FINAL PUBLISHABLE SUMMARY REPORT

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A. FINAL PUBLISHABLE SUMMARY REPORT

A.1. EXECUTIVE SUMMARY

The clear focus of the Duramet project was on the demonstration of the enhanced performance and durability of newly developed or optimized DMFC components, i.e. catalysts, membranes and MEAs, in single cells and in appropriate stacks with realistic cell area and under practical operation for portable and auxiliary power unit applications.

Specifications and protocols for assessing direct methanol fuel cells components and devices have been delivered and available to the public through the project website (http://www.duramet.eu).

Cost-effective membranes for low temperature operation with improved conductivity and reduced methanol cross-over mainly included sulfonated polysulfone (sPSf) and polyetheretherketone (sPEEK) containing zirconium phosphate filler, new generation perfluorosulfonic acid (PFSA) membranes, mixed functionality membranes comprising PFSA and a long chain phosphonic acid, and composite zirconium phosphate PFSA-based polymers. MEAs based on Fumatech sPEEK and PFSA membranes showed power densities higher than Nafion in the range 60 °C - 90 °C. Such characteristics derived from lower methanol cross-over and suitable area specific resistance. These membranes are characterized by significantly lower polymer cost than Nafion. For the high temperature range, mixed functionality and composite membranes provided a proton conductivity approaching 50 mS cm^{-1} at 120 °C with 50% R.H.

For DMFC electrodes, the focus was on the reduction of noble metal loading to less than 1 mg cm^{-2}. Composite electrocatalysts consisting of a high surface area TiO_2 or IrO_2 and PtRu/C have been developed. The composite electrocatalyst provided an increase of performance of about 20-30 % vs. baseline catalysts. 50 wt.% Pt_3Co_1/C cathodes (3 nm mean particle size) have provided better performance than conventional Pt cathodes. A specific study, aided by atomistic simulations applying both ab-initio density functional (DFT) and classical molecular dynamics to model the structural and electronic properties, has been undertaken to replace Pt with cheaper electrocatalyst formulations including ZrOx, TaOx and metal silicides supported on carbon.

By using the components developed in the project, MEA performances of 30 and 70 mW cm^{-2} using low Pt total MEA loading of 1.5 mg cm^{-2} have been achieved at 30 °C under passive mode and at 60 °C. Using the new generation membranes and a low noble metal loading of 1 mg cm^{-2} a performance of 250 mW cm^{-2} was obtained at 130 °C. A modelling work was carried out to drive the search and optimisation of improved MEAs formulations and stack operating conditions.

Two types of short stacks have been designed and tested. A monopolar configuration operating at low temperature under passive mode for portable applications and a bipolar stack configuration for high temperature operation (10 cells, 100 cm^2 bipolar or 4 cm^2 monopolar configuration, respectively). The ministack operating under passive mode has provided an ouptput power of 1.3 W compared to 1 W project target whereas the bipolar APU stack tested at high temperature has provided an output power of about 200 W compared to 150 W project milestone. The APU stack showed, in a > 500 hrs life-time test, a performance decay less than 5% during operation under mild conditions (~70 °C) using the novel Fumatech PFSA membrane and 100 µV/h/cell voltage decay at T> 100 °C using a CNRS composite sPEEK-ZrP membrane. A scale-up study was carried out to evaluate the impact on the cost of the single components and to estimate costs for mass production.

Dissemination of project results was achieved through various ways including implementation of a dedicated project website (http://www.duramet.eu/), journal publications (> 14 published articles), conference presentations (25 contributions), edition of a brochure and a dedicated workshop on direct alcohol fuel cells held in Montecatini, Tuscany in June 2014 at the CIMTEC conference.

A.2. SUMMARY DESCRIPTION OF PROJECT CONTEXT AND OBJECTIVES

Direct Methanol Fuel Cells (DMFCs) working at low (≤ 60 °C) and intermediate temperatures (up to 130 °C) and employing solid protonic electrolytes have been postulated as suitable systems for power generation in the field of portable power sources, remote and micro-distributed energy generation as well as for auxiliary power units (APU) in stationary and mobile applications.

