	143 ± 3	90 ± 5	84 ± 1	No cracking

For the case of pulsed plasma deposited poly(maleic anhydride) and poly(trifluoromethyl-maleic anhydride) films, the measured proton conductivities are on a par with Nafion (80-90 mS cm^{-1} at room temperature). In the case of poly(trifluoromethyl-maleic anhydride) films, a threefold beneficial effect is achieved by utilising a trifluoromethyl group substituted variant of maleic anhydride: firstly it provides stabilization of anhydride radicals within the electrical discharge (thus enhancing rate of polymerization and suppressing ablation); secondly its electron-withdrawing effect gives rise to a stronger carboxylic acid group; and thirdly, it provides a degree of hydrophobicity which helps to avoid cracking (due to less hydrophilicity and therefore swelling/internal mechanical stress within the layers). These films were characterised using XPS, FTIR, and impedance measurements. Testing for fuel cell applications by IRD was found to be unsuccessful.

Further experiments were undertaken in relation to the atomized spray plasma deposition (ASPD) of the sulfonate ester provided by UNIBA (Figure 8).
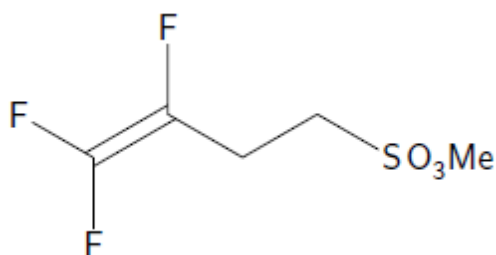

Figure 8: Structure of UNIBA monomer.

The UNIBA monomer was deposited under both continous wave conditions and pulsed conditions without using the ASPD setup (i.e. conventional plasma polymerization at a vapour pressure of 0.18 mbar). This gave low film deposition rates of 6 nm min^{-1} for the continuous wave and 2.7 nm min^{-1} for the pulsed deposition. Though the films were smooth and of good quality, their low thickness rendered them not easily analyzable. In contrast, the atomised spray-plasma-deposited films were very thick (with a deposition rate in the order of 100's of nanometres per minute). This gave rise to a dark brown film, with sharp infrared peaks. There is still a significant peak due to the $CF_2=CF$ vinyl stretch after plasma deposition, but this could easily be reduced by tailoring the reaction conditions, such that the flow rate and therefore pressure inside the chamber was optimised.
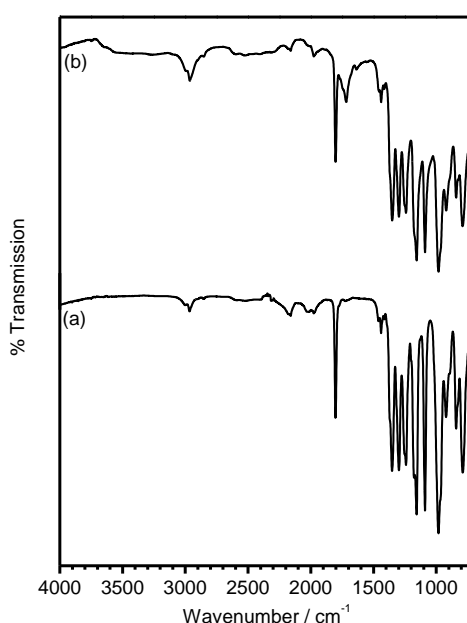

Figure 9: FTIR spectra for (a) UNIBA monomer; and (b) UNIBA monomer having been spray-plasma deposited

2.3.1 Catalytic electrodes development

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UNIBA had to optimize nano-composite coatings consisting of platinum clusters embedded in a polymeric matrix by means of plasma deposition. The approach consisted in simultaneous plasma polymerization and sputtering of a Pt target. This is depicted in Figure 10.
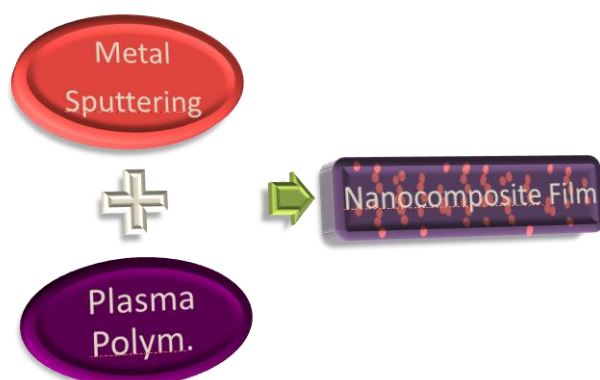

