# PROJECT FINAL REPORT


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**Project acronym:** *QUASIDRY*

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# FINAL PUBLISHABLE SUMMARY REPORT

# 1. EXECUTIVE SUMMARY

The primary objective of QuasiDry was the development of selected highly innovative approaches to polymer and membrane design to open up the possibility for fuel cells to operate at temperatures of around 120 °C, a desirable, yet currently impractical operating point with currently available materials. The QuasiDry partnership of six technical partners provided a balance between industry and academia that pooled its complementary skills and competences. The partnership was structured to cover the range of expertise required to carry the project through and achieve its objectives, for full exploitation and use of the results, and for professional project management and dissemination of project results.

The work plan comprised work packages dedicated to the main developmental RTD activities on polymers and membranes (WP2), catalyst development (WP3), and validation of the project materials in membrane electrode assemblies (MEAs, WP4). The focus of WP1 was the development of protocols for functional materials characterisation and evaluation of MEAs under project-specific conditions. WP5 and WP6 were dedicated to dissemination and use of results, and to project management, respectively.

WP2 targeted the development of new concepts for fuel cell electrolyte membranes. Its ambition with regard to conductivity values was considerable. Proton conducting materials, polymers and membranes (i) functionalised only with phosphonic acid groups (ii) incorporating polymer-bound sulfonic and phosphonic acid functionalities (iii) cross-linked high acid doping level membranes and (iv) mixed functionality membranes incorporating phosphonic and phosphoric acids, have been developed and their properties characterised, and transferred to WP4. Key outcome includes the novel properties offered by mixed functionality (sulfonic-phosphonic, and phosphoric-phosphonic), distinct from those observed for the separate components alone. Target conductivities have been achieved with two of the above membrane classes. Overall, the boundaries in the field of novel approaches to proton conducting membranes have been expanded and some very promising results achieved with significant progress over the state of the art.

In WP3, new ternary alloy catalysts for cathodes (PtXY) demonstrated improved kinetic mass activity (while retaining high stability) for operation at high temperatures from 120-180 °C and was successfully scaled-up to 200 g for further MEA development studies. A composite Pd-Pt catalyst with ultra-low Pt content produced a synergistic effect and showed a much larger activation effect for the Pd-based catalyst than a conventional Pt-alloy. This makes such composite Pd system quite appealing for application under automotive conditions characterised by intermediate temperature and low relative humidity operation. The use of heteropolyoxometalate promoters further increased the catalytic activity of a Pd catalyst under automotive conditions. Alternative non-carbon catalyst supports with specific architectures have been developed that show high electrochemical corrosion resistance.

A wide range of innovative materials from WP2 and WP3 were evaluated in WP4 using both in situ and ex situ techniques. Three new catalysts, four novel classes of membranes and the compatibiliser concept were all investigated under a wide range of conditions and constructions. Several of these new materials show significant improvements and potential compared to the initial benchmark materials. At the low RH, 120 °C, ambient pressure target conditions of the project, peak power densities >0.4 W/cm2 were achieved at useable cell voltages with the cross-linked acid doped membranes, more than doubling the initial benchmark material's performance. Target power density could also be achieved by raising both humidification and pressure using mixed functionality sulfonic –phosphonic functionalised membrane materials. Durability was validated with one of the new catalysts and one of the new membranes demonstrating durability on par with the benchmark material. Overall some very promising practical results have been achieved from the new membrane classes, which demonstrate that significant progress has been made over the three years of the project and reveals their obvious potential.

Project results have been disseminated in conferences (25 presentations) and journal publications (9 articles).

## 2. SUMMARY DESCRIPTION OF PROJECT CONTEXT AND OBJECTIVES

Fuel cells using oxides or polymers hold great promise in the future diversification of energy supply for applications ranging from the portable electronics market, through automotive use and stationary power generation to other niche areas related to the leisure market or military purposes. Real impact of the potential in terms of reduced emissions and alternative fuels allowed by fuel cell technology awaits introduction of a mass market application, and it is considered that the greatest bearing in this arena will be brought by fuel-cell electric vehicles.

In recent years, a vast number of polymers have been proposed and evaluated as possible materials for proton exchange membrane fuel cells (PEMFC), in particular for automotive application. Sulfonic acid functionalised perfluorinated polymers are a class of benchmark materials having excellent proton conductivity, mechanical and chemical stability. Nafion®, the 3M™ and Aquivion® membranes are representative perfluorosulfonic acid (PFSA) ionomers. Despite the wide use of Nafion® and other state of the art PFSAs, their maximum performance in a fuel cell is at moderate operation temperatures (≤80 °C). This falls significantly short of the automotive industry long-term targets, which is for a cell temperature of 120 – 130 °C, with no humidification of reactant hydrogen and air, since humidification increases systems complexity and costs. It is agreed by the automotive industry that the too low temperature of operation and the need for humidification of current polymer exchange membrane fuel cell membranes is an obstacle to widespread implementation of fuel cell vehicles (FCV). High temperature of operation is required to enable the heat generated by the fuel cell stack to be exchanged efficiently.

In the above PFSA membranes, the proton is transferred by water molecules. Over the last decade, new concepts have evolved engaging alternative proton carriers that mark a move towards reducing the need for high levels of hydration of the fuel cell membrane. The ideal protogenic group in a "quasi-anhydrous" membrane environment should be amphoteric, exhibit proton donor and acceptor properties and show a high degree of self-dissociation. It also should have a high dielectric constant to enhance the charge separation and be stable under fuel cell operation conditions. Candidate "solvents" alternative to water include nitrogen heterocycles and phosphonic acids. While initial results effectively showed that such solvents could be immobilised on to polymer backbones, the low concentration of functional groups in this first work led to rather low proton conductivity values.

The objective of QuasiDry was to develop the fuel cell electrolyte membranes of the next generation of fuel cells, satisfying the long-term automotive targets. The increase of proton conductivity with temperature, including at low RH, will allow continuous increase in fuel cell performance with temperature, rather than the drop in performance for all sulfonic acid functionalised membranes above ca. 80-90 °C. QuasiDry membranes were evaluated by electrode and MEA development, to the scale of small-scale (50 $cm^2$) single cell demonstrators. The end result has been a step-change in the properties of the materials, as is required to underpin the future of European fuel cell research.

Several approaches to automotive fuel cell membranes were screened within the framework of Framework 6 Integrated Project Autobrane (completed 31st October 2009), including advanced perfluorosulfonic acid (PFSA) type membranes, and their composites containing an inorganic component, novel hydrocarbon type polymers with sulfonic acid functions, consideration of some novel polymers with protogenic functions other than sulfonic acid, as well as novel processing routes. Using a state-of-the-art PFSA membrane, Autobrane achieved its goal of fuel cell stack operation to 120 °C, although performance dropped severely as the temperature was increased, anode and cathode gases were hydrated, and some over-pressure was applied.

It was the intention of QuasiDry to build on some of the achievements of Autobrane by concentrating efforts on some of the most promising long-term options developed in its framework. The materials selected were those functionalised with phosphonic acid groups; since we have shown that phosphonic acid containing

polymeric materials have the possibility of operating at higher temperature at low humidity conditions. Their properties are in clear contrast to those of any PFSA, or any sulfonic acid containing polymer.
The project covered the following topics:

- Development of innovative polyphosphonic acid functionalised polymers and materials and membranes from them, phosphoric acid doped membranes and mixed functionality membranes, corresponding electrolyte dispersions, and characterisation of polymer and materials components, and membrane properties:

  *Despite considerable progress in formulating and implementing new approaches leading to novel proton conducting membrane systems that have high proton conductivity at high temperature through the full range of relative humidity remains a most difficult challenge. Phosphoric and phosphonic acid derivatives in particular were considered suitable candidates as ionomers because of their efficient proton transport at high temperature that involves proton hopping via hydrogen bonds. Recent results on phosphonated polymeric membranes and their associations with sulfonic acid functionalised polymers have indicated that very high local concentrations of phosphonic acid, forming large hydrogen bonded aggregates, are needed in order to reach high proton conductivities. Innovative synthetic immobilisation strategies have to be developed to minimise local dilution effects and aggregation constraints of the acid units.*

- Design and development of supported electrocatalysts with high activity in the appropriate electrolyte environment:

  *Electrocatalyst development was required to accompany the above step-changes in high temperature, low RH properties of proton conducting membranes. Significant progress beyond the state of the art was expected by concentrating efforts in specific directions most relevant to QuasiDry objectives, including designed Pt-alloy catalyst compositions to overcome strong activation control at low current density, using stabilised carbon supports as well as non-carbon (oxide and carbide) supports to avoid high temperature corrosion, and reducing costs by developing Pt-free or ultra-low Pt loaded catalysts in conjunction with anchored heteropolyacid promoters to enhance reaction kinetics (oxygen diffusion coefficient, oxygen solubility, proton transfer at the electrode-electrolyte interface).*

- Development of electrodes and MEAs adapted for the novel polymer membranes and characterisation of the MEAs in single cells:

  *An MEA having an inappropriate electrode structure and membrane-electrode interface as required to translate the potential of the novel membranes to proven MEA performance in a fuel cell, and thus there was a major effort on the development of appropriate electrode structures. Electrode development itself, has studied the impact of key structural and compositional variables, including electrode thickness, pore volume, pore size distribution, hydrophobicity, catalyst loading requirement, and level of ionomer incorporation. This electrode development study went hand-in-hand with developing the processes by which the catalyst layer is formulated and applied. A fundamental study of the interface involved studying the effectiveness of materials capable of electron transfer to the electrode and proton transport to the membrane (mixed ionic-electronic conductors.*

The final target of QuasiDry was to achieve the development of membrane materials having conductivity at 120 °C and <25% RH of >50 mS/cm, in the range 50-100 mS/cm, and which have low dependence of conductivity on RH and also temperature (<factor 2-3 over the RH range 20 – 95%), in addition to having satisfactory properties with respect to hydrolytic and mechanical degradation. This will enable increase in fuel

cell performance (power density) at 120 °C and even beyond, and with anode/cathode RH of <25%, compared with that given by reference state of the art PFSA membranes at the beginning of the project.

The project provided the opportunity to vastly add value to some exciting new results consistently showing the promise of phosphonic acid functionalised polymeric membrane systems and maintain the lead of European researchers in this field. To carry the project through to its conclusion, a consortium of world-leading polymer and materials chemists was assembled, experienced in the field of materials developments for fuel cells. Participation by Johnson Matthey Fuel Cells Ltd and FuMA-Tech GmbH showed the credibility and the potential of the proposed research, and guaranteed the future high impact of the research results.

# 3. Main Scientific and Technical Results

## 3.1 WP1: Specification & protocols – WPL: FUMA

### *Objectives*

To establish a set of characterisation and test protocols for ex situ and in situ characterisation of baseline and novel membranes, catalysts and supports, and MEAs, including both non-accelerated and accelerated stress testing conditions;
To establish benchmarks against which progress could be assessed by characterisation using QuasiDry protocols of baseline membranes and MEAs.
To derive composition – property – performance relationships from ex situ properties and in situ evaluation data.

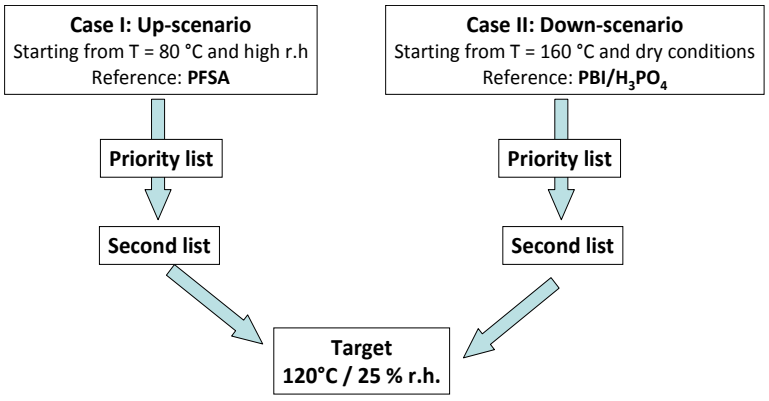
***To achieve deliverables D1.1 in RP1, and D1.2 in RP2.***

### *Summary of Output from WP1*

**The key output of WP1 (Task 1.1 - 1.3) was the definition of characterisation and test protocols for assessment of high temperature - low RH performance and stability of the novel QuasiDry polyphosphonic acid based MEAs and the correlation of the observed electrochemical characteristics with physicochemical properties of membrane, catalysts and their interfaces (deliverable report D1.1). These protocols allowed for a comparison of characterisation data between the project partners and to the benchmark membranes and MEAs, which have been identified at the beginning of the project.**

### *Detailed Summary of Achievements in WP1*

In WP1, characterisation and test protocols for assessment of high temperature - low RH performance and stability of the novel QuasiDry polyphosphonic acid based MEAs have been defined and the observed electrochemical characteristics have been correlated to physicochemical properties of membrane, catalysts and their interfaces. The characterisation and test protocols were established at the beginning of the project (deliverable report D1.1). These protocols enabled a comparison of characterisation data between the project partners and to the benchmark membranes and MEAs, which have been defined also at the beginning of the project. The general structure for the protocols for membrane, catalyst, support characterisation, and MEA testing is shown below:



All partners have carried out a complete set of measurements according to the protocols defined in D1.1 on benchmark membranes and MEAs. Measurements on low and high temperature benchmark membranes and MEAs have been conducted and cross-comparison between project partners has shown similar results. It is particularly worth mentioning that the results of the MEA measurements based on benchmark MEAs for the high-temperature and low-temperature approach obtained at JMFC, CNR-ITAE and FUMATECH were in good agreement in spite of the differences in MEA preparation and testing facilities.

In Task 1.4, a characterisation matrix for cross-comparison of membrane and MEA properties has been achieved including comparison of ex situ conductivity data and in situ single cell performance data determined under similar or equivalent conditions and derived from different project partners. Single cell performance values has been achieved for the various membranes in MEAs are reported in terms of power densities under specific operating conditions in terms of cell voltage, temperature, pressure, relative humidity, type of oxidant and in conjunction with the specific MEA characteristics i.e. Pt loading in the electrodes, type of anode and cathode catalysts, backing layer. Cross-comparison of ex situ resistance data and in situ single cell resistance data under realistic operation conditions T = 120 °C has shown good agreement, and is summarised in deliverable report D1.2 (Characterisation matrix: Characterisation table with cross-comparison of membrane and MEA properties).

It could be shown that the observed high conductivities for cross-linked PBI-PA membranes as well as for the mixed sulfonic-phosphonic acid functionality membranes do reflect the improved cell performance data derived at high temperatures and low relative humidity.

Regarding mixed functionality sulfonic-phosphonic acid membranes, the best performance at high temperature and low relative humidity is obtained with the membrane AC-925. This performance is higher than achieved with the other membranes reaching good power density values in MEAs under conditions where conventional PFSA membranes such as Nafion show a strong decrease of conductivity e.g. T>100 °C, RH≤50%. The key advantages of these membranes over other polymer electrolyte systems capable of operation at intermediate and high temperature are the possibility to provide good performance in the presence of a low catalyst loading (Pt≤ 0.3 mg $cm^{-2}$) and a fast cold start-up which is assured by the sulfonic acid functionalities whereas the phosphonic acid provide suitable conductivity for operation up to 110-120 °C. These characteristics appear suitable for automotive operation.

## 3.2 WP2: Innovative Phosphonated Polymers, Materials and Membranes - WPL: CNRS

### *Objectives*

To design and prepare novel membrane systems incorporating phosphonic functionalities for operation in dry and quasi-dry operation conditions by developing new concepts for fuel cell electrolyte membranes considering the need for high degrees of functionalisation, local aggregation of protogenic groups and microphase separation of membrane morphology:

- Grafting poly(phosphonic acid) to polymer backbones or side chains, with architectural control of the polymer backbone composition through development of multiblock phosphonic acid functionalized systems;
- Associating two types of protonic functionality in interpenetrating network type membranes to exploit synergies and develop specific microphase separated membrane architectures;
- Developing phosphonic acid functionalised organic crystals and methods for dispersion of phosphonic acid molecules in a polyphosphonic or polysulfonic acid functionalised membrane.