The main objective of the DURAMET project was to develop cost-effective components for direct methanol fuel cells (DMFCs) with enhanced activity and stability in order to reduce stack costs and improve performance and durability. The project concerned with the development of DMFC components for application in auxiliary power units (APU) as well as for portable systems.

DMFCs utilize liquid fuel to deliver continuous power and they have low fuel storage and handling constraints than hydrogen fuelled fuel cells. These systems are promising candidates for portable electric power sources and auxiliary-power-units because of their high energy density, lightweight, compactness, and simplicity as well as easy and fast recharging. Nevertheless, according to the international state-of-the-art, before this technology can reach a large-scale diffusion, specific problems related to the high cost of fuel cell components and the low performance and stability must be solved.

In particular, in order to be competitive within the portable and distributed energy generation markets, direct methanol fuel cell must be reasonably cheap; they should be characterised by high durability and capable of delivering high power densities.

At present, there are some challenging problems to the development of such systems. These mainly consist of developing:

i) anode electro-catalysts which can effectively enhance the electrode-kinetics of methanol oxidation
ii) electrolyte membranes which have high ionic conductivity and low-methanol/Ru cross-over
iii) methanol-tolerant cathode electro-catalysts with high activity for oxygen reduction.

Furthermore, all aspects related to fuel cell stack development are of particular relevance, in particular, materials and design of cell housing, bipolar plates, gaskets and stack auxiliaries.

All these materials and components contribute to the final characteristics of the practical devices determining their performance, efficiency and cost. Thus, before these technologies can reach a full-scale production, specific problems have to be solved especially the high cost and the short-term stability. All these aspects have been addressed in the project and specific quantitative project milestones have been achieved.

The project has dealt specifically with cost effective and enhanced durability components for high temperature direct methanol fuel cells amenable to be integrated in auxiliary power units, for portable powers sources and in general for applications related to energy supply systems for micro-distributed and remote generation.

The work plan comprised work packages dedicated to the main developmental RTD activities on membranes (WP3), electro-catalysts (WP4), development of membrane- electrodes assemblies (MEAs, WP5) and validation of the novel materials and components in passive mode operation monopolar ministacks and high temperature bipolar stacks (WP6). The focus of WP2 was the development of protocols for materials characterisation, evaluation of MEAs and assessment in stacks under project-specific conditions. WP1 and WP6 were dedicated to project management and to dissemination and use of results, respectively.

The specific topics and objectives covered by the project are summarised in the following:

The objective of the workpacakge dealing with "Specifications" was to define characterisation and test protocols for the assessment of performance and durability of the newly developed DMFC membranes and electro-catalysts, for DMFC MEAs and for DMFC stacks. These protocols were developed with the aim to propose harmonized characterisation and test procedures, common to the DMFC research community, establishing agreed and shared "modus operandi" among different research performing entities. Another objective was dealing with a cost analysis applied to a selected stack configuration.

A work package was aiming at developing "innovative direct methanol fuel cell membranes" for two specific applications i.e. portable and APU uses and corresponding targeted temperatures (up to 60 °C or up to 130° C). The required properties for the new membranes were high proton conductivity at the specific targeted temperatures, low methanol crossover and stability under operation in a wide temperature range. The activities included preparation of the membranes, ex-situ characterization, provision of the most promising formulations to MEA fabrication, scaling up of the most promising membrane formulations for stack testing.

The "catalyst development" workpackage aimed at enhancing the stability, reduce the cost and increase the performance of DMFC electro-catalysts. Specific objectives concerned with:

- Enhancing the reaction rates with respect to the state of art catalyst/ionomer assemblies
- Decrease of oxygen reduction and methanol oxidation overpotentials in the presence of low noble metal loading electrodes.
- Increasing catalyst chemical and electrochemical stability as demonstrated by accelerated stress tests.
- Decreasing cost of catalysts used in DMFCs by developing Pt-free and non-noble metal based catalysts.