Figure 10: Scheme of the single step plasma deposition of Pt containing nanocomposite coatings at UNIBA

For this reason a gas feed containing both a monomer, precursor of the matrix and Argon has been considered. As monomer both fluorocarbon and inorganic gas have been considered. Chemical analysis of the surface as well as electron microscopy characterization of the coating has been carried out to assess the structure of the coating. Furthermore to define the performance of the coatings for their potential use as an electrocatalytic layer in fuel cell, the cyclovoltammetric measurements have been carried out for samples deposited on graphite rotating discs. This test gives information on the specific "active" area of the catalytic materials, and in turn, indirectly, on their efficiency of conversion of fuel.

Basically 2 systems have been considered
a) C_2H_4 + Pt target
b) C_3F_6 + Pt target
for the system a the monomer was admitted both continuously and pulsed. The second approach allows for reducing the unwanted deposition on the target that limits the sputtering of metal and in turn its amount in the coating. In this mode lower RF power can lead to higher Pt content in the catalytic layers.

A typical effect of RF power on the composition of the coating is reported in Figure 11, in the case of plasma fed with C_3F_6. The amount of metal in the coating is increased with the power at a fixed content of monomer in the gas feed.

The nanocomposite structure of the catalytic layer deposited in this way was demonstrated by means of transmission electron microscopy (TEM). In Figure 12A it can be appreciated that the coating (about 60% atomic percent of platinum) consists of well dispersed small agglomerates of Pt clusters (less than 10nm in diameter) in a polymeric matrix. Furthermore, and this has been confirmed by chemical analysis the Pt is not oxidised, and it is organised in crystalline form.

Much more as displayed in Figure 12B the film for Pt% higher than 55% grows columnar, as typically found in coatings deposited by classic sputter deposition.
In terms of Electrocatalytic activity the results are summerized in Table 3, reported in terms of SECSA (specific electrocatalytic surface area).
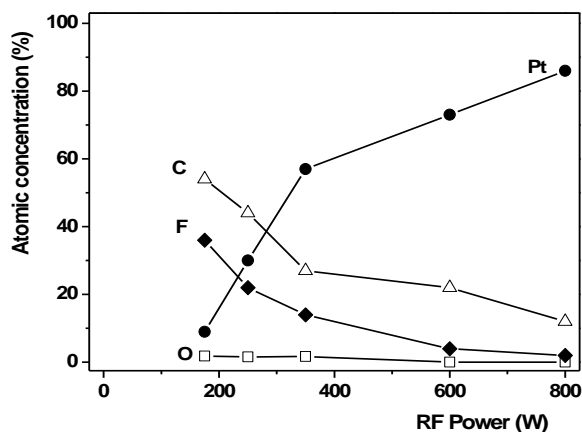
Figure 11: XPS elemental analysis of the surface as a function of the power ignition of the plasma, when a C_3F_6/Ar system is considered.
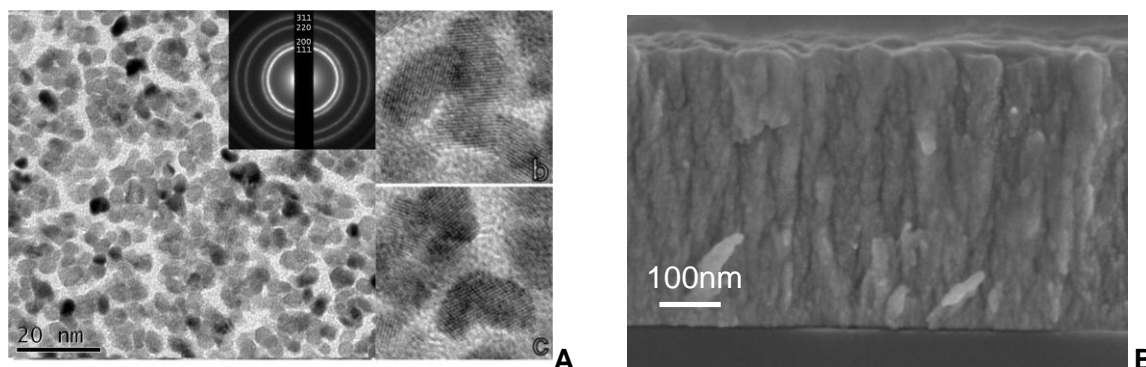
Figure 12 : Morphological characterization of Pt/CHx coating, A) TEM and B) SEM analysis