- Scale-up of polymers and membranes.

***To achieve deliverables D2.1-2.7 and milestone MS1 in RP1, and deliverables D2.8-2.12 and milestones MS2 and MS3 in RP2.***

### *Summary of Output from WP2*

**The focus of activities was in four main directions: membranes for fuel cell operation (i) functionalised only with phosphonic acid groups (ii) incorporating sulfonic and phosphonic acid functionalities (both polymer-bound) (iii) cross-linked high acid doping level membranes and (iv) mixed functionality membranes incorporating phosphonic and phosphoric acid. Membrane types (i) and (ii) correspond to the approach of increasing the temperature of operation of "low" temperature membranes, while approaches (iii) and (iv) are aimed at lowering the temperature of operation of high temperature membranes. The membranes have all been investigated for their conductivity at the target conditions of 120 °C and low RH, while many other types of characterisation have been carried out specific to each membrane type. In all cases, greater understanding has been reached on the relation between polymer/membrane composition (which includes consideration of the types of protogenic function, and the extent of functionalisation) and conductivity under these target conditions.**

**It is a remarkable result that several of the WP2 membranes exceeded the conductivity of the low temperature (PFSA) and high temperature (phosphoric acid doped AM-PBI) benchmarks. At low relative humidity, the mixed functionality sulfonic-phosphonic acid membranes systematically displayed higher conductivity than the PFSA benchmark, even higher than conditioned plain PFSA membrane. These results support the original concept of the proposal. Although the absolute values of the target conductivity were not achieved with this type of membrane system, the observation that the dependence of conductivity on relative humidity for mixed functionality sulfonic-phosphonic acid membranes is lower than for either type of component (sulfonic or phosphonic acid functionalised polymers) alone, is of great significance for future exploitation, in the use of membranes in the low RH, high temperature regime. These results could not have been achieved without the large numbers of materials exchanges that exemplify the close collaboration between partners.**

**The target conductivity values are exceeded with membranes based on cross-linked acid doped PBI, even in a dry conductivity cell. Furthermore it has been shown that phosphonic acid functionalised polyaromatic molecular species may be readily integrated as proton conducting component into a composite membrane system, as typified by the mixed functionality phosphonic-phosphoric acid membranes that also surpass target conductivity at low RH at 120 °C. It is notable result of the project that despite the novelty of the polymer chemistry developed; membrane scale-up has also been achieved, using the membrane production line at FUMA. Overall the boundaries in the field of novel approaches to proton conducting membranes have been expanded and some very promising results achieved with significant progress over the state of the art.**

### *Detailed Summary of Achievements in WP2*

WP 2 targeted the development of new concepts for fuel cell electrolyte membranes considering the need for high degrees of functionalisation to ensure high conductivity, local aggregation of protogenic groups to ensure percolation of charge carriers, and microphase separated membrane architectures to develop the proton conducting channels that are conducive to high conductivity. Its ambition with regard to conductivity values was considerable (milestone targets MS2 and MS3 at months 24 and 33 of 50 and 50-100 mS/cm respectively at 120 °C and low (<25% relative humidity, RH), as well as a reduced dependence of the conductivity on RH compared with what is observed with reference perfluorosulfonic acid membranes. Each

partner has contributed to significantly advancing the state of the art on non-conventional proton conducting materials and membranes, which have been developed and characterised within WP2, and transferred to WP4 for the confection and testing of functional membrane electrode assemblies. The originality of the approaches is a major feature of the results of the programme. The key outputs from WP2 in months 19-36 are:

At **CNRS**, significant advance has been made in the development of an original approach allowing cross-linking of acid-swollen PBI polymer in solution, and subsequent membrane casting and curing. These membranes display conductivity that exceeds the project target and their surface properties and high acid doping levels allow for simplification of the membrane electrode assembly fabrication steps. These results are described in D.12.

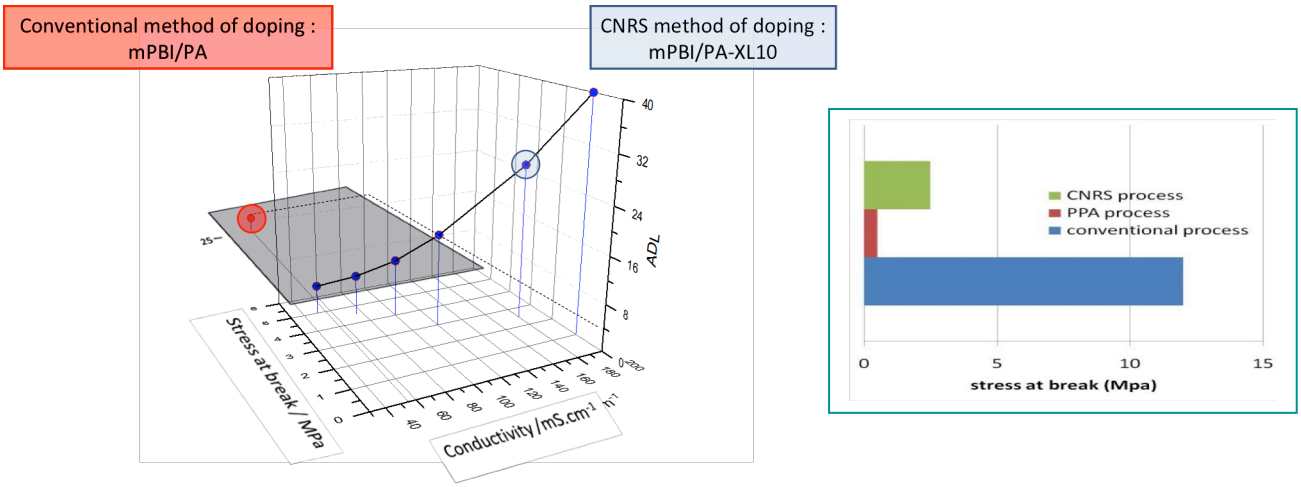



***Table 3.2-1: Relation between ADL, conductivity and mechanical properties of XL-PBI membranes (left); comparison of stress at break for BASF PPA process membranes, CNRS process membranes, and conventionally imbibed membranes (right).***

The development of mixed functionality membranes incorporating p-6PA-HPB into acid doped PBI (or sulfonated PBI) leads to membranes that surpass the conductivity target, and which have given surprisingly high and durable fuel cell performance.

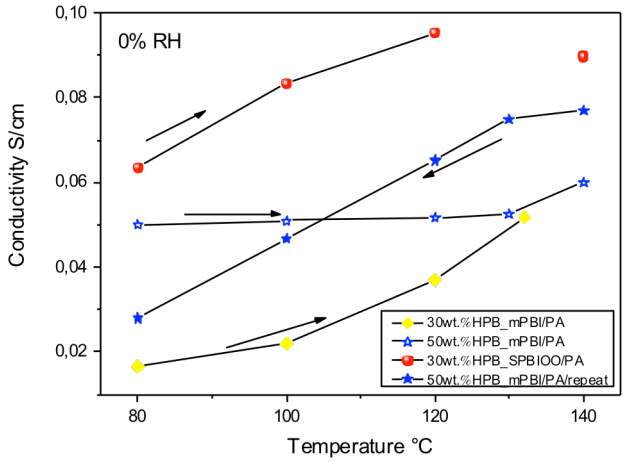
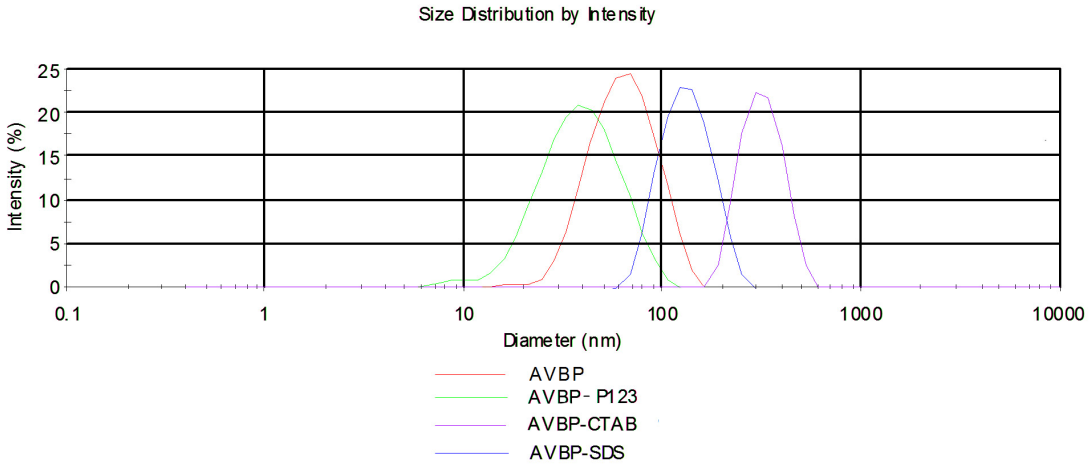



***Table 3.2-2: Conductivity (dry cell) of 30 and 50 wt% HPB / m-PBI and 30 wt% HPB / sPBI-OO composite membranes***

CNRS has also developed a deposition method for phosphonic acid functionalised molecules based on electrospinning (D2.11). In the early stages of the project, CNRS described a sulfonic-phosphonic mixed functionality all-hydrocarbon membrane displaying low dependence of its conductivity on RH at 120 °C (D2.4), and made available a phosphonic acid functionalised dispersion for use in WP3 and WP4 (described in deliverable report D2.1).

***Table 3.2-3: DLS measurement of p(vinylbenzylphosphonic acid) polymerised in the presence of surfactants***




In **ULund**, synthetic strategies have been developed and several series of novel block and graft copolymers prepared with different chain architectures containing phosphonated blocks of either PVPA or PTFSPA. By this synthetic strategy, densely phosphonated phases were immobilised and stabilised in nanostructured membranes to promote proton conductivity. Relationships between structure and membrane properties were established for the different systems. The combined results confirm the positive effect of the strategy on the membrane properties, provided that a favourable set of structural parameters of the copolymer are found. The anhydride formation, which hampers the conductivity of alkyl- and arylphosphonic acids at high T/low RH conditions, was greatly depressed by employing the more acidic PTFSPA, instead of e.g. PVPA, segments in the copolymers. Moreover, the inclusion of PTFSPA in PFSA membranes proved to quite significantly increase the proton conductivity also at low RH, in relation to neat PFSA membrane. ULund supplied samples of copolymers and PTFSPA to QuasiDry partners for pilot-scale membrane preparation and further characterisation.

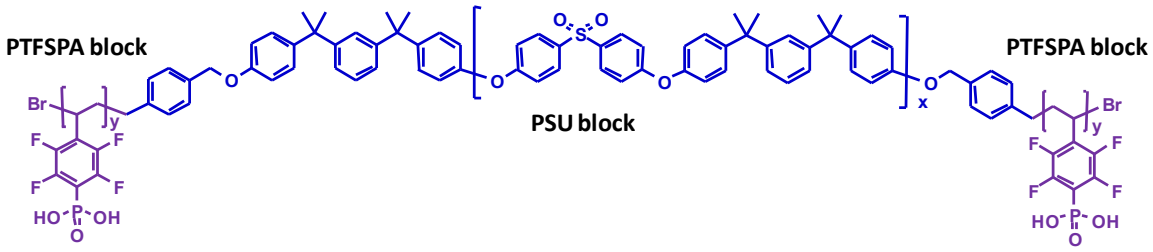



***Table 3.2-4: Structure of the PTFSPA-PSU-PTFSPA triblock copolymers synthesised via ATRP***.

***Table 3.2-5: IEC, water uptake and proton conductivity of phosphonic acid membranes under fully hydrated conditions***.

| Phosphonated triblock copolymers | Sample # | Theoretical IEC[b] (mmol $g^{-1}$) | Water uptake[c] (wt%) | $[H_2O]/[-PO_3H_2]$ (l)[c] | σ at 120 °C (S $cm^{-1}$) |
|---|---|---|---|---|---|
| $PTFSPA_{15}$-$PSU_{44}$- $PTFSPA_{15}$ | **3p** | 1.4 | 1 | 0.8 | 0.001 |
| $PTFSPA_{46}$-$PSU_{44}$- $PTFSPA_{46}$ | **4p** | 3.2 | 5 | 1.7 | 0.028 |
| $PTFSPA_{62}$-$PSU_{44}$- $PTFSPA_{62}$ | **5p** | 3.8 | 7 | 2.0 | 0.028 |
| $PTFSPA_{72}$-$PSU_{44}$- $PTFSPA_{72}$ | **6p** | 4.2 | 25 | 6.6 | 0.080 |
| $PTFSPA_{113}$-$PSU_{44}$-$PTFSPA_{113}$[a] | **7p** | 5.0 | - | - | - |

[a]Unable to form water-stable membranes. [b]Determined from NMR data. [c]Immersed at 25 °C.

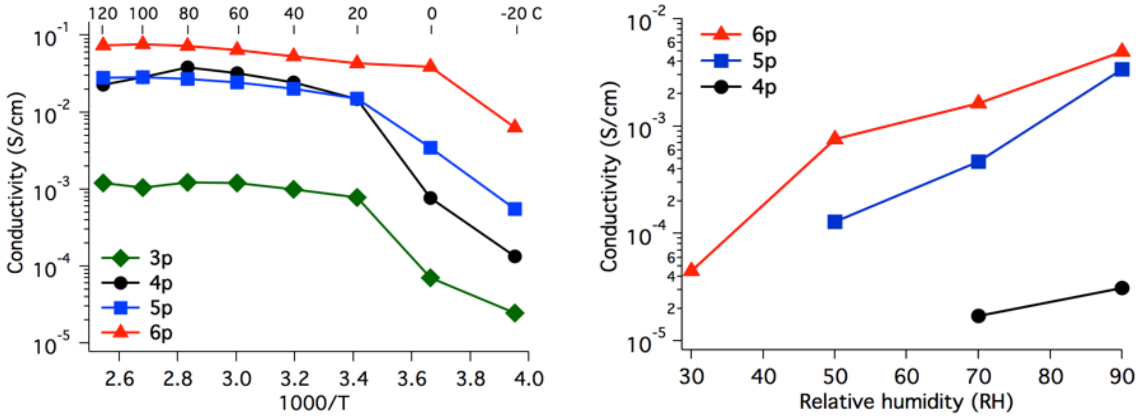



***Table 3.2-6: Proton conductivity of block copolymer membranes as a function of temperature under fully hydrated conditions (left) as measured by EIS using a two-probe method, and the proton conductivity of block copolymer membranes at 80 °C as a function of RH (right), as measured by EIS using a four-probe method.***

**MPIP** has proposed a completely novel approach to increase proton mobility that is based on self-assembly and pre-organisation of multifunctional molecular organics. Among all investigated topologies (see **D2.3**, **D2.7** and **D2.11**), the hexagon structure of *p*-6PA-HPB was identified as the most promising material providing a proton conductivity value of $6 \times 10^{-3}$ S/cm, which remains constant with temperature. It was furthermore demonstrated that metal-organic frameworks based on those phosphonated molecules can compete with commonly used acid-functionalized polymers as membrane material for fuel cell applications. They can be easily prepared and optimized due to the broad availability of the required building blocks. By that, proton conductivity in the range of Nafion can be achieved. Remarkably, acid-doped p-6PA-HPB-based aluminum phosphonates exhibit a very high proton conductivity of about $5 \cdot 10^{-2}$ S $cm^{-1}$ at 120°C and 50% RH.