The aim of the workpackage dealing with "membrane-electrode assembling" was concerning with the validation in terms of stability and performance of the novel acid functionalised polymer membranes in combination with the enhanced durability catalysts in practical MEAs with reduced noble metal loading under practical operation in single cell at the targeted temperatures. In this regard, the main objective was to demonstrate both performance enhancement and cost decrease for the new developed materials over the baseline components. Another relevant objective of this work-package was to carry a modelling work to drive the search and optimisation of improved MEAs formulations and stack operating conditions.

The aim of the workpackage dealing with "DMFC stacks" was regarding an assessment of the new developed components in verification units i.e. short stacks for testing under realistic operating conditions and validation with respect to the project objectives. The main objective was thus a validation of MEAs in terms of performance and stability in short stacks (10 cells, 100 cm^2 bipolar or 4 cm^2 monopolar configuration, respectively) as proof-of-concept in order to reach the aimed power output at the targeted temperatures of ≥ 100 °C for APU and room temperature, passive mode (ministack) for portable applications. Another important objective of this work-package was to individuate stack designs for low and high temperature operation and carry out stack durability tests.

The objectives of this workpackage were:

- Provide the maximal dissemination of the results and implementation of developed DMFC components in industry by using different information and dissemination tools such as, publications, conference attendances, workshops, project web site, etc.
- Contribute to public understanding of scientific research and technological development in Europe by means of articles and conferences in popular science media. Extension of public dissemination through dedicated website with special efforts in the direction of education and promotion actions.

Development of membrane electro-catalysts and MEAs for direct methanol fuel cells, satisfying the required targets of proper performance and durability by using cost-effective materials such as novel hydrocarbon membranes and low PGM loading electrodes for portable as well as APU applications is a challenging topic. The activities of this project were focused on new cost-effective membranes with better resistance than Nafion to methanol cross-over as well as to the drag of Ru ions. Improved durability electro-catalysts were developed with the aim to reduce costs, degradation and noble metals content. To validate the new membranes and electro-catalysts materials, specific development of membrane-electrode assembly with tailored hydrophobic-hydrophilic electrode characteristics was carried out. The new developed components were thus validated in short stacks to assess their performance and durability under practical operation.

The final target of the project was to demonstrate the newly developed or optimized DMFC components, i.e. catalysts, membranes and MEAs, in single cells and in short stacks. The main quantitative project milestones concerned with the achievement of membrane conductivity better than 50 mS/cm (up to 120 °C) and MeOH cross-over lower than $5x10^{-7}$ $mol.cm^{-2}.min^{-1}$, low overpotentials for anode/cathode reactions (PGM loading ≤1 mg cm^{-2}; ORR overpotential< 0.4 V; MOR overpotential < 0.3 V at 0.125-0.5 A cm^{-2} for low temperature and high temperature operation), and the obtainment of a performance better than 250 mW cm^{-2} for high temperature operation and > 50 mW cm^{-2} for low temperature operation. These targets represent a suitable progress beyond the state-of-the-art (from 20% to 50% better).

The project also aimed to achieve an MEA decay factor of 2-times smaller than benchmark MEAs and validation of the components in short stacks (150 W active mode, 10-cell stack with 100 cm^2 active area, operating above 100 °C and 1 W passive mode, 10-cell stack with 4 cm^2 active area, operating at room temperature) with durability test of at least 500 hrs.

Go/no go decision points for membrane, catalysts and membrane-electrode assembly development were addressed in the project and essentially concerned the achievement of proper protonic conductivity and low methanol cross-over for the membranes at specific operating conditions as well as proper electro-catalytic activity for methanol oxidation and oxygen reduction catalysts (with suitable methanol tolerance for the latter) and appropriate MEA performance and stability.

The second set of decision points for stack demonstration was concerning with MEA performance results in single cell. The achievement of quantitative milestones for the membrane/electro-catalysts and an appropriate MEA development have led to successful MEA performance results in line or better than the project targets. MEA performance stability test were promising and in line with the specific project milestone.

Aspects dealing with the choice of bipolar plate design and MEA configuration for high temperature operation has initially introduced some risks regarding durability. These were addressed by the use of a 7-layer MEA configuration equipped with proper high temperature resistant sub-gaskets.