Table 3

Process	thickness (nm)	Pt loading (mg·cm^{-2})	SECSA (cm^2 Pt mg^{-1})
Pt/CHx continuous	500	0.342	85
Pt/CHx continuous	500	0.513	263
Pt/CFx continuous	500	0.652	94
Pt/CHx pulsed monomer		0.56	202
Pt/CHx continuous	250	0.278	173

The following observations can be done:
1) The performance is at least comparable with the commercial catalysts
2) Hydrocarbon based monomer leads to better catalytic character
3) Even at thickness as low as 250nm a considerable catalytic activity is obtained

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MOCVD (direct liquid injection) has been used for the deposition of the C_xF_yCOOH/Pt coatings. The reactive species (Pt precursors Complex $PtMe_2(COD)$ purchased from Strem Chemicals) are solubilised in Toluene (Aldrich) and injected with nitrogen and oxygen at high pressure by liquid injectors. Synthesis of the proton conductive matrix occurs from the polymerization of C_4F_8 with water vapours which is also injected with nitrogen at high pressure by liquid injector. Platinum deposition occurs from the thermal (plasma assisted) decomposition of the precursor's carbonated ligands.

Preliminary experiments were done without water, to check the ability of depositing composite C_xF_y/Pt films. We studied the growth rate of the films, as well as the electronic resistivity. Indeed, near the catalytic sites, low electronic resistivities are required for a good evacuation of electronic charges. The figure below shows the impact of the C_4F_8 flow on the growth rate, for various r.f. power. Visually, the colour of the membrane deposited in glass substrate varies from metallic grey for the low C_4F_8 flow to dark grey for the elevated C_4F_8 flow. This modification of the aspect of the films can be correlated with a variation of the Pt/C ratio in the coating. In parallel, the growth rate is strongly impacted by the fluorocarbon flow and the r.f. power, showing thus that the plasma polymerization of the fluorinated gas should have occurred. For a C_4F_8 flow of 100sccm, a maximal growth rate close to 100nm/min could be reached.
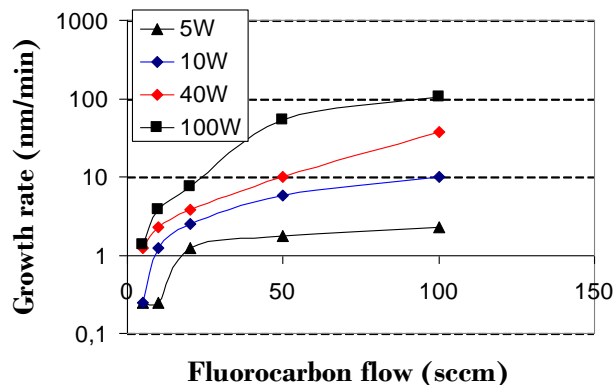

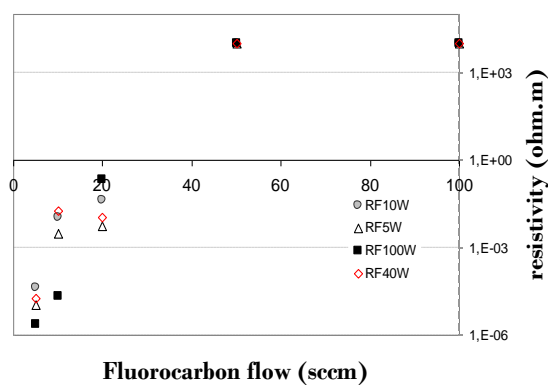**Figure 2 :** Impact of the C_4F_8 flow and the r.f. power on the growth rate of C_xF_y/Pt films.

Figure 14 : Impact of the C_4F_8 flow and the r.f. power on the electronic resistivity of C_xF_y/Pt films[14].