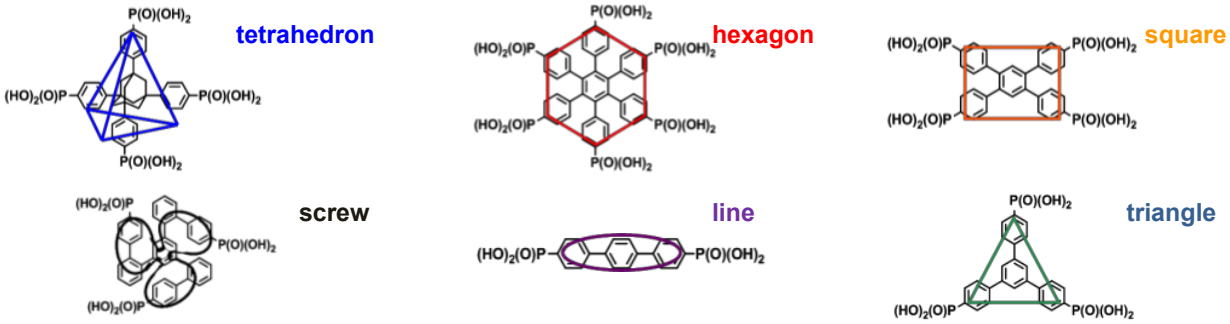



**Table 3.2-7**: Different topologies of synthesised phosphonated organic crystals**.**

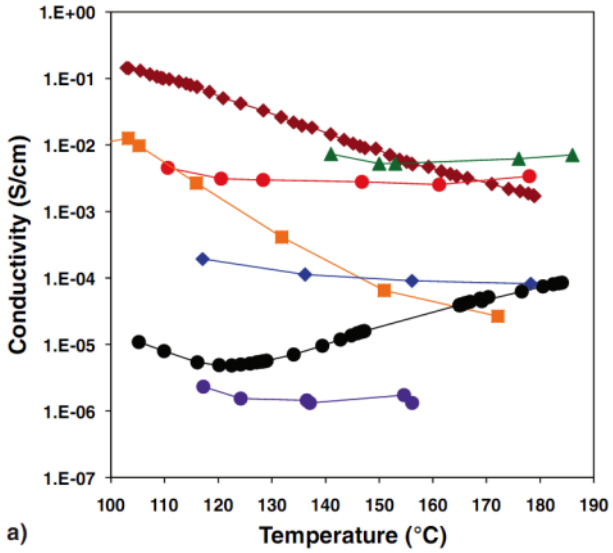



***Table 3.2-8: Plots of proton conductivity vs. temperature under 1 bar $H_2O$ atmosphere. Each compound is depicted with a colour: line (purple), triangle (green), screw (black), square (orange), tetrahedron (blue) and hexagon (red). The curve of Nafion® 117 (brown) is shown for comparison***

**FUMATECH** has developed novel mixed functionality membranes based on PFSA (polymer-bound sulfonic acid) and various phosphonic acid components R-$PO_3H_2$ including (i) molecular-bound phosphonic acids and (ii) polymer-bound phosphonic acids such as phosphonated pentafluorostyrene (PTFSPA) provided by ULund. Composite membranes based on sulfonated polysulfone polymer (fumion® S-360) and molecular-bound phosphonic acid R-$PO_3H_2$ and phosphoric acid $H_3PO_4$, respectively, have been prepared and characterised as well. These membranes have demonstrated high conductivities at intermediate temperature (120 °C) and low relative humidity. The evaluation on morphology and properties revealed some crucial parameters related to production conditions, membrane processing conditions, and up-scaling issues, which are relevant for obtaining high conductivities. FUMATECH has supported the work of other partners in task 2.1, 2.2, 2.4, by the preparation and supply of matrix polymers for sulfonation and preparation of interpenetrating networks, and woven material for membrane preparation. Several types of polymers have been supplied as polymer matrix such as perfluorinated sulfonic acid polymers (PFSA), PBI materials (AB-PBI, meta-PBI, PBI-OO...) and highly sulfonated polyarylene, e.g. polysulfone (S-360 and STO-305) and poly(ether ketone) (sPEEK).
These tasks have been summarised in deliverable D2.5 (1st generation composite membranes), D2.10 (optimised mixed functionality interpenetrating network membranes), and D2.12 (composition-structure property relationships in phosphonic acid functionalised fuel cell membrane).

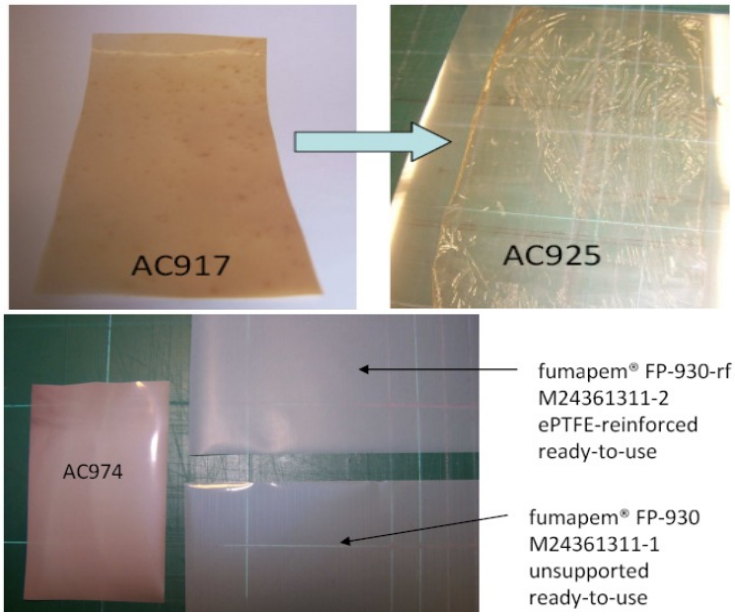



***Table 3.2-9: Appearance of selected blend membranes based on PFSA and PTFSPA***

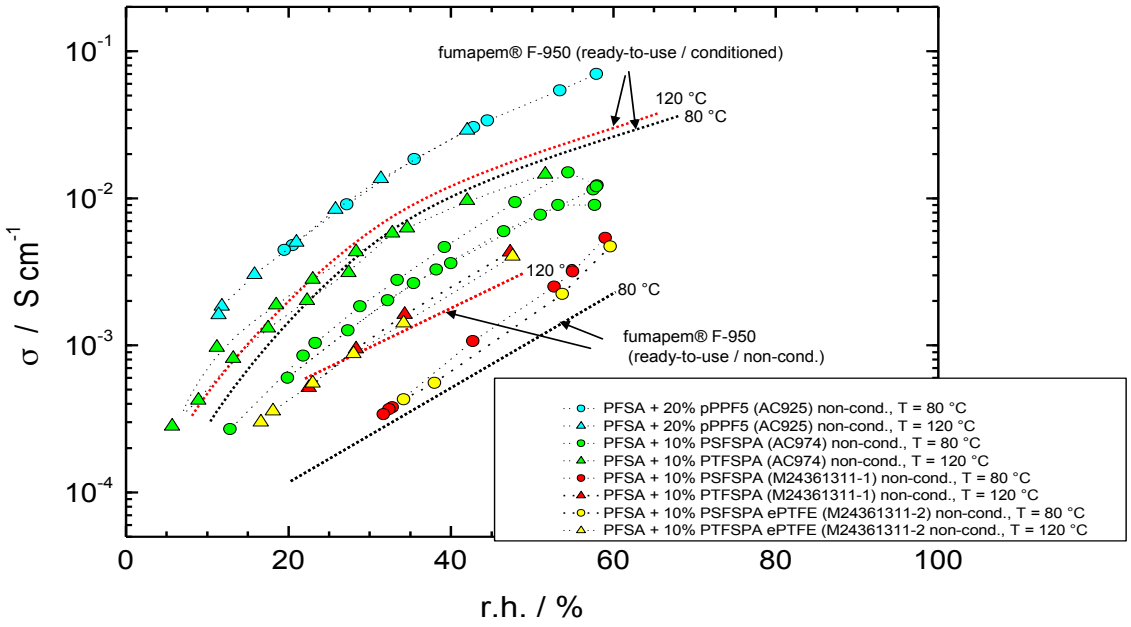
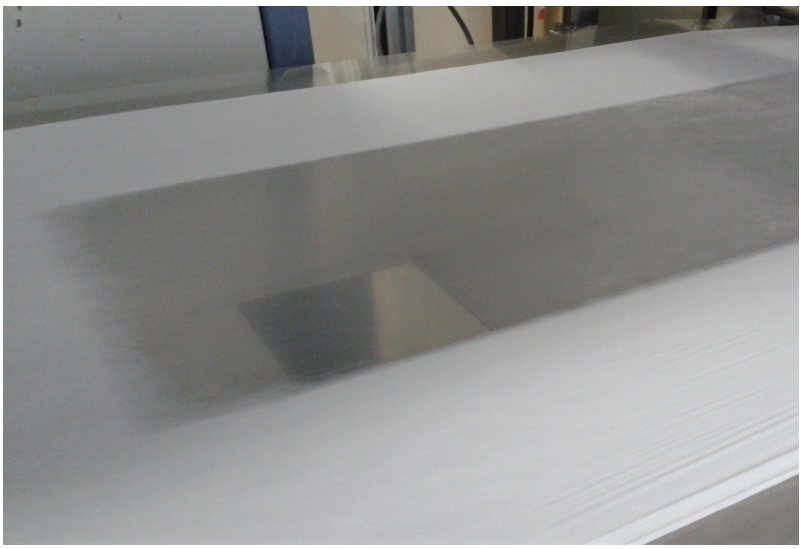



***Table 3.2-10*: *Conductivity of selected blend membranes based on PFSA and PTFSPA*.**



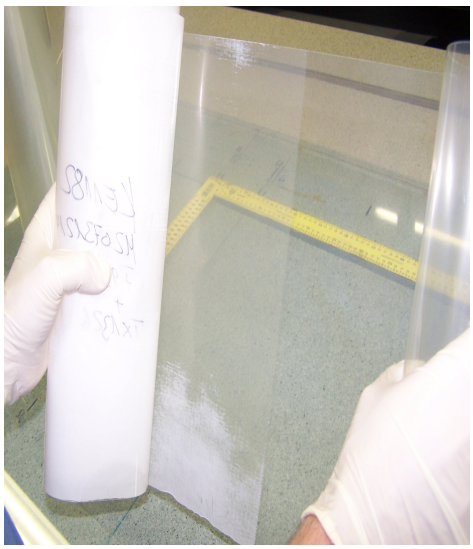


*Table 3.2-11: Roll-to-roll production of blend membranes of PFSA polymer (polymer-bound sulfonic acid) and pentafluorostyrene phosphonic acid (= PTFSPA) with ePTFE on continuous production line.*

## 3.3 WP3: DESIGNED ANODE AND CATHODE ELECTROCATALYSTS – CNR-ITAE

### *OBJECTIVES*

To develop non-carbon catalyst supports and screen them for their properties, compare their resistance to electrochemical corrosion with that of standard carbon supports, and select best candidates for catalysation, and to select stable carbon supports on the basis of their surface area and degree of graphicity;
To design and develop novel Pt-based electrocatalysts demonstrating enhanced catalytic activities and high temperature corrosion stability and down-selection on the basis of mass activity, performance and electrochemical stability;
To prepare low Pt electrocatalysts in ternary compositions based upon Pd/Co;
To investigate the advantages of catalyst promoters.

***To achieve deliverables D3.1 and 3.2 and milestone MS4 in RP1, and deliverable D3.3 and milestones MS5 and MS6 in RP2.***

### *SUMMARY OF OUTPUT FROM WP3*

**The first period of the project has addressed a screening of promoter-free electrocatalysts, whereas the second phase was addressed to further investigation of the down-selected formulations from the first phase, the utilization of promoters and the full achievement of WP3 milestones at targeted operating conditions, in terms of temperature and relative humidity, for automotive applications.**

**Novel supports included Ti-oxide, and sub-oxides, Ta or Nb-doped titania, Nb-doped $SnO_2$, high surface area tungsten carbide (WC) and WC/C composites, whereas highly graphitic supports were investigated at JMFC. Novel synthesis procedures were developed for the oxides and carbides including colloidal approaches and methodologies leading to spherical and fibrous support architectures. The developed supports showed excellent corrosion resistance (at least one order of magnitude better than a benchmark carbon black), appropriate surface area (100-250 $m^2/g$) and capability to favour a high dispersion of the active noble metal phase and to stabilise the catalyst metal particles due to a high metal-support interaction. The results dealing with supports only have been described in detail in the mid-term report. The supports down-**

**selected from the first phase have been used in the second phase to prepare enhanced stability Pt and Pt-Co catalysts.**

**Four ternary alloy cathode catalysts supported on a highly stabilised carbon black have been investigated at two different sintering temperatures and compared to the current high temperature reference alloy. The aim of this activity was to develop a highly durable catalyst to operate at high temperature (120 °C upwards) with increased kinetic activity. The catalysts were also designed for application with PBI type membranes/phosphoric acid electrolytes, such as Fumapem AM, with a highly open structure to help retain free acid within the resulting catalyst layer structure.**
**Most of the efforts were focused on the oxygen reduction reaction (ORR), with attention addressed to alloying Pt with Co and tailoring the particle size. Practical procedures that can produce an enrichment of Pt in the outermost layers of supported nanoparticles were developed to induce Pt surface segregation by high-temperature annealing and a removal of the less noble transition metal from the surface by pre-leaching the alloy in an appropriate acid. The electrochemical activity of ordered and disordered Pt-Co alloy phases was investigated, and specific efforts addressed to examine the role of the thermal treatment in determining the occurrence of possible different surface compositions and structures. This electrocatalyst was combined with an insoluble heteropolymetallate promoter to further increase the catalytic activity at the interface.**

**Pd-based electrocatalysts were investigated for both the ORR and hydrogen oxidation reaction. Its cost is at the present significantly lower than Pt and its reserves much wider. Pd-based electrodes may thus represent a consistent way to reduce the Pt content in PEMFCs and provide a performance that is not significantly lower than Pt/C. Results obtained in RP2 show that there is a promoting effect of temperature on the electrocatalytic activity of Pd-based electrocatalysts. To further improve activity in the ORR, Pd-Pt alloys were considered, in which a thin Pt overlayer (<15 µg/cm$^2$) satisfies the aim to reduce costs while maintaining suitable activity and stability at intermediate temperatures.**

### *DETAILED SUMMARY OF ACHIEVEMENTS IN WP3*

At JMFC, selected new ternary alloys for cathodes (PtXY) supported on graphitised high surface area carbon blacks were evaluated for improved kinetic mass activity (while retaining best highest stability possible) for operation at high temperatures from 120-180 °C. Mass activity was measured using the high temperature activity cell within a half cell test set-up using 99% phosphoric acid as the electrolyte at 180 °C.

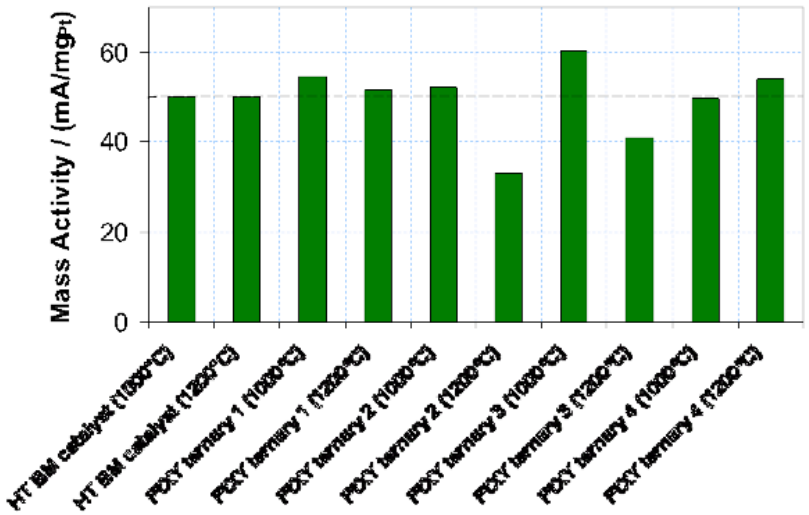



***Table 3.3-1*: Mass activity of JMFC ternary alloy catalysts (HTBM: high temperature baseline material)**

The ECA, effective catalytic area, at room temperature was also measured by cyclic voltammetry using the adsorbed hydrogen peak using a 10 mV/s scan between 0 and 1.2 V. All catalysts studied were annealed at both 1000 and 1200 °C, to improve their corrosion resistance. "Ternary 3" at 1000 °C was the most promising catalyst as it demonstrated a 20% increase in activity compared to the high temperature baseline material. The catalysts were then subjected to accelerated ageing at high temperature. Sample "ternary 3" has the same stability as the high temperature baseline material at 1000 °C, while "ternary 2" shows improved stability at 1000 °C. Based on these results "ternary 3" was selected for scale-up as it met the QuasiDry project requirement for a higher performance catalyst. These results are described in deliverable report D3.1.