The achieved performance for the passive mode operation ministack and APU stack were in line with the project targets.

Duramet was addressing the FCH-JU MAIP, Application area: Early Markets. This application area aimed to develop and deploy a range of fuel cell-based products capable of entering the market in the near term. The main goal was to show the technology readiness of portable and micro fuel cells for various applications; portable generators, back-up power, assisted power units (APU) and UPS-systems etc.

A.3. DESCRIPTION OF THE MAIN S&T RESULTS/FOREGROUNDS

I. WP1. PROJECT MANAGEMENT – WPL: CNR-ITAE

The activity of WP1-Project management was essentially addressed to provide efficient project coordination and management to support the partners in their achievement of the project objectives, to interface with the FCH JU and to provide tools for communication between partners inside the consortium. This was achieved by the development of web-based tools (Intranet), as well as representing the project to outside audiences through the public web site (http://www.DURAMET.eu).

The coordination activity has been specifically addressed to ensure that each of the technical work packages started effectively and in a timely manner, so as to avoid any delays with respect to the project schedule.

Significant efforts were addressed to allow completion and submission of all deliverables due by the end of the project as well as to the achievements of the general objectives of the project and the specific milestones.

The project rapidly acquired a public face through the implementation of the project website, as well as a user-friendly and highly efficient shared workspace where project documents are uploaded and stored. These sites are maintained and updated on a continuous basis.

Steering committee and technical progress meetings have been attended by the partners (a list of these meetings and the relative agendas are reported at the end), with active participation and discussion especially in relation to protocols, methods, activities, results, achievements and dissemination.

No deviations or changes have been occurred in the Consortium. Some experimental activities e.g. those dealing with stack durability studies and high temperature stack testing were continued also after M36 to fully achieve the project milestones. At the end of the project all main objectives have been achieved.

The coordinator has represented the project at international conferences, in particular at the FCH-JU review days 2012, 2013, 2014.

II. WP2. SPECIFICATION, PROTOCOLS & TESTING – WPL: FUMATECH

In the framework of the Duramet project, specifications and protocols (WP2) for assessing direct methanol fuel cells components and devices such as membranes, catalysts, MEAs and stacks have been delivered. This allowed to correlate of the observed electrochemical characteristics with physicochemical properties of membrane, catalysts and MEAs. The selected procedures allowed to assess the achievement of project milestones and validate the developed materials in stack devices. The protocols allowed to compare properly the results achieved in different laboratories or dealing with different materials and components as well as a comparison with baseline materials identified the project.

Deliverables dealing with specifications and protocols are available to the public through the project web-site (http://www.duramet.eu). Characterisation and testing protocols for ex situ and in situ characterisation of innovative membranes, catalysts and supports, MEAs and stacks have been defined in Workpackage 2. In particular, these protocols allow for a comparison of characterisation data between the partners, and enable a homogeneous screening and evaluation of the newly developed components. Baseline components have been identified against which progress was assessed.

During the second reporting period, WP2 activities were further addressed to apply the procedures and protocols to the down-selected components and devices and adapt protocols to specific instrumentation in the different laboratories.

Specification of membrane characteristics, e.g. appropriate thickness to achieve a good compromise in terms of low ohmic resistance and cross-over, was addressed. Catalyst loading, and catalysts amounts for provision to WP4 for MEA development were determined.

The physicochemical characterisation procedures and methodologies for assessing the main properties of large area membranes and large batch catalysts down-selected for application in practical DMFC stacks were used. These mainly included proton conductivity, permeation tests, swelling and mechanical measurements on the membranes, diagnostic techniques for catalysts such as cyclic voltammetry, polarisation curves, rotating disc electrode experiments and ac-impedance spectroscopy measurements. Electrochemical characterisation protocols regarded the determination of electrocatalytic parameters such as electrochemical active surface area, Tafel slopes, polarisation resistance. Accelerated stress test protocols such as potential cycling supported by ex situ post-test analysis allowed to evaluate the degradation of membrane and catalysts.