The Figure 14 presents the variation of the electronic resistivity of these same coatings. The resistivity is strongly correlated to the C_4F_8 flow. For C_4F_8 flows superior to 20sccm, the coatings are insulating, C_4F_8 flow as low as 5sccm are required to reach low resistivity between 10^{-4} and 10^{-6} ohm.m. The impact of the r.f. discharge is less clear. Indeed, for C4F8 flow of 5sccm, the high power coatings present the lowest resistivity of 2.10^{-6} ohm.m. But from C_4F_8 flow of 20sccm, the tendency is reversed and the resistivities seem decreased for the r.f. power of 5watt. This tendency should be confirmed, but it can be explained by the competitive action of the r.f. discharge for the platinum deposition and the polymerization of the carbon matrix. For the low C_4F_8 flow, an increase of the plasma power will mainly affect

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[14] Electronic resistivity superior to 10^{-1} ohm.m cannot be measured with our 4 probe apparatus; consequently, values of 10^4ohm.m have been plotted – meaning insulating coating.

the platinum growth rate while for enhanced C_4F_8 flow, event if the platinum deposition yield should probably be increased, the r.f. power mainly impacts the deposition of C_xF_y matrix. From these results, the C_4F_8 flow has been set below 20sccm. Hence, water vapours were added for formation of ion conductive carboxylic functions. As oxygen, H_2O is known as an oxidative specie and act for the degradation of the carbonated ligands[i]. For the trimethyl aluminium precursor, H_2O introduction causes reduction of the aluminium growth rate (with respect to oxygen). This is interpreted by the different reactions of trimethyl aluminum with the oxygen species of O_2 and H_2O in the vapour phase prior to the growth region[ii].

The addition of water was shown to act positively on the growth rate for the films deposited with C4F8 5sccm, while it has a negative impact on the growth rate for the film with C_4F_8 flow superior or equal to 50sccm. It was shown previously that the decreased of the C_xF_y growth rate is related to the formation of carboxylic functions and consequently, an equilibrium has to be found between electronic resistivity (low C_4F_8 flow) and ionic conductivity (C_4F_8 flow high enough for formation of carboxylic functions).

From these results, growth conditions were chosen to reach electronic resistivity between 4.10^{-6} and 2.10^{-5} ohm.m. XPS analyses confirmed the presence of platinum, carbon, oxygen, and fluor.

In parallel with the material developments, fuel cells were built onto polyimide substrates. We present here the results for the ionic membrane CFS type, deposited by PECVD, and for the catalytic materials deposited by MOCVD. The fuel cells were built according to the following stack: first, a 500nm thick gold collector was deposited via sputtering. Then a C/Pt ink (home made, from commercial catalysts – pt load $0.2mg/cm^2$) was deposited on the drilled polyimide substrate. The CFS membrane was then deposited under the following plasma conditions: plasma discharge 10Watt, He bubbling flow 0.1SLM, C_4F_8 flow 80sccm, pressure 0.25mbar, duration between 8 to 64hrs. The cathode was deposited via spraying a C/Pt ink ($0.3mg/cm^2$). A cathodic gold collector (500nm thick) was then deposited.

The open circuit voltage is the difference of electrical potential between the cathode and the anode when there is no external load connected. The theoretical value for a PEM fuel cell is of 1.23V. Practically, open circuit voltage of 0.9 to 1.1V can be measured with a majority of the commercially available PFSA materials. For thicknesses between 10 and 20µm, maximal OCV of 850-900mV are measured. These values remain stable in time but inferior to the one measured with a commercial NafionXL membranes, meaning that the hydrogen crossover through the CFS membranes is superior to the hydrogen crossover through Nafion membranes. This can be related to the low reticulation of the CFS plasma membranes since low deposition power are requires to conserve the acidic functions.

Chrono amperometric curves for the CFS fuel cells at a potential / cell of 0.6V were carried on (Figure 15). Even if power outputs as high as $5mW/cm^2$ can be reached, the current is stabilized at values around $1mA/cm^2$ ($0.6mW/cm^2$). No influence of the membrane thickness could be depicted.
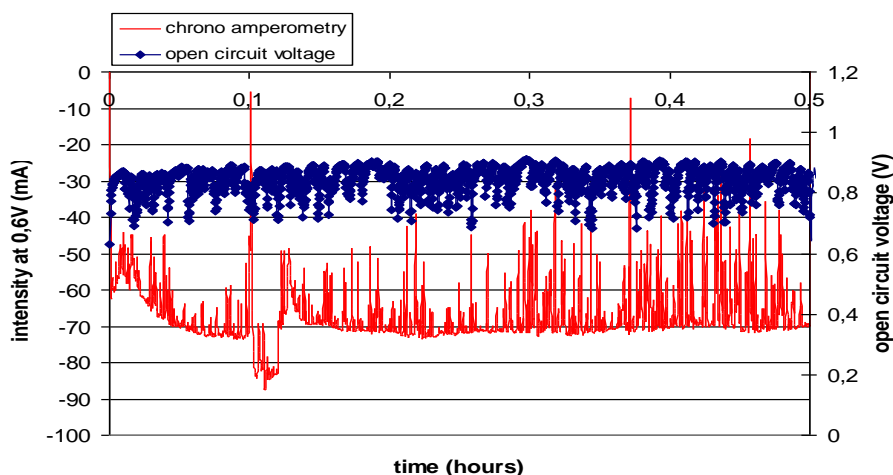
Figure 15: Sample AllinOne 5, in blue, open circuit voltage and in red chrono amperometric curve for a cell potential set at 0.6V.