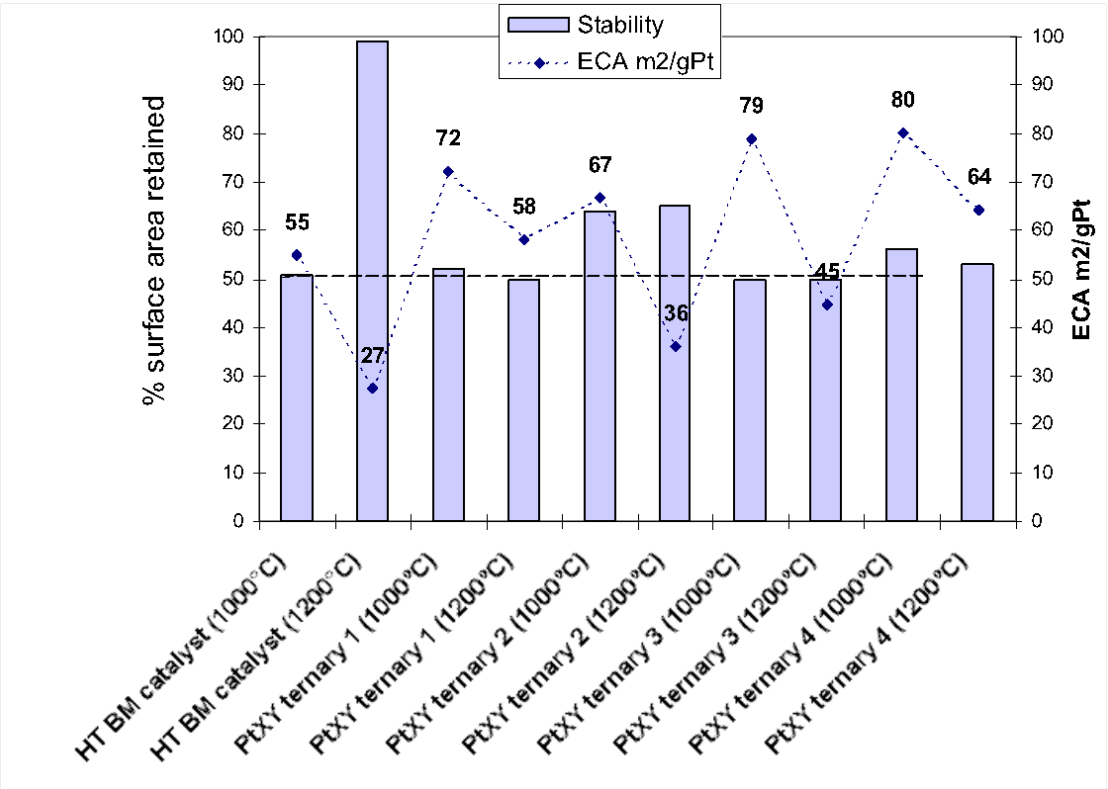



***Table 3.3-2*: *JMFC ternary alloy catalyst stability***

Following on from the down-selection the "ternary 3" formulation has been scaled-up to 200 g batches in readiness for MEA development activities and cell testing in WP4. Successful scale-up was confirmed by characterisation using XRD for alloy lattice parameter and average crystallite size, ECA for platinum surface area and electron microscopy for particle size distribution, which showed that the scaled up samples had similar key characteristics to the original laboratory-scale samples.

At **CNR-ITAE**, 50 wt. % Pt–Co/C catalyst with nominal alloy composition $Pt_3Co_1$ (at.) and Pd-alloy catalysts with 5% Pt have been prepared using methods described in the mid-term report. The characteristics are provided below.
Electrocatalytic activity, performance and stability characteristics for these catalysts were investigated.

***Table 3.3-3***: ***Physico-chemical properties of CNR-ITAE enhanced Pt-Co alloy catalysts***

| **Catalysts** | **Treatment** | **Overall Pt/Co at. Ratio (XRF)** | **Pt/Co at. Ratio in the outermost layer (LE-ISS)** | **Structure** | **$A_{220}$ nm** | **at. % Co in the alloy (XRD)** | **Crystallite size (XRD) nm** | **Particle size (TEM) nm** | **ECSA (CV) m2/g** | **Pt $4f_{7/2}$ orbital B.E eV** | **Co2p $_{3/2}$ orbital B.E eV** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 50%PtCo/C 6T | 600 °C pre-leached | 3.4 | 05:01 | Face centered cubic disordered | 0.383 | 23.8 | 2.9 | 2.9 | 46.7 | 71 | 779.0 |
| 50%PtCo/C 8T | 800 °C pre-leached | 3.0 | 4.1 | Primitive cubic ($L1_2$) ordered | 0.381 | 29.4 | 3.3 | 4.2 | 49.2 | 71 | 778.7 |

***Table 3.3-4***: ***Physico-chemical properties of Pd-based catalysts***

| Sample | Crystallite size XRD nm | Pt;Pd;Co XRF Bulk atomic content % | Pt:Pd:Co XPS Near-surface atomic content % | Pt:Pd:Co LE-ISS Outermost-layer atomic content % |
|---|---|---|---|---|
| 5%Pt-$Pd_3Co_1$/C one-step | 4.4 | 2.8; 72.7; 24.5 | 8.13; 72.44; 19.43 | 7.2; 80.3; 12.5 |
| 5%Pt-$Pd_3Co_1$ two-steps | 6.2 | 2.6; 73.1; 24.3 | 15.42; 79.43; 5.14 | 15.6; 80.6; 3.8 |

The two-step process showed an enrichment of Pt on the surface and a smaller content of Co in the outermost layers.

Using the PtCo/Ketjenblack 8T cathode catalyst, the MS4 targets of $O_2$ reduction mass activity> 0.1 A/mg @ 0.9 V RHE and 110-130°C with 18-33% R.H. using enhanced Pt-based formulations is achieved in the full range (110-130°C with 18-33% R.H.) with an optimised electrode configuration consisting of 50% Fumion as ionomer and PtCo/KB as cathode electrocatalyst. At 130 °C, 18% RH, the achieved performance provides 73% of this milestone.

***Table 3.3-5**: **Mass activity results for the ORR at the CNR-ITAE PtCo catalyst (50% Fumion ionomer, F-950 membrane, 0.3 mg Pt/cm$^2$ anode and cathode, oxygen feed, P=1.5-3 bar abs. 30% Pt/Vulcan at the anode)***

| **Temperature °C** | **Mass activity @ 0.9 V vs. RHE mA / $mg_{Pt}$** | **Relative humidity %** |
|---|---|---|
| 110 | 227 | 18-33 |
| 110 | 253 | 100 |
| 120 | 160 | 18-100 |
| 130 | 73 | 18 |
| 130 | 120 | 25 |
| 130 | 100 | 33 |

At conventional operating conditions, the composite palladium catalysts showed lower performance than the down-selected PtCo. For the composite Pd-based catalyst, the platinum loading was only Pt 0.015 mg $cm^{-2}$, with Pd 0.24 mg $cm^{-2}$ whereas in the PtCo catalyst, the loading was Pt 0.3 mg $cm^{-2}$. However, at high temperature, the composite Pd catalyst outperforms the PtCo catalyst characterised by the same disordered structure (despite the much lower Pt content) even if the performance is slightly lower than that of the PtCo catalyst with ordered structure. These results also satisfy the milestone MS4. Furthermore, there was no observable decay after $10^4$ cycles at 110 °C and 33% RH, 0.6-0.9 V.

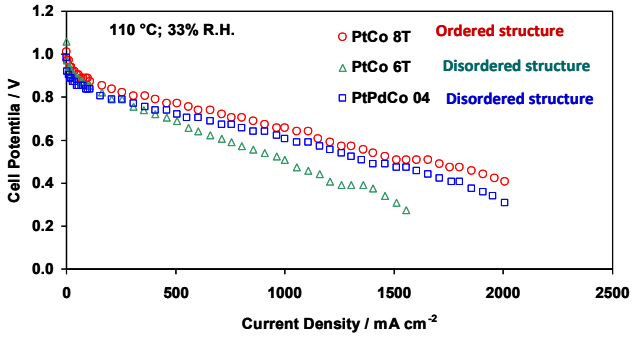



***Figure 3.3-1**: Comparison of the high temperature polarization behaviour for the carbon-supported 5 % wt. Pt-95 % wt. $Pd_3Co_1$ and the $Pt_3Co_1$ electrocatalysts at 110 °C and 33 % RH. Catalyst loadings: Pt 0.015 mg $cm^{-2}$, Pd 0.24 mg $cm^{-2}$ in the Pd-based electrode; Pt 0.3 mg $cm^{-2}$ in the $Pt_3Co_1$ alloy electrode.*

Using the Pd-Pt catalyst, the ORR potential at 0.5 A $cm^{-2}$ is about 0.75 V vs. RHE in a wide temperature range in the presence of the standard Nafion 115 membrane and, after correction for the ohmic drop (50 mV ≈0.1 Ohm $cm^2$ · 0.5 A $cm^{-2}$), the IR-free potential is 0.8 V vs. RHE corresponding to 380-400 mV overpotential for the oxygen reduction. Thus, the milestone MS5a Oxygen reduction overpotential at 0.5 A $cm^{-2}$ < 0.4 V IR-free at 110 -130 °C with 33% R.H. for Pt-free catalysts is achieved, in almost the full temperature range at low relative humidity (excluding the high temperature 130 °C limit), in the presence of a composite Pd-based catalyst with ultra-low loading Pt content (15 μg Pt /$cm^2$). Using a Pd-only cathode catalyst, overpotential characteristics are η @ 0.5 A/$cm^2$≈0.5 V vs 0.4 V target both at 80 °C 100% RH and 110 °C 33% RH. This corresponds to about 80% of the milestone MS5 at 110 °C. Regarding the use of the bare Pd/ C catalyst as anode, the results match the project targets, with MS5b achieved with Pd/C anode up to 130 °C and 100% RH, and at 110 °C and 33% RH.

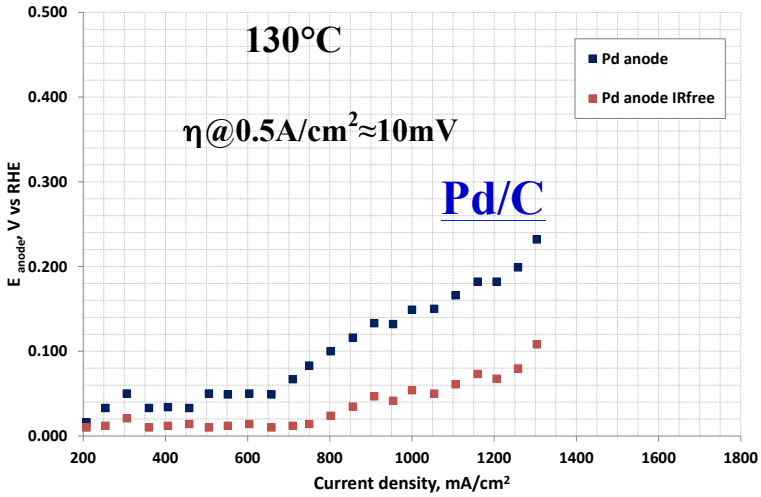



***Figure 3.3-2**: Anodic polarisation behaviour at 130 °C of Pd/C catalyst (anode). Cathode: 0.3 mg Pd/$cm^2$*

The effect of a heteropolyoxometallate promoter at the cathode was investigated using the PtCo catalyst. At 130 °C, 100% RH, 3 bars, the MEA containing the promoter performs definitively better, however no difference in intrinsic electrocatalytic activity at low current density is observed. The effect of the promoter is therefore not significant at low current density, whereas it is relevant at current densities of practical interest and at high temperature operation. The effect of the promoter becomes more important with the decrease of RH even at low temperatures. The effect is again observed at high current densities in a range of practical interest. This is relevant for the milestone MS6: Performance better than that achieved for the corresponding promoter-free catalytic formulations as determined from electrochemical measurements. Accordingly, milestone MS6 is achieved.

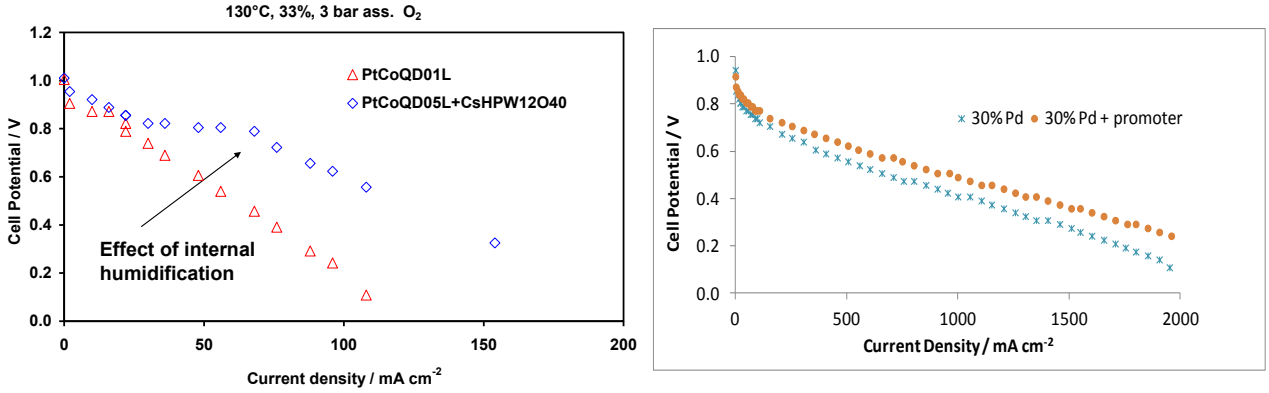



***Figure 3.3-3**: Effect of promoter on the polarisation behaviour of the PtCo cathode catalyst at 130 °C, 33% RH and Pd cathode at 80°C.*

At **CNRS**, non-carbon electrocatalyst support materials have been prepared having unusual morphologies, including microspheres and nanofibres, the latter deposited by electrospinning. A small range of material types has been explored, in order to rapidly screen for most promising systems in terms of surface and electrochemical properties, and that can be developed using a robust preparation methodology. In initial work, CNRS carried out a study comparing microspherical and nanofibre niobium-doped titanium oxide. To satisfy the electronic conductivity requirement, attention was turned to tungsten carbide, which was prepared as microspheres, and niobium-doped tin oxide, prepared as nanofibres and in a highly original fibre-in-tube architecture, where clear effects of the influence of the composition and preparation process parameters are being observed on the properties of the final support oxide, and where particle growth in Nb-$SnO_2$ is limited by the presence of niobium.

A microwave-assisted polyol method was used to deposit up to 21 $\%_{wt}$ of Pt onto the Nb-$SnO_2$ support. The resulting electrocatalysts were characterised for their chemical and electrochemical properties, both ex situ and in situ. The 21 $\%_{wt}$ Pt/Nb-$SnO_2$ electrocatalyst has shown a better stability to prolonged voltage cycling (0.05-1.2 V/RHE in 0.1 M $HClO_4$) compared to commercial Pt/C, by retaining 77 % of the ECSA after 2000 cycles versus 22 % for the Pt/C support. The loss of mass activity is also less significant when compared to the commercial electrocatalyst.

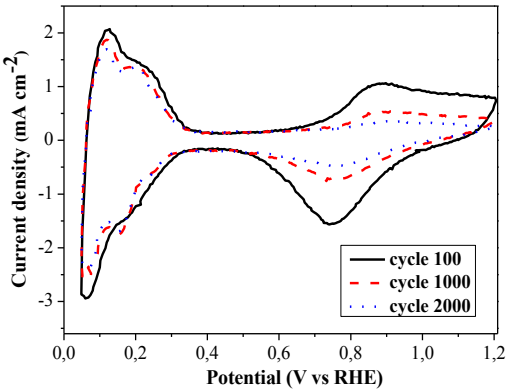



***Figure 3.3-4: CVs of CNRS Pt/Nb-$SnO_2$ on cycling 0.05 – 1.2 V at room temperature***

The above results are described in detail in deliverable reports D3.1-3.3.