The characterisation and test protocols were applied to the membrane-electrode assemblies prepared using the down-selected catalysts and membrane formulations as well as to the different MEA configurations e.g. 5-layers or 7-layers. The assessment of results allowed for a down selection of the most promising MEAs for validation in a low temperature monopolar stack and high temperature bipolar stacks. Protocols mainly included steady-state, accelerated durability tests and freezing / thawing cycling as well as performance evaluation in relation to the specific applications.

Cross-comparison of MEA performance using the novel Duramet components was carried out in various laboratories.

Stack characterisation and test protocols were applied during the second phase to low temperature monopolar stack and high temperature bipolar stacks.

Protocols mainly included performance and life-time (durability) assessment of DMFC stacks. Polarization tests (voltage vs. current density or j-V) and electrochemical impedance (EIS) measurements at beginning of test (BoT), and end of test (EoT) were carried out. Post operation analysis was conducted according to a failure analysis procedure to identify the causes of premature stack failure. This was particularly useful when a specific MEA configuration (5-layers) was used in the stack. The ex-situ failure analysis procedure allowed the identification of the problem and the implementation of an improved MEA configuration (7-layers) that allowed to reach the durability targets.

A cost analysis for the laboratory DMFC stack prototype was carried out within this WP (CRF). This regarded essentially an analysis of prototype costs and it was not dealing with the cost estimates for series production. The latter are treated in WP6.

The Duramet prototype was compared in terms of costs with a prototype ideally assembled with commercial materials representing the state of the art of the DMFC technology. Particular attention was addressed to the analysis of cost saving by effect of the new materials developed in the project. This analysis was essentially addressed to laboratory prototypes whereas scale factors related to mass production have been analysed in WP6.

The DMFC stack architectures taken into consideration in the cost analysis were a bipolar stack made of ten cells assembled in series, and a monopolar stack composed by two strings of 5 cells (10 cells in total) connected in parallel configuration. The first stack configuration was operating in the active mode while the monopolar stack was working in passive mode.

The impact of the single stack component on the overall cost was assessed for both commercial and Duramet components as reported in Figure II–1. The cost savings for the Duramet materials compared to commercial state of the art components are corresponding to 37% for the bipolar stack and 22% for the monopolar stack. The two main components of the MEA (excluding GDL) i.e. catalysts and membranes represent a consistent part of the total cost of the stack. The impact of the MEA on the overall cost is lower for the passive mode operation ministack than the APU bipolar stack.

Thus, with regard to the bipolar stack, cost savings for the prototype are almost entirely due to the following components:

1. Lower loading of noble-metal catalysts in electrodes (both anode and cathode) or catalytic layers (CCM).
2. Supported catalysts with higher catalytic activity.
3. The membrane cost saving is about 89%, this because the new membrane developed has a thickness almost about one third of that of a benchmark commercial Nafion 115 membrane; the latter is characterised by even larger methanol permeation. Moreover also the base material is cheaper than Nafion.