Surface Innovations Limited

One main objective was to screen a range of existing SIL precursors previously used for plasma deposition of metal containing organic layers. Out of these, plasma-enhanced deposition of copper(II) hexafluoroacetylacetonate and platinum(II) hexafluoroacetylacetonate were chosen as suitable precursors for plasma enhanced chemical vapour deposition (Figure 16).
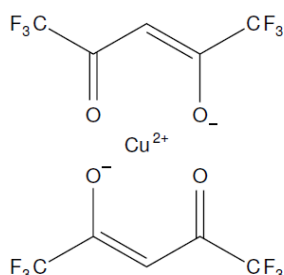
Figure 16: Structure of copper(II) hexafluoroacetylacetonate (the platinum(II) analogue is identical except for the replacement of the Cu^{2+} with Pt^{2+} metal ion).

Electron microscopy showed that for both copper(II) and platinum(II) hexafluoroacetylacetonate films metal nanoparticles (size of less than 10 nm) embedded within the film were produced.
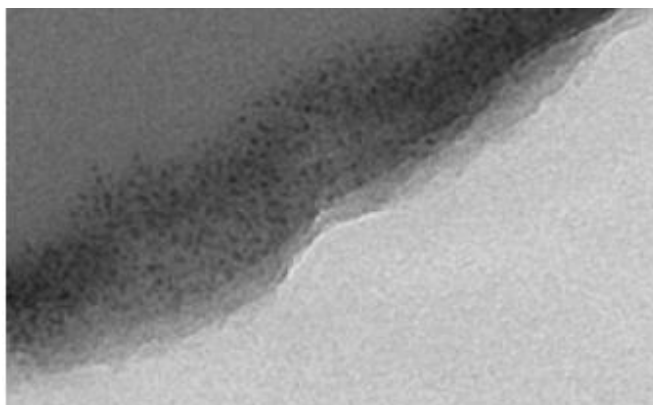
Figure 17: TEM showing metal nanoparticles.

These films were not successfully tested in fuel cells.

2.4.1 Potential impact

Potential 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[15,16]. 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 and the specificity of the allinone architecture can clearly help in this way. Of course, costs must also be competitive and costs of $10/W are targeted but we can also point out the fact that the business model can affect this threshold value. Indeed, due to the fact that for the small systems, hydrogen will appear as a cartridge which could be disposable, the total price of the system fuel cell/N cartridge will be mainly determined by the price of the cartridge. Then costs superior to $10/W could be attractive.

In the light of the results we have had, we think that the initial commercial targets of the project should be refocused on small scale, portable application rather than the more demanding automotive or stationary applications, with a particular emphasis on planar micro-power fuel cells for portable devices. Indeed, the materials itself as well as the solution proposed for their integration might bring opportunities to miniaturize the systems but the materials developed until now cannot sustain the working conditions required for automotive and stationary applications.

Process scalability
The approach selected to assess process scalability was to use a return on investment model, to rate the economical interest of SmallinOne technology findings in front of current and targeted fuel cell performances.
The inputs needed to this model are typically costs and capacity information for the tools and materials, price and volume information for the market side.
It was decided to focus on the micro-fuel cells market and realistic cost and throughput expectations for SmallinOne deposition technologies were then collected from partners.
Current cost and price schemes were taken out of www.quintech.de.
A specific model was build to calculate typical return of investment input figures out of the available data.

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[15] Connolly, D. J.; Gresham, W. F. U. S. Patent No. 3,282,875, 1966.
[16] Mauritz, K. A.; Moore, R. B. *Chem. Rev.* **2004**, *104*, 4535.