## 3.4 WP4: VALIDATION OF MEMBRANES BY MEA DEVELOPMENT – WPL: JMFC

### *OBJECTIVES*

To design and develop an adapted high temperature electrode structure and catalyst layer using benchmark catalysts;
To assemble and characterise MEAs according to the WP1 protocols using start-point benchmark membranes and model electrolyte systems;
To commence validation of the potential of novel membranes designed and developed in WP2 and the prospective catalysts prepared in WP3 by demonstrating the performance of MEAs in single cell testing.
To develop functionalised polycyclic aromatic phosphonic acids having mixed protonic/electronic conduction as compatibilising components for the membrane/electrode interface.

***To achieve deliverables D4.1 and D4.2 and milestones MS7 in RP1, and deliverables D4.3-D4.5 and milestones MS8 and MS9 in RP2.***

### SUMMARY OF OUTPUT FROM WP4

**Work package 4 has targeted some significant milestones for QuasiDry relating to achievement of cell power densities at 120°C under realistic operating conditions (milestone targets MS8 and MS9 of 0.2W $cm^{-2}$ and 0.4 $Wcm^{-2}$ respectively at 0.65 V, 120 °C, $H_2$/Air, <50 kPag, <25%RH). This has required each partner being able to integrate novel ionomer components developed in WP2 and catalysts from WP3 to produce and test functional membrane electrode assemblies (MEAs).**

**JMFC and CNRS Montpellier concentrated on testing MEAs using the "T down" protocol of evaluating MEAs from 160 °C to 120 °C comprising various phosphoric acid-doped cross-linked PBI membranes and a novel double functionality membrane based on a phosphoric and phosphonic acid doped PBI membrane as well as the new JMFC ternary catalyst cathode layer.**

**Testing at CNR-ITAE and FUMATECH primarily focused on the "T up" protocol to evaluate MEAs fabricated from double functionality membranes (based on perfluorosulfonic and phosphonic acid functionality) at temperatures from 65 °C to 120 °C using Pt/Co and 5%Pt-$Pd_3Co_1$ alloys.**

**The extremely challenging targets set by the project were not completely met, with only the mid-term 0.2 $W/cm^2$ power density target (MS8) at 0.65 V being close to being delivered, at the specific practical test conditions, using the cross-linked phosphoric acid doped PBI membrane. However, it was noted that peak power densities of 0.4 $W/cm^2$ were also achieved at still useable voltages, which represents a real achievement, which more than doubled the initial benchmark material's performance. It was also demonstrated that the target power densities could be achieved at 120 °C by raising both humidification and pressure using membranes based on the mixed perfluorosulfonic/phosphonic acid functionality materials. This work was reported in the Deliverable Report D4.5 "Data from MEA tests, showing performance and stability as a function of T and RH – novel ionomers and catalysts".**
**The innovative use of mixed ionic-electronic conductors within MEAs capable of electron transfer to the electrode and proton transport to the membrane was synthesised at MPI and investigated at CNR-ITAE. MPIP also focused on the proof of electron conductivity on a molecular level using various ex-situ techniques such as scanning tunnelling microscopy and spectroscopy, Terahertz time-domain-spectroscopy, device performance in field effect transistors and time-of-flight experiences. This work was reported in Deliverable D4.3 "Feasibility of comptabiliser components for enhancing electrode/membrane interface".**

**The performance and stability at the cathode of the novel Pt/Nb-$SnO_2$ catalyst has also been investigated by CNRS Montpellier using both electron optic techniques and in-situ cell testing, and was reported in Deliverable Report D4.4 "Ex situ characterisation of electrode and MEA structures from down-selected ionomers and catalysts".**

## *DETAILED SUMMARY OF ACHIEVEMENTS IN WP4*

At **JMFC**, a new catalyst layer structure was successfully tested which showed a notable performance improvement at higher current density at elevated temperatures.

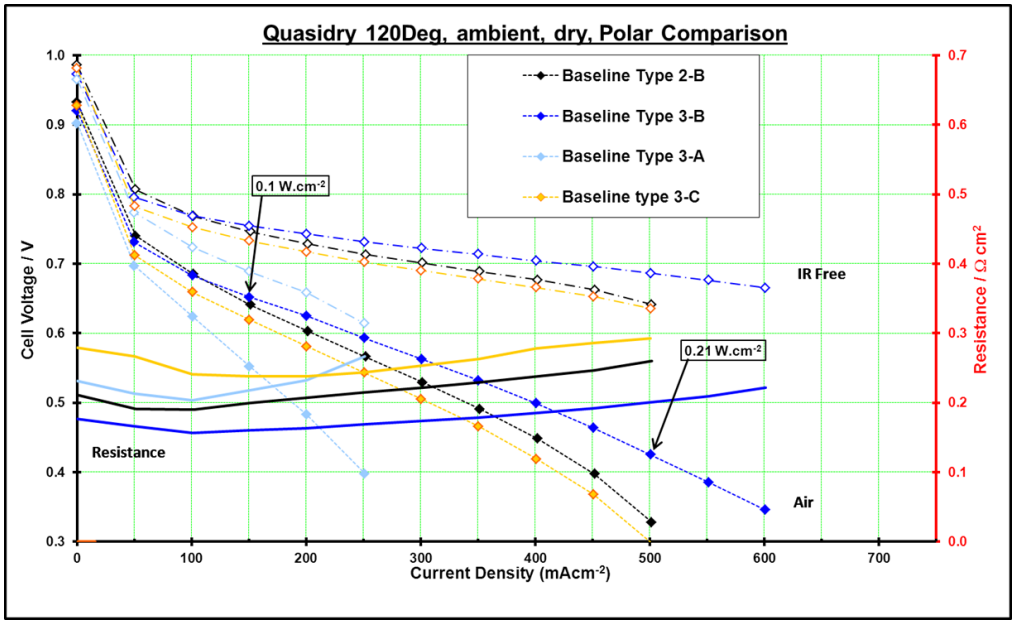



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***Figure 3.4-1**: Standard ternary catalyst with type 3 layer design at 120 °C*

At the target 120 °C the lower resistance observed was very significant, in addition to the finding that the performance increase was also accessed at higher current densities which go beyond just an ohmic improvement. The MEA was repeated successfully and evaluated on a durability test for over 2,500 hrs at 160 °C. The performance was then assessed via air and oxygen polarisation curves every 500 hrs at 120 °C and 160 °C. The durability was very successful with the performance fairly constant over the first 2,000 hrs and the ohmic resistance only starting to increase at 2,000 hrs.

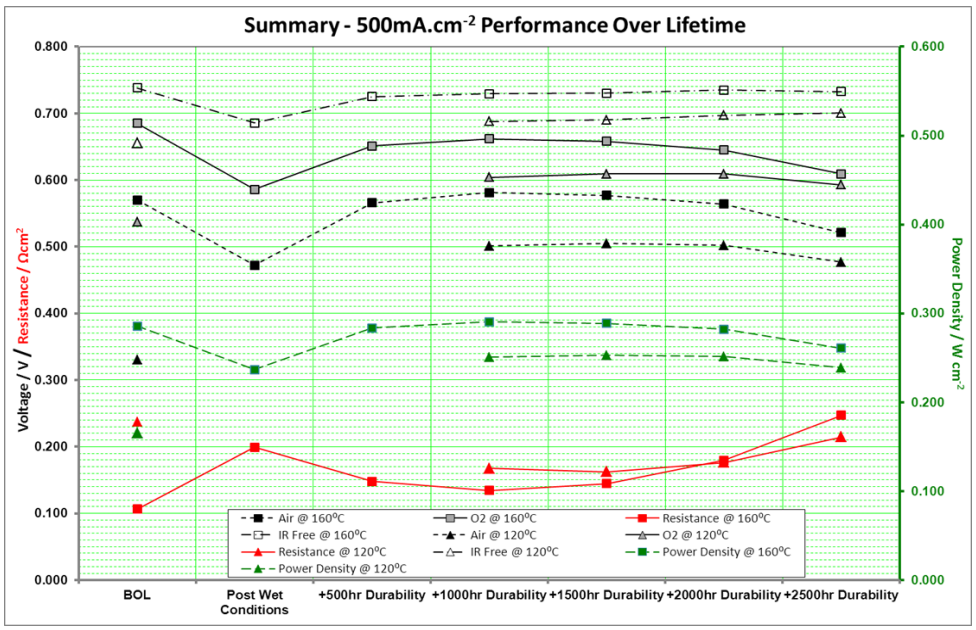


***Figure 3.4-2**: **Standard ternary catalyst with type 3 layer design durability***

The cross-linked phosphoric acid doped PBI membrane from CNRS Montpellier also demonstrated a remarkable peak power density of 0.336 W/cm$^2$ and membrane resistance of 0.07 Ω.cm$^2$, which is best in class under these conditions for these materials. The XL membrane also revealed excellent manufacturing potential, by removing the need for both lamination and doping but also demonstrating good acid life. However, both technologies developed remain to be successfully demonstrated together and issues with the recent material in cell stability still need to be resolved and would warrant further work. Full results are described in deliverable report D4.5.

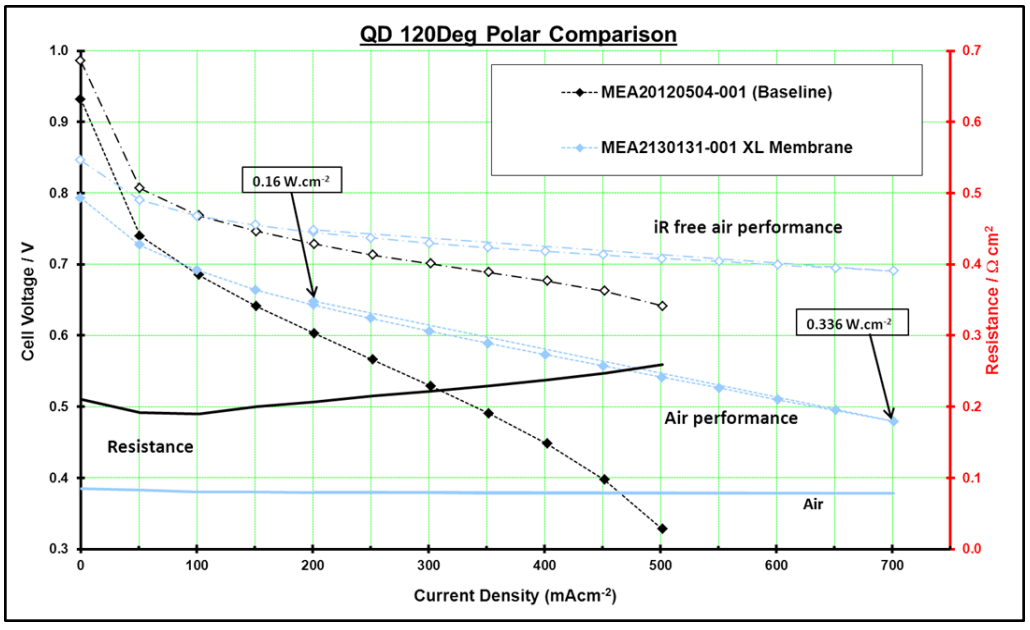


***Figure 3.4-3**: **XL01 membrane testing at 120°C***

At **CNRS**, results from cross-linked membrane based MEAs also showed that performances were higher than a state-of-the-art commercial MEA. Based on cross-linked membranes, ten MEAs have been fabricated and the influence of polymer source, acid doping level and proton conductivity on MEA performances have been studied.

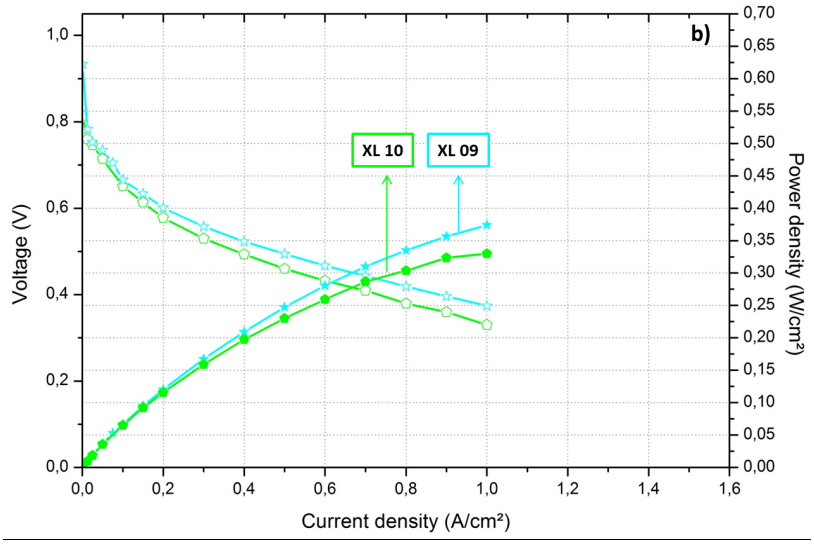


***Figure 3.4-4**: I/V and power density curves of MEA-XL09 and MEA-XL10 at 120 °C, dry $H_2$/air, electrodes 1.4 mg/cm²*

For MEA-XL09, a power density of 0.2 W/cm$^2$ was achieved for a voltage of 0.53 V at 120 °C, with dry hydrogen and air. This is close to the ambitious MS8 milestone of MEA performance in single cell at 120 °C and low RH (< 25 %) achieving 0.2 W/cm$^2$ at 0.65 V. Furthermore, the performance of MEA-XL09 at 120 °C under dry conditions is 0.375 W/cm$^2$ at a voltage close to 0.4 V.

A mixed functionality membrane associating phosphonic and phosphoric acids has shown very promising performance. The power density delivered by MEA-MF01, at 120 °C and dry conditions, is 0.2 W/cm$^2$ at 0.55 V and 0.4 W/cm$^2$ at 0.4 V. MEA-MF01 shows significant improvements in the mass transport region. MEA-MF01 has been operated for more than 2000 hours. Results were further developed in deliverable report D4.5.

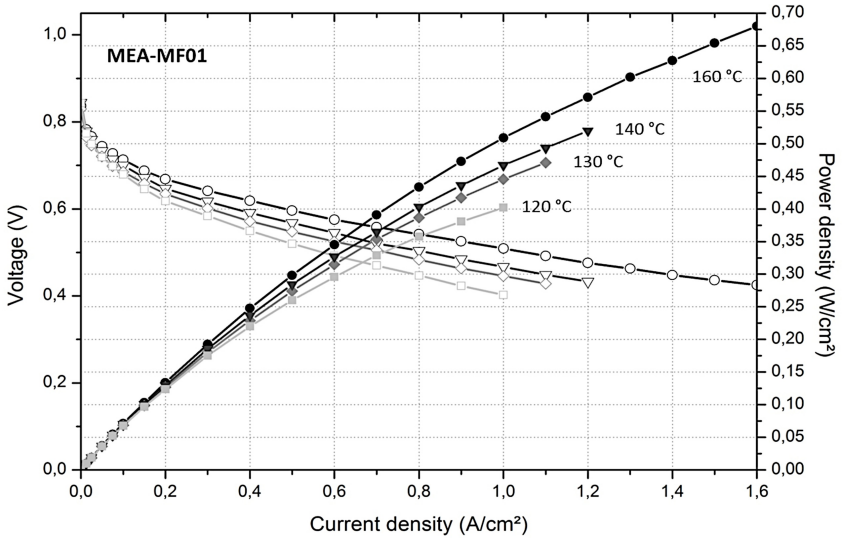


***Figure 3.4-5**: I/V and power density curves of MEA-MF01 at 120 – 160 °C, dry $H_2$/air*

CNRS has also performed accelerated ageing testing in situ using non-carbon Nb-$SnO_2$ support materials developed in WP3, followed by ex situ characterisation of the aged MEAs. It was concluded that the significantly increased resistance to electrochemical oxidation of the non-carbon support material at the cathode directly impacts the stability of the supported Pt catalyst with regard to dissolution and migration. This observation is interpreted as indicating that a strong metal – support interaction has formed between Pt and Nb-$SnO_2$ that is effective in stabilising the Pt to dissolution at high cell voltage. Since support oxidation and Pt dissolution could, in principle, each be considered as separate degradation phenomena, this

observation further shows that these degradation phenomena are in fact related when carbon supports are used, but can be decoupled by use of an oxide support. These results are described in deliverable report D4.4.