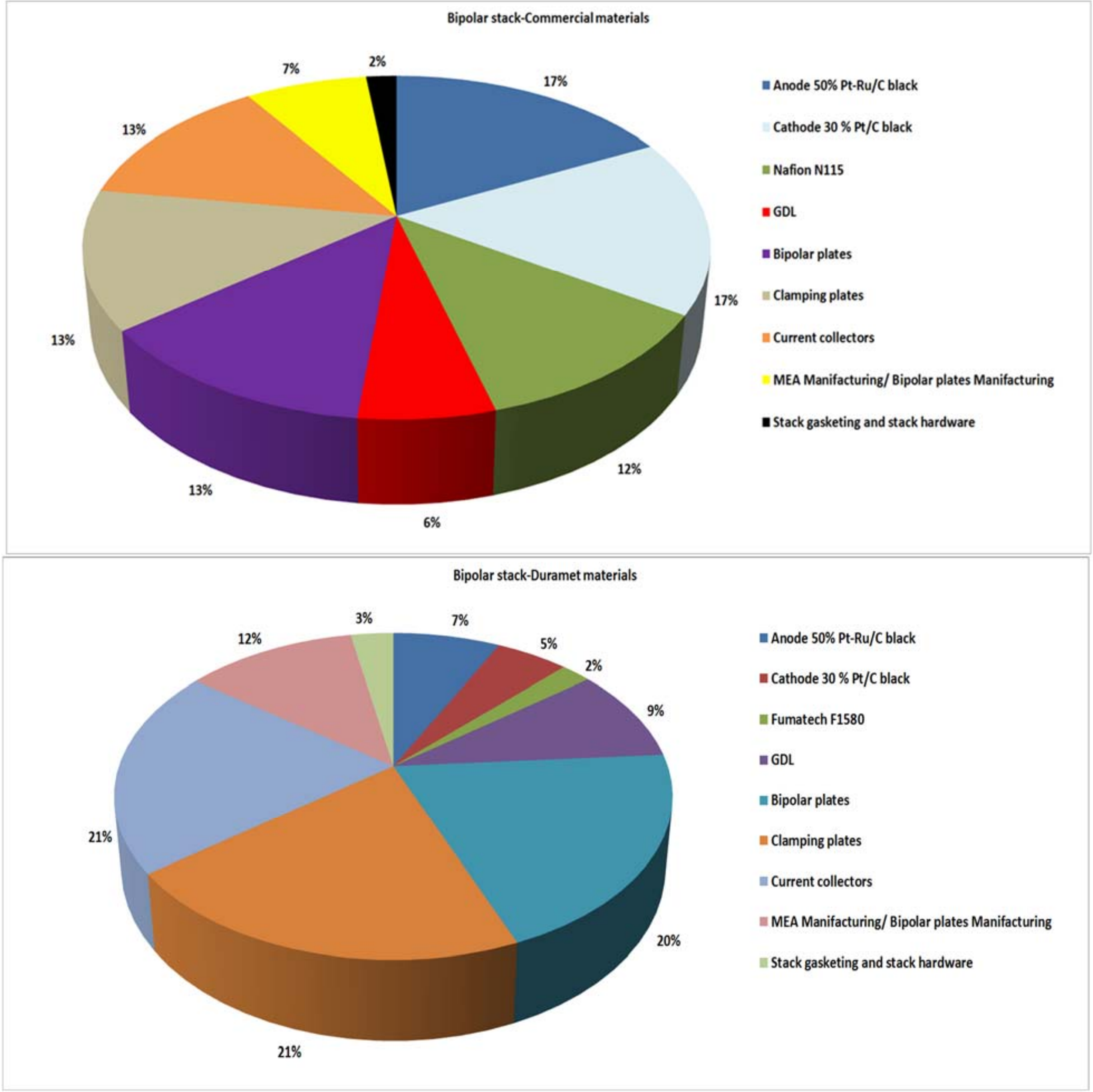


***Figure II–1**: Cost analysis of DMFC stack components at the prototype level (CRF)*

With regard to the monopolar stack, miniaturisation or compact volume requirements for portable applications always cause a strong influence on cost of the hardware components and design. Of course the major cost savings for the monopolar passive mode stack compared to the bipolar active mode stack would be in terms of Balance of Plant.

Summary output from WP2

Characterisation and test protocols have been defined in WP2 for the assessment of performance and durability of the newly developed DMFC membranes and electrocatalysts for DMFC MEAs and for DMFC stacks. Protocols have been applied especially during the second phase of the Duramet project to the down-selected components and devices. A cost analysis for the laboratory prototypes was made during the second phase on the most promising stack configurations. The cost savings for the Duramet materials compared to commercial state of the art components are corresponding to 37% for the bipolar stack and 22% for the monopolar stack. The two main components of the MEA (excluding GDL) i.e. catalysts and membranes represent a consistent part of the total cost of the stack. The impact of the MEA on the overall cost is lower for the passive mode operation ministack than the APU bipolar stack.