The output of the return on investment calculations is summarized below:

- The ASPD & PECVD deposition techniques are potentially profitable for next generation portable fuel cells membranes.
- The use of ASPD tools and ATO based Nanoparticles catalysts are potentially very profitable for next generation portable fuel cells electrodes.
- The use of the same ASPD equipment for both the membrane and electrodes deposition only adds to the economical interest of the SmallinOne findings.

On the whole, various materials were developed with different maturity level. Even if the from a process point of view, the ASPD and the PECVD technique were found profitable for the next generation fuel cell, their behaviour still needs optimization for being useful in fuel cell systems. The catalysts systems are at an advanced maturity level and could probably be used at an industrial level within few years.

2.4.2 Dissemination and exploitation of results

The exploitation and dissemination in SMALLINONE project followed each 6 month via sessions at the project meetings and the actions were recorded carefully. At M30, an EC Exploitation Strategy Seminar was organized that helped in the brainstorming on final project results.

Various publications and patents have been submitted or identified.

The publications submitted by CEA, UNIBA, SIL, IRD and BIU are:

- J.Thery, S.Martin, V.Faucheux, L.Le Van Jodin, D.Truffier-Boutry, A.Martinent, J.-Y. Laurent, Fluorinated carboxylic membranes deposited by plasma enhanced chemical vapour deposition for fuel cells applications, J. Power Sources, 195, 17, 5573-5580.
- E.Dilonardo, A.Milella, P. Cosma, R.d'Agostino, F.Palumbo, Plasma deposited electrocatalytic films with controlled content of Pt nanoclusters, Plasma Processes and Polymers, 8, 5, 452-458.
- T.J.Wood, W.C.E.Schofield, J.P.S. Badyal, Single step solventless deposition of highly protonconducting anhydride layers, J. Mater. Chem., 22 (2012) 7831-7836.
- A.M.Coclite, F.Palumbo, P.Lund, R.DiMundo, R.d'Agostino, Novel hybrid fluoro-carboxylated copolymers deposited by initiated Chemical Vapor Depostion as protonic membranes, J. Mater. Chem., submitted.
- A.Peled, M.Naddaka, J-P.Lellouche, Controllable photodeposition of metal nanoparticles on a photoreactive silica support, J. Mater. Chem., 22 (2012) 7580-7583.

In addition, CEA presented its results at the FDFC 2011 (Fundamentals and developments of fuel cells, January 2011, Grenoble-France), and UNIBA at the XX AIV (May 2011, Padova-Italy) and CIP 2011 (June 2011, Nantes-France). Several conferences were attended as invited speaker by SIL.

The consortium co-organised together with CEA-Liten and the FCH JU a workshop on "materials issues for fuel cells and hydrogen technologies" on the 26-28th of March 2012 in Grenoble, France that gathered actors in European projects on fuel cells. The workshop was connected to the final SMAllinOne meeting. CEA gave a presentation of our project and it was an occasion for the SMAllinOne consortium to exchange about the state of the art on the materials bottlenecks for fuel cells and hydrogen storage.
For more information: http://www.fch-ju.eu/event/workshop-materials-issues-fuel-cells-and-hydrogen-technologies

2.5 Consortium and contact information

2.5.1 Coordinator

J. THERY, jessica.thery@cea.fr, www.smallinone.eu

Commissariat à l'Energie Atomique et aux Energies Alternatives – France

2.5.2 Partners

- Universita degli Studi di Bari – Italy/ A. MILELLA, milella@chimica.uniba.it
- Surface Innovations Ltd – United Kingdom/ K. ARMOUR, Ken.Armour@p2i.com
- Bar-Ilan University – Israel/ J-P. LELLOUCHE, lellouj@biu.ac.il
- Federal Mogul Systems Protection – France/ B. LAURENT, benoit.laurent@federalmogul.com
- IRD Fuel Cells A/S – Denmark/ M. J. LARSEN, mjl@ird.dk
- ALMA Consulting Group SAS – France/ J. KERANEN, jkeranen@almacg.com