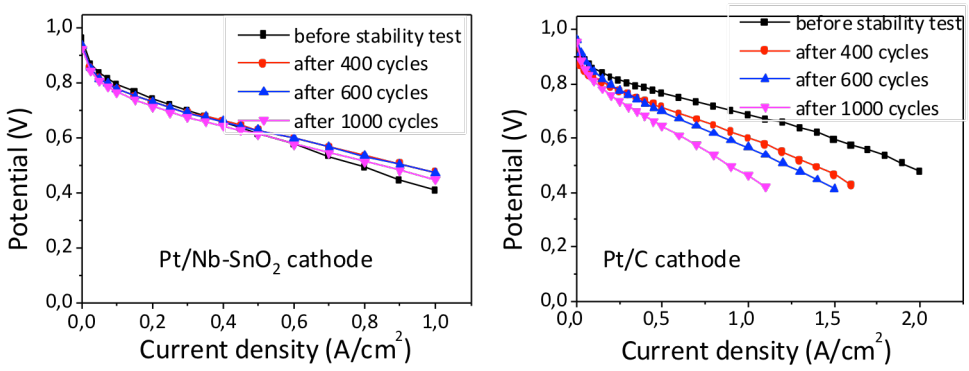


***Figure 3.4-6*: Polarisation curves after voltage cycling between 0.9 and 1.4 V with Pt/Nb-$SnO_2$ cathode (left) and Pt/C cathode (right). Measurements at 80 °C, $H_2$-$O_2$. Anode/cathode feed gases hydrated at 80/64 °C.**

**CNR-ITAE** has assembled and investigated MEAs comprising membranes provided by FUMA, and CNR-ITAE electrodes based on electrocatalysts down-selected from WP3. Some of the FUMA membranes included polyphosphonic acid polymers synthesised at ULund. For mixed functionality sulfonic-phosphonic membranes, the best performance at high temperature and low RH was obtained with the membrane AC-925, where high power density was obtained under conditions where conventional PFSA membranes such as Nafion/Fumion (e.g. F950) showed a dramatic decrease of conductivity. At 110°C 33% RH, the membrane AC-925 allowed to achieve a peak power density of 730 mW $cm^{-2}$ and a performance of 300 mW $cm^{-2}$ at 0.6 V. The key advantage of these membranes over other polymer electrolyte systems capable of operation at intermediate and high temperature is the possibility of providing good performance in the presence of a low catalyst loading (Pt≤ 0.3 mg $cm^{-2}$), low pressure and a fast cold start-up which is assured by the sulfonic acid functionalities whereas the phoshonic acid provide suitable conductivity for operation up to 110-120 °C. These characteristics appear suitable for automotive operation. Key results at the MEA level, obtained at CNR-ITAE, showing the progress beyond the state of the art for mixed functionality sulfonic-phosphonic membranes over PFSA membranes are clearly illustrated in Figure 4.7, and described in deliverable report D4.5.

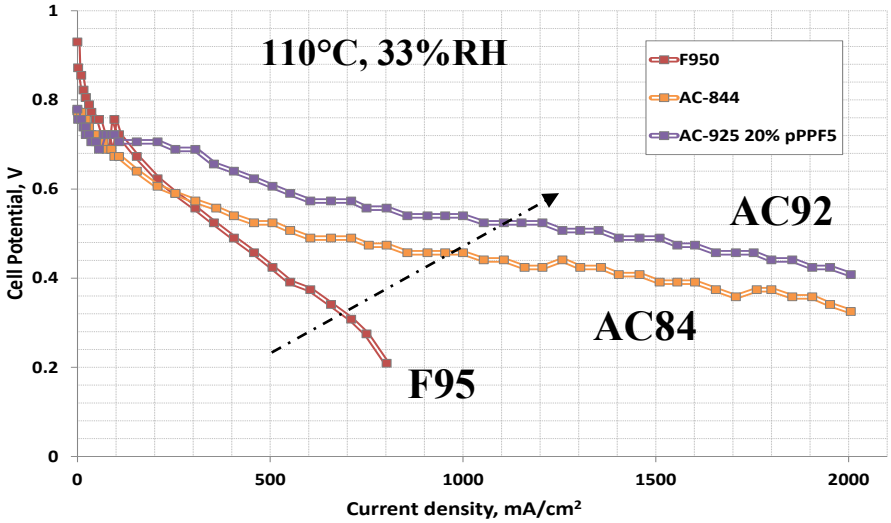


***Figure 3.4-7*: Polarisation curves for MEAs based mixed functionality membranes and PFSA (F-950), using CNR-ITAE catalysts and electrodes at 110 °C and 33% RH, 1.5 bara, 0.3 mg/$cm^2$ Pt**

A comparison of high temperature operation, at 120 °C, for the best performing membrane AC-925 in the presence of air and oxygen as oxidant feed is shown in Figure 4.8.

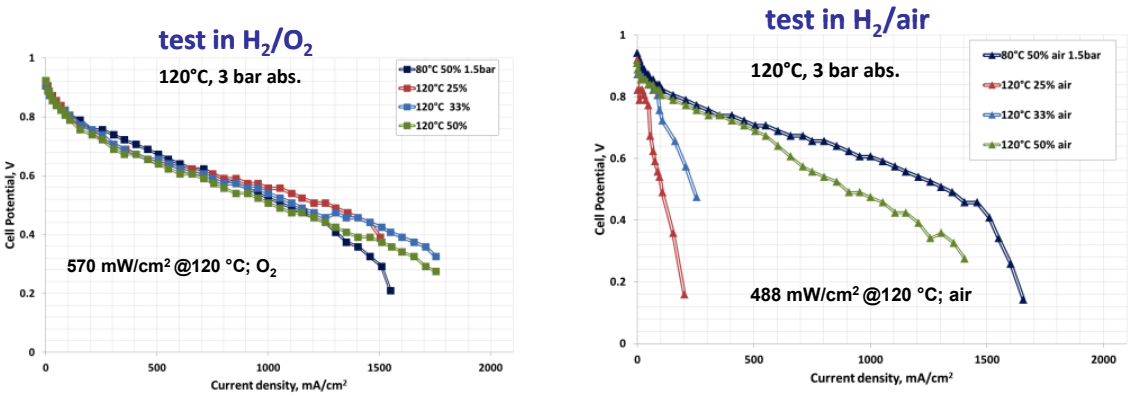


***Figure 3.4-8**: **Comparison of the high temperature (120 °C), low RH polarisation behaviour of mixed functionality membranes in the presence of air and oxygen feeds.***

The AC-925 membrane reaches a maximum power density of 570 mW/cm$^2$ at 120 °C, 50%RH in $O_2$ and a maximum power density of 488 mW/cm$^2$ at 120 °C, 50%RH in air in the presence of CNR electrodes with 0.3 mg Pt cm$^{-2}$ catalyst loading. Milestone MS9 power density targets were thus attained at a useful cell voltage, by tuning the pressure and humidity conditions at the target temperature.
Progress beyond the state of the art is provided by the significant improvement registered for the AC-925 -based MEA with respect to the F-950 PFSA reference membrane at intermediate temperatures and low RH.

At **MPIP**, activities were dedicated to a fundamental study of the interface between electrode and membrane by synthesising a material able to transport electrons to the electrode and protons to the membrane. Functionalised polycyclic aromatic hydrocarbons (*PAHs*) such as triphenylene (*TP*) or hexa-*peri*-hexabenzocoronene (*HBC*) were considered as potential candidates. $H_2PO_3$-containing PAHs are expected to self-organize into more stable and more defined columnar superstructures in direct comparison to hexaphenylbenzene (*HPB*) derivatives. They form discotic mesophases due to pronounced π-stacking, which results in high values for conductivity. These molecules might possess at the same time proton- and electron-conducting properties and could act as compatibilizers at the interface between electrolyte and electrode. MPIP synthesised four different types of compatibilizer components comprising a triphenylene or an HBC core respectively and a phosphonic acid-functionalised periphery. The triphenylene compatibilizer was chosen as model compound for further investigations. Proton conductivity studies were carried out under 1 bar $H_2O$ atmosphere by increasing temperature until 180 °C, when the conductivity was observed to be 9 mS/cm over the whole temperature range.

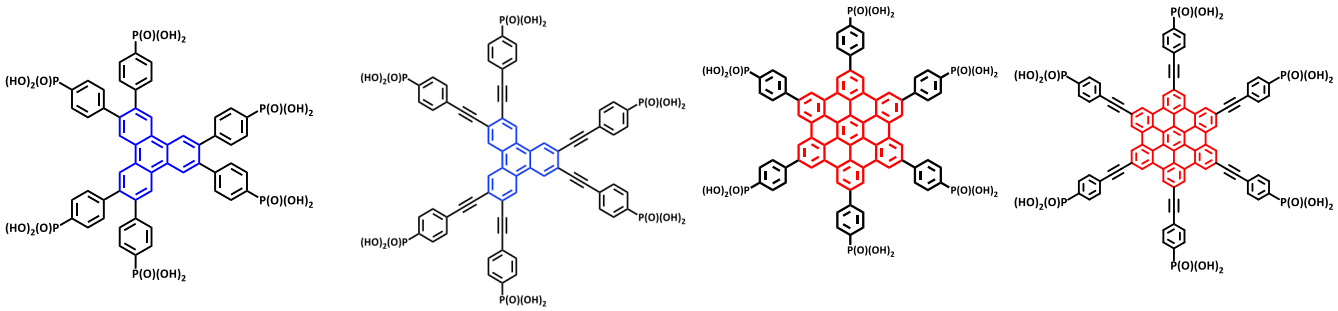

***Figure 3.4-9**: **Compatibilizer components in phosphonic acid form based on triphenylene (blue) and HBC (red).***

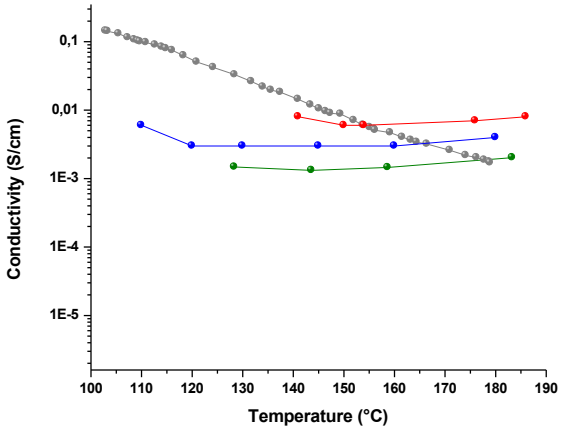


***Figure 3.4-10*: Plots of proton conductivity vs. temperature under 1 bar $H_2O$ atmosphere for 2,3,6,7,10,11-hexakis(phosphonatophenyl)triphenylene (●), p-3PA-TPB (●), p-6PA-HPB (●) and Nafion® 117 (●).**

MPIP has also focused on the proof of electron conductivity on a molecular level using scanning tunneling microscopy and spectroscopy (STM and STS), Terahertz time-domain-spectroscopy (THz-Tds), device performance in field effect transistors (FET) and time-of-flight experiences (TOF).

At **CNR-ITAE**, an extensive ex-situ spectroscopic and electrochemical characterisation was carried out to assess the relevant properties of the triphenylene compatibiliser material in order to formulate deposition onto carbon and related catalytic ink formulation. The aim of the spectroscopic characterisation was to identify if electron transfer may occur at the molecular level by studying the optical absorption in the UV-Vis-NIR region corresponding to electronic transitions. Macroscopic electronic conductivity was investigated by using ac-impedance spectroscopy. The material shows suitable proton conductivity but modest electronic conductivity. Preliminary investigations were performed to use the phosphonic acid fuctionalised triphenylene in the MEA as a catalytic additive, however a suitable solvent could not be found within the timeframe and further efforts are necessary to find a solvent capable of dissolving the compatibiliser at the molecular level while being removed by moderate thermal processing without causing constraints to the MEA characteristics. In this regard, further research is necessary. These results are described in deliverable report D4.3.

## 3.5 WP5 – DISSEMINATION, USE AND OUTREACH – WPL: PXO

### *OBJECTIVES*

To provide a framework for dissemination of project foreground;
To create a public face for the project through a dedicated website;
To monitor dissemination activities and promote them through the project website;
To provide intermediate and final assessments of membrane development routes, and potential ease of MEA fabrication with these membranes, with view to their future use;
To produce a flyer promoting QuasiDry.

***To achieve deliverables D5.1-D5.3 in RP1, and D5.4-D5.6 in RP2.***

### *SUMMARY OF OUTPUT FROM WP5*

**WP5 has provided the framework for the dissemination and use of results from the project. A template for presentations at internal meetings was prepared, and a logo developed for use on internal documents and when reporting from the project at conferences. Abstracts of publications arising from the project, a list of conference presentations, the project flyer, are all available from the project website. The full papers are available in open access through institutional repositories. The dissemination protocol agreed between partners has been followed to manage the knowledge generated by the project. Selected membrane development routes coming out of WP2 have been cost-evaluated and assessed with a view to potential upscale and commercial development, as has the MEA fabrication route from one of these novel membranes.**

### *DETAILED SUMMARY OF ACHIEVEMENTS IN WP5*

A dissemination protocol took into full account the open access special clause. This dissemination protocol was used each time a partner planned to present results at a conference or to submit a paper for journal publication.

The QuasiDry project website (http://www.quasidry.eu/) has been updated on a regular basis with information on project activities (news, meetings, publications, public deliverables…) and project resources (links, related events…). It is described in deliverable report D5.1.
Over the 3 years of the project, the Quasidry public web site has been consulted on a regular basis with an average of 19 unique visits per month.
Further analysis of this traffic shows that half of the visits arise from new visitors (using "Quasidry" as a main search key word) that are mainly looking for information on the project and its partners. This information reveals that dissemination activities of the consortium have been very efficient, attracting many new visitors.

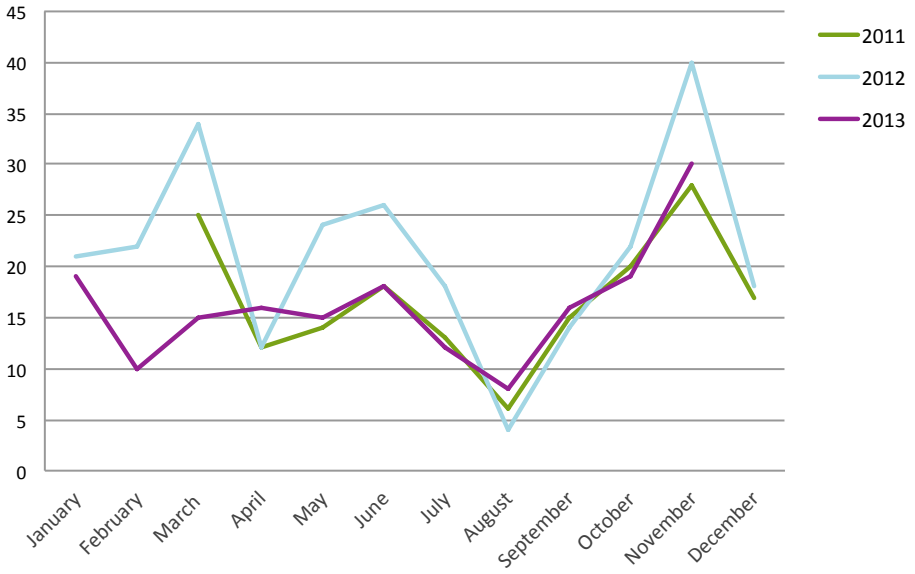


***Figure 3.5-1*: *Quasidry public web site unique visits for the period M1-M36***

A total of 18 presentations of the project results have been made at national or international conferences, 7 journal articles are published, with 6 others in press or in preparation, 1 patent has been filed and extended,

and 2 others are in preparation for filing. A brochure promoting project activities and results has been distributed at international conferences. These dissemination actions are described in deliverable report D5.2.