3. Use and dissemination of foreground

3.1 Section A: Dissemination (Public)

3.1.1 List of scientific (peer reviewed) publications (A1) - Public

Template A1: List of scientific (peer reviewed) publications											
No	WP	Title	Main author	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Date of publication	Relevant pages	Permanent identifiers** (if available)	Is/Will open access*** provided to this publication?
1	WP2	Fluorinated carboxylic membranes deposited by plasma enhanced chemical vapour deposition for fuel cells applications	Jessica Thery/ CEA	Journal of Power Sources	Volume 195, Issue 17	Elsevier	-	2010	5573-5580	-	No
2	WP2	Plasma Deposited Electrocatalytic Films with Controlled Content of Pt Nanoclusters	Antonella Milella/ UNIBA	Plasma Processes and Polymers	Volume 8, Issue 5	Wiley-VCH	-	2011	452-458	-	No
3	WP2-3	Single step solventless deposition of highly protonconducting anhydride layers	J. P. S. Badyal/ SIL	Journal of Materials Chemistry	Volume 22, Issue 16	RSC	-	2012	7831-7836	-	No
4	WP2	Novel hybrid fluoro-carboxylated copolymers deposited by initiated Chemical Vapor Depostion as protonic membranes	Fabio Palumbo/ UNIBA	Journal of Materials Chemistry	Submitted	RSC	-	2012	-	-	No
5	WP1	Controllable photodeposition of metal nanoparticles on a photoreactive silica support	Jean-Paul Lellouche/ BIU	Journal of Materials Chemistry	Volume 22	RSC	-	2012	7580-7583	-	No
6	WP3,5	Joint BIU/ SIL publication: 'Highly Proton Conducting	J. P. S. Badyal/	Chemistry of Materials	Planned in 2012	ACS	-	TBD	TBD	-	No

		Layers'	SIL								
7	WP1,5	Joint BIU/ IRD publication	Jean-Paul Lellouche/ BIU	Journal of Materials Chemistry	Planned mid-2012	RSC	-	TBD	TBD	-	No

* A permanent identifier should be a persistent link to the published version full text if open access or abstract if article is pay per view) or to the final manuscript accepted for publication (link to article in repository).

** Open Access is defined as free of charge access for anyone via Internet. Please answer "yes" if the open access to the publication is already established and also if the embargo period for open access is not yet over but you intend to establish open access afterwards.

3.1.2 List of dissemination actions (A2) - Public

Template A2: List of dissemination activities											
No	WP and (if applicable) result number	Type of activities*	Main leader	Title/ Subject/ Reference	Actual/ planned date or status	Place	Type of audience**	Size of audience	Countries addressed	Draft received (Yes/No)	Final version received (Yes/No-anticipated date DDMMYY)
1	Global project	Website, brochure	ALMA	http://www.smallinone.eu/	Released May-June 2010	-	All public	-	All	Yes	Yes
2	Global project	Public summary	CEA	Public executive summary	Released 20/05/10, 22/11/10, 17/05/11, 18/11/11 and 23/05/12	-	All public	-	All	Yes	Yes
3	WP2	Publication	CEA	J.Thery, S.Martin, V.Faucheux, L.Le Van Jodin, D.Truffier-Boutry, A.Martinent, J.-Y. Laurent, Fluorinated carboxylic membranes deposited by plasma enhanced chemical vapour deposition for fuel cells applications, J. Power Sources, 195, 17, 5573-5580.	Published	-	Scientific	-	All	Yes	Yes
4	WP2	Publication	UNIBA	E.Dilonardo, A.Milella, P.	Published	-	Scientific	-	All	Yes	Yes

				Cosma, R.d'Agostino, F.Palumbo, Plasma deposited electrocatalytic films with controlled content of Pt nanoclusters, Plasma Processes and Polymers, 8, 5, 452-458.							
5	WP2	Communication	CEA	FDFC 2011 – Fundamentals and developments of fuel cells, PECVD synthesis of thin proton exchange membrane for micro fuel cells, D. Truffier-Boutry, J. Thery, A. Martinent	19-21/01/2011	Grenoble (F)	Scientific	>100	All	Yes	Yes
6	WP2	Oral presentation	UNIBA	XX AIV- Plasma deposition of Pt-based nanocomposite films as electrocatalysts in micro fuel cells	17-19/05/2011	Padova (Italy)	Scientific	>100	Italian conference (Academic, Industrial)	Yes	Yes
7	WP2	Oral presentation (invited)	UNIBA	CIP 2011- Plasma processes for fuel cell applications	4-8/06/2011	Nantes (France)	Scientific	>500	All	Yes	Yes
8	Global project	Other : FCH JU corporate leaflet	CEA	Public executive summary	March 2012	-	All public	-	All	Yes	No
9	Global project	Oral presentation (invited)	CEA	FCH JU workshop on "Materials issues for Fuel Cells and Hydrogen Technologies: from innovation to industry". SMALLINONE project presentation.	26-28/03/2012	Grenoble (F)	Scientific	>100	European	Yes	Yes
10	WP2-3	Publication	SIL	T. J. Wood, W. C. E. Schofield, J. P. S. Badyal, Single step solventless deposition of highly protonconducting anhydride layers, Journal of Materials Chemistry 22 (2012) 7831-7836.	12/03/12	-	Scientific	-	All	Yes	Yes
11	WP2-3	Publication	UNIBA /IRD	Anna Maria Coclite, Fabio Palumbo, Peter Lund, Rosa Di Mundo, Riccardo d'Agostino, Novel hybrid fluoro-carboxylated copolymers deposited by initiated Chemical Vapor Depostion as protonic membranes, Journal of	Submitted	-	Scientific	-	All	Yes	To receive

				Materials Chemistry							
12	WP1	Publication	BIU	Anna Peled , Maria Naddaka and Jean-Paul Lellouche, Controllable photodeposition of metal nanoparticles on a photoreactive silica support, J. Mater. Chem., 2012, 22, 7580-7583. DOI: 10.1039/C2JM16785A.	15/02/2012	-	Scientific	-	All	Yes	Yes
13	WP3,5	Publication	SIL	J. P. S. Badyal et al., 'Highly Proton Conducting Layers', Chemistry of Materials	Planned in 2012	-	Scientific	-	All	No	No
14	WP1,5	Publication	BIU/ IRD	In Journal of Materials Chemistry	Planned mid-2012	-	Scientific	-	All	No	No
15	Global project	Oral presentation (invited)	SIL	International Conference on Plasma Processes and Applications	5-7/7/2010	Kirchberg, Luxembourg	Scientific	>100	European	No	No
16	Global project	Oral presentation (invited)	SIL	240th American Chemical Society (ACS) National Meeting	22-26/8/2010	Boston, USA,	Scientific	>100	International	No	No
17	Global project	Oral presentation (Plenary)	SIL	5th International Conference on Advanced Materials and Nanotechnology (AMN-5)	7-11/2/ 2011	Wellington, New Zealand	Scientific	>100	International	No	No
18	Global project	Oral presentation (invited)	SIL	8th International Conference on Polymer Surface Modification	20-22/6/ 2011	Danbury, Connecticut, USA	Scientific	>100	International	No	No
19	Global project	Oral presentation (Plenary)	SIL	5th International Conference on Developments in Materials and Emerging Technologies	27-29/6/ 2011	Alvor, Portugal	Scientific	>100	International	No	No
20	Global project	Oral presentation (Plenary)	SIL	6th International Conference on Surfaces, Coatings, and Nano-Structured Materials	17-20/10/2011	Krakow, Poland	Scientific	>100	International	No	No
21	Global project	Oral presentation (Plenary)	SIL	3rd International Conference on Atomic, Molecular, Optical & Nano Physics	14-16/12/2011	New Delhi, India	Scientific	>100	International	No	No
22	Global project	Oral presentation (Plenary)	SIL	2nd International Conference of Nanomaterials and Nanotechnology	18-21/12/2011	New Delhi, India	Scientific	>100	International	No	No
23	Global project	Oral presentation (Plenary)	SIL	International Conference on Supramolecules and Nanomaterials (ICSNA 2012)	6-8/2/2012	Ahmedabad, India	Scientific	>100	International	No	No

| 24 | Global project | Oral presentation (Keynote) | SIL | 33rd Australasian Polymer Conference | 12-15/2/2012 | Hobart, Australia | Scientific | >100 | International | No | No |
| 25 | Global project | Oral presentation (Invited) | SIL | Smart Coatings 2012 Conference | 22-24/2/2012 | Florida, USA | Scientific | >100 | International | No | No |

* A drop down list allows choosing the dissemination activity: publications, conferences, workshops, web, press releases, flyers, articles published in the popular press, videos, media briefings, presentations, exhibitions, thesis, interviews, films, TV clips, posters, other.

** A drop down list allows choosing the type of public: Scientific Community (higher education, Research), Industry, Civil Society, Policy makers, Medias ('multiple choices' is possible.

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i   C.G. Van de Walle. Phys. Rev. Lett., 85 (2000), p. 1012.

ii   Journal of Crystal Growth Volume 68, Issue 1, 1 September 1984, Pages 157-162