Eight education actions towards non-specialist scientists (general public, non-specialist higher education, and high schools) have been undertaken by the consortium (a complete list of those dissemination actions is reported in the deliverable report D5.6 on Education actions released at M24). They mainly explain the move to alternative energy sources, the role to be played by hydrogen as an energy carrier, and energy conversion by fuel cells.

Two assessments of industrial scaleability were carried out and are described in deliverable reports D5.3 and D5.5. FUMATECH has evaluated the preparation route of materials with respect to their industrial scalability, cost and environmental considerations (deliverable report D5.5 on the feasibility of scale-up - Final Assessment of Industrial Scaleability). This report delivered a view on the feasibility whether selected approaches within WP2 are industrially scaleable in a cost effective way in comparison with today's state of the art PFSA. The following three materials were selected for evaluation: (i) Blend membrane consisting of PFSA + 10% PTFSPA, (ii) XL-PBI and (iii) XL-PBI + p-6PA-HPB composite. The final cost analysis report concluded that the first approach based on blending PFSA with PTFSPA does not change the cost structure of the membrane significantly compared to today's state-of-the-art PFSA membranes. Progress against state-of-the-art membranes can be achieved essentially in the advanced membrane properties of this blend membrane.

The second approach, the use of cross-linked PBI membranes cast from PA / PPA(XL-PBI), shows a significantly lower cost compared to state-of-the-art PFSA membranes, which could be a significant step forward. The third approach based on the fabrication of XL-PBI membranes with incorporated p-6PA-HPB is driven by the high cost of the additive p-6PA-HPB. In order to reduce the cost of this membrane, significant optimisation and modification of the production process of this additive must be achieved.

JMFC assessed the potential for large scale MEA manufacturing using phosphoric acid doped cross-linked XL-PBI membrane compared to current acid doped PBI based membranes. The XL-PBI has been fabricated into laboratory-scale MEAs at JMFC has shown significant potential advantages as it would be compatible with roll-to-roll processing, would not require any added doping stage, nor temperature and pressure lamination, and the acid contained within the membrane does diffuse into each catalyst layer and does not exhibit any significant end of life acid loss. It is easy to imagine a very simple manufacturing process with the membrane on a roll with a tensioner and the discrete electrodes just being tacked in place using a cold roller.

However, from the MEA manufacturing perspective, there are still remaining technical challenges concerning the newly developed membranes that need to be overcome. The single greatest hurdle is one of mechanical strength with the membrane developing tears fairly easily. This is something that can be addressed by using reinforcement for the membrane and which was also demonstrated by CNRS Montpellier but it would have to be a less coarse support to be successful. Overall the phosphoric acid doped XL-PBI membrane shows great promise from an MEA manufacturing point of view.

The plan for dissemination and use of project results is described in deliverable report D5.4.

## 3.6 WP6 – PROJECT MANAGEMENT: CNRS

### *OBJECTIVES*

To distribute project funds in a timely manner;
To coordinate negotiation of the consortium agreement, its finalisation and signature;
To establish communication tools adapted to the needs of the partners and promote their use.
To initiate, coordinate and finalise project intermediate reports and 18 month contractual reporting requirements;
To coordinate the scientific and technical activities of the project and interactions between the partners and between work packages;
To interface between the European Commission officers, the project and its partners.

***To achieve deliverables D6.1 and D6.2 in RP1, and D6.3 in RP2.***

### *SUMMARY OF OUTPUT FROM WP6*

**The coordination activity has been specifically addressed to ensure that each of the technical work packages started in a timely manner and pursued to completion and submission of all deliverables, as well as to the achievements of the general objectives of the project and the specific milestones. Steering committee, technical progress and web-based meetings have been attended by all partners. The coordinator has represented the project at international conferences. Technical and Financial reporting has been completed.**

### *DETAILED SUMMARY OF ACHIEVEMENTS IN WP6*

The activity of WP6 Project management was designed to provide efficient project coordination and management to support achievement by the partners of the project objectives, to interface with the European Commission.

The consortium agreement was completed and signed in line with the commencement of the project. Distribution of the overall pre-financing and second payments were expedited rapidly.

The coordination activity has been specifically addressed to ensure that each of the technical work packages started on time, and carried through to completion and submission of the corresponding deliverables. In many cases this has involved close collaboration between partners, all of which have contributed where relevant to any given deliverable report. The coordination activity has overseen the achievements of the general objectives of the project and its specific milestones.

A user-friendly and effective shared workspace was developed, which was largely used by the project partners, where project documents including meeting agendas and minutes, presentation materials, disseminated items, project reports etc., are uploaded and stored, and where materials exchanges between partners are tracked. This site was maintained and updated on a continuous basis, and will remain open to project partners in the foreseeable future. The total number of visits to the platform by partner and the average number of visits per month for all partners except the PSW manager PXO is shown below.

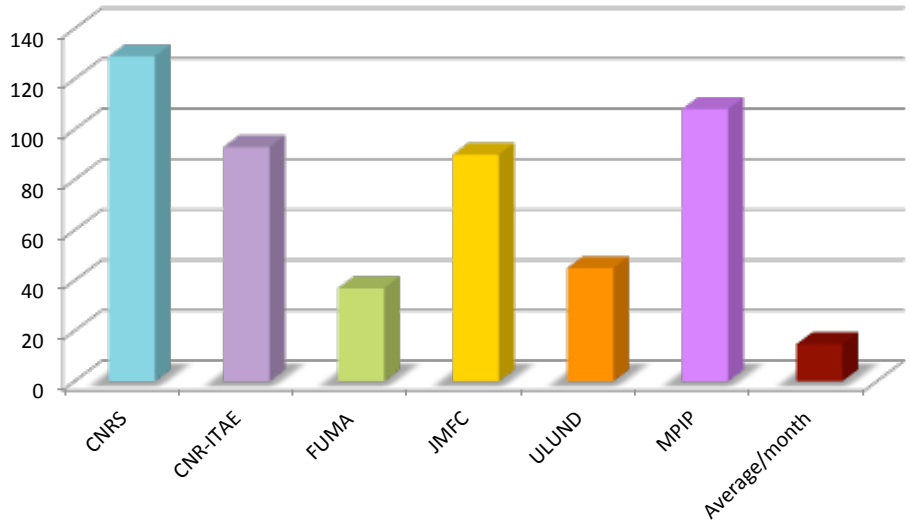


***Figure 3.6-1*: *Use of the Project Shared Workspace. Number of visits during the contract duration.***

Steering committee and technical progress meetings have been attended by the partners, with full participation by partners and discussion in relation to protocols, methods, activities, results, achievements, dissemination and future potential use of results.

**PROGRESS MEETINGS**

- **Kick-off meeting**: 31st January 2011 at JMFC, Sonning Common, UK.
- **6 month progress meeting**: 26th-27th May 2011 in Taormina, Italy, hosted by CNR-ITAE..
- **12 month progress meeting**: 1st-2nd December 2011 in Schriesheim, German, hosted by FuMA-Tech.
- **18 month progress meeting**: 23rd-24th May 2012 in Skanör, Sweden, hosted by ULund. It was attended by all partners.
- **18 month preparation meeting & mid-term review meeting**: 29th-30th October 2012 in Montpellier, France, hosted by CNRS.
- **24 month progress meeting**: 17th-18th January 2013 in Begur, Spain, hosted by CNRS.
- **30 month progress meeting**: 5th-6th June 2013 in Kloster Eberbach, Germany, hosted by MPIP.
- **36 month progress & final meeting**: 21st– 22nd November 2013 in Oxford, UK, hosted by JMFC.

**WEB MEETINGS**

- **QUASIDRY web meeting**: The "Go to Meeting" software was used as from project month 12 to implement a 6 monthly web meeting, alternating with full progress meetings, for an update on results and actions (27th February 2012, 27th September 2012, 22nd March 2013, 30th September 2013).

Reporting is a major component of the activity in WP6. Internal reports have been prepared at Months 6, 12 and 24, the mid-term assessment report at M18, the periodic activity report for the second reporting period M19-36, the present final publishable report, and a plan for the future use and dissemination of results. In addition, WP6 has overseen the preparation and submission of the 31 deliverable reports of the project. Templates for these reports (deliverable and periodic) were prepared and made available to partners on the project shared workspace.

A Materials Tracking Sheet, an on-line editable document, has tracked the exchanges of samples and materials between partners since the beginning of the project. There are currently 79 entries registered in the MTS.

The coordinator has represented the project at international conferences.
Technical and Financial reporting has been completed.

# 4. POTENTIAL IMPACT, USE AND DISSEMINATION OF FOREGROUND

This section describes the dissemination of the results and knowledge arising from the QUASIDRY project, during all the project duration and a plan for future dissemination after the end of the project.
The following dissemination activities are described:

- Research publications in peer-reviewed journals,
- Meetings, conferences,
- Website,
- Brochure,
- Education actions.

In total 9 publications have been produced so far, in peer-reviewed scientific journals and 25 presentations (oral or posters) given at international conferences.
A complete list of journal publications, oral presentation, poster presentations and other is given.
We also provide a list of planned dissemination activities to be continued after the end of the project as well as exploitable foregrounds.

## 4.1 DISSEMINATION ACTIVITIES DURING PROJECT LIFE

### 4.1.1 INTENDED AUDIENCE & OBJECTIVES

The dissemination plan has various objectives depending on the type of audience, as detailed below:

- Scientific community & Industrial fuel cell specialists: promote the diffusion of scientific results and QUASIDRY consortium activities
- General public: fulfil project communication and dissemination needs in the direction of the scientific community and the public
- Non specialist scientists (general public and schools): promote the importance of the move to alternative energy sources, the role to be played by hydrogen as an energy carrier

### 4.1.2 DISSEMINATION CHANNELS

#### 4.1.2.1 Dedicated Project Website

The dedicated project website is one of the main dissemination channels towards the scientific community and the public. The public section features:

- General description of the project and its objectives
- Information about the consortium and links to partners' websites
- Public documents, such as public deliverables, publications (open-access provided), project posters and brochure.
- Contact information

#### 4.1.2.2 Participation in international conferences

The consortium has attended prominent international conferences, workshops and symposia.

- **Organic Pacific Grove Advances in Materials for Proton Exchange membrane Fuel Cells Systems, Asilomar Conference Grounds, California, USA, 20-23 February 2011**, Crystals as proton-conducting materials, M. Klapper, Max-Planck-Institute for Polymer Research, Mainz, Germany
- **219th ECS meeting, 1st – 6th May 2011, Montreal, Canada**, Investigation of Carbon Supported Pt and PtCo Electro-catalysts by Low-Energy Ion Scattering and X-ray Photoelectron Spectroscopy: Influence of the Surface characteristics on Performance and Degradation, A. Stassi, I. Gatto, G. Monforte, E. Passalacqua, V. Antonucci, A.S. Aricò, CNR-ITAE, Italy

- **Fuel Cells and Hydrogen Joint Undertaking Meeting, 17-20 May 2011, Berlin, Germany**, Discussion of CNR-ITAE results, A.S. Aricò, CNR-ITAE, Italy
- **European Fuel Cell Forum, 28th June – 1st July 2011, Lucerne, Switzerland**, Surface properties of Pt and PtCo electro-catalysts and their influence on the performance and degradation of high temperature polymer electrolyte fuel cells, A.S. Aricò, A. Stassi, I. Gatto, G. Monforte, E. Modica, E. Passalacqua, V. Antonucci, CNR-ITAE, Italy
- **Fuel Cells & Hydrogen Joint Undertaking Review day, 22-23 November 2011, Brussels, Belgium**, Presentation of the QUASIDRY project, D. Jones, ICGM-CNRS, Université Montpellier 2, France
- **European Fuel Cell - Piero Lunghi Conference 2011 (paper EFC11013), 14-16 December 2011, Rome, Italy**, Designed Electrocatalysts for High Temperature Operation of Solid Polymer Electrolyte Fuel Cells, A. S. Aricò, A. Stassi, I. Gatto, G. Monforte, E. Passalacqua, V. Antonucci, CNR-ITAE, Messina, Italy
- **Fuel Cells 2012 Science & Technology, 11-12 April 2012, Berlin, Germany**, Next generation high temperature PEM fuel cells incorporating quasi-anhydrous and dry membranes: from components to MEA, D. J. Jones, J. Rozière, N. Donzel , S. Cavaliere, S. Subianto, ICGM-CNRS, Université Montpellier 2, I. Gatto, A. Stassi, A. S. Arico, CNR-ITAE, Messina, S. Buche, G. Hards, Johnson Matthey Fuel Cells Ltd., M. S. Schuster, B. Bauer, fumatech GmbH, A. Sannigrahi, P. Jannasch, Lund University, J. Wegener, M. Klapper, Max-Planck-Institute for Polymer Research, Mainz, Germany.
- **International Society of Electrochemistry Topic Meeting "Nanostructured Electrodes", 15-18 April 2012, Perth, Australia**, Fuel cell electrodes based on electrospun nanofibres, I. Savych, S. Subianto, J. Bernard d'Arbigny, S. Cavaliere, D. J. Jones, J. Rozière, CNRS ICG-AIME, Université Montpellier 2, Montpellier, France
- **E-MRS Spring meeting, 14-18 May 2012, Strasbourg, France**, New catalyst supports for PEMFC electrodes, I. Savych, J. Bernard d'Arbigny, S. Cavaliere, D.J. Jones, J. Rozière , ICGM-CNRS, Université Montpellier 2, France
- **GEI-ERA2012 Conference, 17-22 June 2012, Salina (Aeolian Island), Italy**, A study of Different PtCo/C cathode Electrocatalysts in PEMFCs for Automotive Applications, A. Stassi, I. Gatto, G. Monforte, V. Baglio, E. Passalacqua, V. Antonucci, A.S. Aricò, CNR-ITAE, Messina, Italy
- **4th EuCheMS Chemistry Congress, 26-30 August 2012, Prague, Czech Republic,** Phosphonated small molecules - a multitalent in fuel cell applications -, J. Wegener, L. Jiménez García, A. Kaltbeitzel, R. Graf, M. Klapper, K. Müllen, Max-Planck-Institute for Polymer Research, Mainz, Germany
- **International Symposium on Electrocatalysis: New concepts and approaches, 4-7 November 2012, Maragogi, Brazil**, PEMFC Electrocatalyst Supports Based on Electrospun Nanofibres, I. Savych, S. Subianto, S. Cavaliere, D. J. Jones, J. Rozière, ICGM-CNRS, Université Montpellier 2, France
- **MRS fall meeting, 25-30 November 2012, Boston, Massachusetts, USA**, A Study on Performance and Degradation of PtCo/C Electrocatalysts for High Temperature Polymer Electrolyte Membrane Fuel Cells, A. Stassi, I. Gatto, G. Monforte, V. Baglio, E. Passalacqua, V. Antonucci, A.S. Aricò, CNR-ITAE, Messina, Italy
- **ASILOMAR Conference, February 17th - 20th 2013, Pacific Grove, CA, USA**, Phosphonated small molecules - a multitalent in fuel cell applications, M. Klapper, J. Wegener, L. Jiménez-Garciá, A. Kaltbeitzel, K. Müllen, Max Planck Institute for Polymer Research, Mainz, Germany
- **ASILOMAR Conference, February 17th - 20th 2013, Pacific Grove, CA, USA,** Proton-conducting Phosphonated Nanochannels, J. Wegener, A. Kaltbeitzel, R. Graf, M. Klapper, K. Müllen, Max Planck Institute for Polymer Research, Mainz, Germany
- **Nordic polymer Days "Polymers for a Sustainable World", 29-31 May 2013, Helsinki, Finland**, Ring Opening Metathesis Polymerization - A New Pathway to Well-Defined Phosphonic Acid Functional Polymers, B. Bingöl and P. Jannash, Lund University, Sweden
- **Electrochemical Society 223rd Meeting, 12-16th May 2013, Toronto, Canada**, Electrospun materials as electrocatalyst supports for PEM fuel cells. S. Cavaliere, I. Savych, S. Subianto, D. J. Jones, J. Rozière, ICGM-CNRS, Université Montpellier 2, France
- **European Fuel Cell Forum, 2-5 July 2013, Lucerne, Switzerland,** Next Generation High Temperature PEM Fuel Cells Incorporating Quasi-Anhydrous and Dry Membranes: from Components to MEA, [1]D. Jones, J. Rozière, N. Donzel and S. Cavaliere, [2]I. Gatto, A. Stassi and A. Arico,; [3]S. Buche and G. Hards, [4]M. Schuster and B. Bauer, [5]A. Sannigrahi and P. Jannasch, [6]J. Wegener and M. Klapper**,** [1]ICGM-CNRS, Université Montpellier 2, France, [2]CNR-ITAE, Messina, Italy; [3]Johnson Matthey Fuel Cells Ltd., Sonning Common, U.K.; [4]fumatech GmbH, Germany; [5]Lund University, Sweden;

[6]Max-Planck-Institute for Polymer Research, Mainz. Germany.

- **Euromat 2013, 8-13 September 2013, Seville, Spain,** Optimization of perfluorosulphonic ionomer amount in gas diffusion electrodes for PEMFC operation under automotive conditions, I. Gatto, A. Stassi, V. Baglio, A. Carbone, E. Passalacqua, A.S. Aricò, CNR-ITAE, Messina, Italy - M. Schuster, B. Bauer, FuMA-Tech, Germany
- **Euromat 2013, 8-13 September 2013, Seville, Spain,** Proton conduction membranes based on highly phosphonated polymer, A. Sannigrahi, Z. Shao, B. Bingöl, P. Jannasch, Lund University, Sweden
- **64th Annual Meeting of the International Society of Electrochemistry, 8-13 September 2013, Queretaro, Mexico,** PEMFC Electrocatalyst Supports Based on Electrospun Nanofibres, I. Savych, S. Subianto, S. Cavaliere, D. J. Jones, J. Rozière, ICGM-CNRS, Université Montpellier 2, France.
- **64th Annual Meeting of the International Society of Electrochemistry, 8-13 September 2013, Queretaro, Mexico,** A Study of Pd-based Electrocatalysts for Automotive Applications, S. Stassi, I. Gatto, G. Monforte, A. Patti, E. Passalacqua, V. Baglio, A. S. Aricò CNR-ITAE, Messina, Italy
- **246th ACS National Meeting & Exposition, 8-12 September 2013, Indianapolis, Indiana,** Proton-conducting phosphonated frameworks. J. Wegener, A. Kaltbeitzel, G. Glaber, R. Graf, M. Klapper, K. Müllen, Max-Planck-Institute for Polymer Research, Mainz. Germany
- **246th ACS National Meeting & Exposition, 8-12 September 2013, Indianapolis, Indiana,** Phosphonic acid-functionalized polymers vs. phosphonated small molecules: David vs. Goliath? M. Klapper, J. Wegener, L. Jiménez-Garcia, A. Kaltbeitzel, K. Müllen, Max-Planck-Institute for Polymer Research, Mainz. Germany
- **246th ACS National Meeting & Exposition, 8-12 September 2013, Indianapolis, Indiana,** Direct synthesis of phosphonated polymers via ring opening metathesis polymerization, B. Bingöl, A. Kröger, P. Jannasch, Lund University, Sweden

#### 4.1.2.3 Journal publications & proceedings

The Consortium has submitted and will continue to submit a number of individual or joint publications to scientific journals. Each publication has followed the QUASIDRY dissemination protocol. Published articles have been made available through institutional repositories (generally the CNRS HAL repository).

#### 4.1.2.4 Journal publications

- **Electrospinning: designed architectures for energy conversion and storage devices**, *Energy Environ. Sci.* (2011), ***4,*** *4761-4785,* S. Cavaliere, S. Subianto, I. Savych, D. J. Jones and J. Rozière, CNRS, France - **DOI:** 10.1039/C1EE02201F - http://hal.archives-ouvertes.fr/hal-00624576
- **The effect of thermal treatment on structure and surface composition of PtCo electro-catalysts for application in PEMFCs operating under automotive conditions**, A. Stassi, I. Gatto, G. Monforte, V. Baglio, E. Passalacqua, V. Antonucci, A. S. Aricò , CNR-ITAE, Italy - *accepted in Journal Power Sources DOI: 10.1016/j.jpowsour.2012.02.014* - http://hal.archives-ouvertes.fr/hal-00753348
- **An electro-kinetic study of oxygen reduction in polymer electrolyte fuel cells at intermediate temperatures**, I. Gatto, A. Stassi, E. Passalacqua, A.S. Aricò, *Int. J. Hydrogen Energy DOI: 10.1016/j.ijhydene.2012.05.155.* - http://hal.archives-ouvertes.fr/hal-00753331
- **Investigation of Pd-based electrocatalysts for oxygen reduction in PEMFCs operating under automotive conditions**, A. Stassi, I. Gatto; V. Baglio; E. Passalacqua; A.S. Arico', DOI: CNR-ITAE, Messina, Italy *Journal of Power Sources* (2013) 390-399 – DOI: 10.1016/j.jpowsour.2012.09.002 - http://hal.archives-ouvertes.fr/hal-00753342
- **Oxide-supported PtCo alloy catalyst for intermediate temperature polymer electrolyte fuel cells,** A. Stassi, I. Gatto, V. Baglio, E. Passalacqua, A. S. Aricò**,** CNR-ITAE, Messina, Italy, *Applied Catalysis B: Environmental*, Volumes 142–143, October–November 2013, Pages 15–24 – DOI: 10.1016/j.apcatb.2013.05.008 - http://hal.archives-ouvertes.fr/hal-00845171

- **Block selective grafting of poly(vinylphosphonic acid) from aromatic multiblock copolymers for nanostructured electrolyte membranes,** A. Sannigrahi, S. Takamuku and P. Jannasch , ULund, *Polym. Chem., 2013,* **4**, 4207-4218- DOI: 10.1039/C3PY00513E - http://hal.archives-ouvertes.fr/ hal-00845189

- **Dopant-driven architectures of nanostructured SnO2: from dense to "loose-tube" fibers,** S. Cavaliere, S. Subianto, I. Savych, M. Tillard, D. J. Jones, and J. Rozière, CNRS, France, *J. Phys. Chem. C, 2013, 117 (36), pp 18298–18307 - DOI: 10.1021/jp404570d - http://hal.archives-ouvertes.fr/hal-00903703 (open access in November 2014)*

- **Poly(tetrafluorostyrenephosphonic acid) block copolymers for proton conducting electrolyte membranes,** Z. Shao, A. Sannigrahi, P. Jannasch, ULund, *Journal of Polymer Science Part A: Polymer Chemistr,* Volume 51, Issue 21, pages 4657–4666, 1 November 2013 – DOI: 10.1002/pola.26887 -*http://hal.archives-ouvertes.fr/ hal- 00904746*

- **Well-defined phosphonated polymers via direct ring opening metathesis polymerization**, B. Bingöl, C. Rosenauer, P. Jannasch, ULund, *Polymer*, *Available online 15 October 2013 – DOI: http://dx.doi.org/10.1016/j.polymer.2013.10.018 - http://hal.archives-ouvertes.fr/hal-00904767*

#### 4.1.2.5 Proceedings

1. **Proton-conducting phosphonated frameworks**. J. Wegener, A. Kaltbeitzel, G. Glaber, R. Graf, M. Klapper, K. Müllen, Max-Planck-Institute for Polymer Research, Mainz. Germany, *Prepr. Pap.-Am. Chem. Soc., Div. Energy Fuels* 2013*, 58 (2), xxxx*

2. **Phosphonic acid-functionalized polymers vs. phosphonated small molecules: David vs. Goliath?** M. Klapper, J. Wegener, L. Jiménez-Garcia, A. Kaltbeitzel, K. Müllen, Max-Planck-Institute for Polymer Research, Mainz. Germany, *Prepr. Pap. Am. Chem. Soc., Div. Energy Fuels* 2013*, 58 (2), xxx*

#### 4.1.2.6 Education actions & brochure

Eight education actions towards non-specialist scientists (general public and schools) have been undertaken by the consortium. They mainly promote and explain the importance of the move to alternative energy sources, the role to be played by hydrogen as an energy carrier, and the role of fuel cells. A leaflet presenting the consortium activities for a more specialised public has also been released.

#### 4.1.2.7 List of Education actions

1. **International Renewable Energies, Energaïa exhibition, Montpellier, France, 8 – 11 December 2010,** *Scientific stakes for tomorrow energies* - Deborah Jones, ICGM, Montpellier, France.
   This is an annual international exhibition on all renewable energies with participation and attendance by industry and research. A scientific programme aimed at an interested and energy-aware but non-specialist general public runs alongside the exhibition, and the above lecture was delivered in this context. CNRS-Université Montpellier 2 also participated in the exhibition to explain fuel cells through a series of small demonstrators including hands-on experiments.

2. **Master of Renewable Energy and Energy Saving Technologies (Master T.E.R.R.E.), University of Messina, Italy, 25-26 November 2011**, Lectures to graduate students on *the hydrogen production, from renewable sources and not, for use in fuel cell*, - S. Siracusano, CNR-ITAE, Messina, Italy

3. **International Renewable Energies, Energaïa exhibition, Montpellier, France, 7 – 9 December 2011**, *Presentation of the UM2 Masters degree in Energy: Sources/resources, conversion, storage and energy management* – Deborah Jones, ICGM, Montpellier, France. Université Montpellier 2 opened a two-year Masters course in *Energy: Sources/resources, conversion, storage and energy management* in 2011 and the year 1 students developed a project around an energy technology and manned a booth with small demonstrators during this exhibition.

4. **International Renewable energies exhibition, Energaïa, Montpellier, france, 7 – 9 December 2011**, *Fuel Cells Challenges & Progress* – J. Bernard d'Arbigny, ICGM, Montpellier, France.

This lecture was delivered as part of the general public oriented scientific programme of this Energaïa exhibition.

5. **Master Energy – (**http://www.master-energie.univ-montp2.fr**), Montpellier, France, 2011-2012,** Lecture course on *Hydrogen generation & storage* – Jacques Rozière, ICGM, Montpellier, France.
   This is a lecture course run within the Masters course on *Energy: Sources/resources, conversion, storage and energy management* - 250 hours, 30 students annually.

6. **UM2 open days – Montpellier, France, 3 March 2012,** *Visit & explanation of the Fuel Cell Experimental Platform* at University Montpellier 2 – Y. Nedellec & M. Dupont, ICGM, Montpellier, France.
   The Fuel Cell Experimental Platform was opened up to the general public as part of the University Open Day. This kind of event generates a lot of local interest in novel energy technologies, hydrogen and fuel cells in particular.

7. **Future Materials – University of Lund, Sweden, 3 September 2012,** Polymers for new energy and clean water – P. Jannasch, University of Lund, Sweden;
   The lecture series "Future Materials" was aimed at high school and undergraduate students to arouse their interest into science in general and material science in particular. The talk was given 4 times on Sept. 3. to approximately 400 students.

8. **Secondary schools (5$^{th}$-12$^{th}$ grade) – Mainz, Germany - from 2010 to 2012,** Markus Klapper (MPIP, Mainz, Germany) teaches frequently in secondary schools (5th-12th grade) in the local area of Mainz.
   The focus is to demonstrate how modern research is done at the university and in research centres to attract young people to study chemistry for modern energy technologies, especially polymers for fuel cells.
   *Examples of some secondary schools are Otto-Schott-Gymnasium, Maria-Ward-Gymnasium, Mainz, berufsbildendes Gymnasium, Mainz and Gutenberg-Gymnasium, Mainz.*

#### 4.1.2.8 Brochure

To focus more on dissemination towards academic and industrial fuel cell specialists, according to the direction advised during the mid-term review meeting by the reviewers and the project officer, a leaflet presenting QUASIDRY objectives, consortium and output has been prepared by PXO & CNRS (figure 2). This brochure has been circulated among the partners for their feedback and then printed and made available for distribution during conferences, workshops … This brochure is also available for download from the QUASIDRY public web site *(http://www.quasidry.eu/publications.html - bro)* .

### 4.1.3 Dissemination Material

The visual identity of the QUASIDRY project has been assured at conferences, workshops, meetings etc., by the use of a project logo, presentation template and brochure.

*Quasidry logo*

## 4.2 Future Dissemination and Plans for Use of the Results

### 4.2.1 Future Dissemination

The consortium will be engaged in conducting further activities for promoting and disseminate the project

results. The following measures are planned so far in the near future to follow up the project:

### 4.2.2 QUASIDRY WEBSITE

The QUASIDRY website will be kept as an information source of the activities performed in the project. The website will also continue to receive and publish papers online related to the project. The website will be updated to reflect the current status of the project as finished. Reports and final results will be clearly communicated through relevant news items and reports.

### 4.2.3 JOURNAL PUBLICATIONS

Future academic articles and reports will be produced. This is an important component in the continuation of communicating the results from the research undertaken. Two publications are accepted for publication, and five others are in the course of preparation:

1. **Proton Conductivity in Doped Aluminum Phosphonate Sponges,** J. Wegener, A. Kaltbeitzel, R. Graf, M. Klapper, K. Müllen, *ChemSusChem 2013, DOI 10.1002/cssc.201301055*
2. **On the Effect of Non-Carbon Nanostructured Supports on the Stability of Pt Nanoparticles during Voltage Cycling: a Study of TiO2 Nanofibres**, I. Savych, J. Bernard d'Arbigny, S. Subianto, S. Cavaliere, D. Jones and J. Roziere, CNRS, France, *accepted in J. Power Sources*
3. **Conductivity enhancement in mixed functionality membranes based on sulfonic and phosphonic acids**, N. Donzel, D. Jones, J. Roziere, M. Schuster, P. Jannasch et al, co-authored CNRS, FUMA and ULund, to be submitted to J. Mater. Chem. A,
4. **Pushing back the frontiers of phosphoric acid doped polybenzimidazole membranes. Highly conducting mixed functionality phosphonic/phosphoric acid doped PBI giving exceptional fuel cell performance.** N. Donzel, K. Angjeli, D. Jones, J. Roziere, J. Wegener, M. Klapper, co-authored CNRS and MPIP, to be submitted to Angew. Chem.
5. **Palladium-based electrocatalysts for oxygen reduction and hydrogen oxidation in intermediate temperature polymer electrolyte fuel cells**, CNR-ITAE, Italy, to be submitted to Int. J *Hydrogen Energy*
6. **Optimization of perfluorosulphonic ionomer amount in gas diffusion electrodes for PEMFC operation under automotive conditions**, CNR-ITAE, Italy, to be submitted to Int. *J. Hydrogen Energy*
7. **Electrochemical investigation of mixed functionality membranes for intermediate temperature polymer electrolyte fuel cells**, CNR-ITAE/Partners involved to be submitted to *Fuel Cells*

### 4.2.4 CONFERENCE PRESENTATIONS

Conference presentations will continue to engage QUASIDRY partners. The following two planned attendances are listed below:

1. **Fifth European Fuel Cell Technology & Applications Conference - Piero Lunghi Conference December 11-13, 2013, Rome, Italy**, Palladium-based electrocatalysts for oxygen reduction and hydrogen oxidation in intermediate temperature polymer electrolyte fuel cells, A.S. Aricò, A. Stassi, I. Gatto, G. Monforte, A. Patti, E. Passalacqua and V. Baglio, CNR-ITAE, Messina, Italy
2. **6th Forum on New Materials (CIMTEC 2014), 15-20 June 2014, Montecatini Terme, Italy,** New polymer electrolyte membranes for fuel cells, Lund University, Sweden

### 4.2.5 QUASIDRY BROCHURE

An update of the QUASIDRY brochure including the main non-confidential results and potential impacts will be edited after the agreement of all the partners and will be made available on the public website.

### 4.2.6 EXPLOITATION OF FOREGROUND

Eight exploitable foregrounds have been identified and are listed below (IPR exploitable measures have been and will be taken.

### 4.2.7 FUTURE COLLABORATIONS

The QUASIDRY project work and results has established a solid base for future developments that shall be taken into account in future collaborations.

## 5. PROJECT WEBSITE AND CONTACT INFORMATION


***http://www.quasidry.eu***

### CONTACT INFORMATION :

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