III. WP3 INNOVATIVE MEMBRANES - WPL: CNRS

In the first phase of the project, a significant number of polymer electrolytes (WP3) have been developed at CNRS and Fumatech varying in terms of composition, equivalent weight, thickness, filler and reinforcement. There was also a small contribution of CNR-ITAE to this activity. The developed membranes include, beside those indicated in the DoW, also other promising polymer electrolytes which during the execution of the project activities appeared to be characterised by properties that could match properly the aims and milestones of the project. The developed membranes are essentially hydrocarbon membranes such as sulfonated polysulfone (including silica fillers) and sulfonated polyetheretherketone containing zirconium phosphate filler, new generation perfluorosulfonic acid membranes different from Nafion, mixed functionality membranes comprising PFSA (sulfonic acid component) and a long chain phosphonic acid, and composite zirconium phosphate PFSA-based polymers. All materials have been screened in terms of proton conductivity, methanol cross-over, mechanical and hydrolytic stability. Interesting relationships were obtained and provided a guideline to predict which level of performance may be achieved in the DMFC providing that the mechanical and interfacial properties are appropriate. The activity of the first period on WP3 was essentially addressed the screening of the most promising membranes, on the basis of the relevant properties individuated in WP2, that were validated in short stacks in the second phase of the project. The main conclusions are summarized below:

Membranes developed at Fumatech showed promising characteristics for DMFC applications. Among these, the down-selected sulfonated polyetheretherketone E-730 FUMATECH has several advantages compared to Nafion:

- The power densities achieved with E-730 based MEAs are similar or higher than Nafion 115-based MEAs in the range 60 °C - 90 °C as confirmed by three different laboratories within the Consortium (about 77 mW cm^{-2} as compared to 64 mW cm^{-2} at 60 °C on a low catalyst loading basis). Such characteristics are the result the lower methanol cross-over (47 mA cm^{-2} for E-730 vs. 120 mA cm^{-2} Eq. Curr. Dens. for Nafion 115 at 60°C) and suitable area specific resistance (0.15 Ohm cm^2 for E-730 vs. 0.22 Ohm cm^2 for Nafion 115) properties.
- Lower cross-over for the E-730 despite the much lower thickness resulting in a better fuel utilization and higher energy density
- Significantly lower polymer cost for E-730 than Nafion. E-730 consists in a cheap hydrocarbon membrane (PEEK), no fluorine chemistry is involved, obtained by a cost-effective process instead of the

perfluorinated Nafion membrane; the lower cost is also associated to the much lower amount of polymer used in the cell due to the low thickness.

Also the sulfonated polysulfone hydrocarbon membranes showed good characteristics for low temperature operation especially low cros-over (6 mA cm^{-2} and 20 mA cm^{-2} Eq. Curr. Dens. at 30 °C and 60 °C, respectively) approaching the project target.

Fumatech membrane F-1850 was very promising and potentially can cover a wide range of operating temperatures (up to 130 °C) as assessed in different laboratories. This membrane is also reasonably cheap even if based on PFSA. The F-1850 is also down selected due to its novelty and its expected robustness. In particular, for high temperature applications, F-1850 has provided the highest power density at 120 °C in the presence of high catalyst loading on both air (214 mW cm^{-2}) and oxygen (357 mW cm^{-2}). Increase in thickness from 50 to 120 µm had a strongly detrimental effect. As a blend membrane, F-1850 already provides a cost advantage over non-blended PFSA (Nafion etc.). Regarding high temperature operation, also sulfonated PEEK-ZrP composite membranes (CNRS) have shown suitable properties and good performance in MEA testing. According to the screening activity carried out in the first period essentially two membranes for the low temperature and another two for the high temperature were individuated with specific advantages over the benchmark membrane. Composite polyphosphonic acid membranes which represented an important topic of this project have revealed interesting performances at intermediate temperature but more work appeared necessary to improve their stability for DMFC application.

A scaling-up production of down-selected membranes was carried out; these were provided for membrane-electrode assembly manufacturing and integrated in bipolar and monopolar DMFC stacks.

Regarding membrane scale-up, at Fumatech, selection, production capability and supply of the most promising polymer and membrane materials was carried out. Two most promising concepts have been selected for further evaluation in stack testing and for assessment of scale-up capability. These approaches are (1) the high-equivalent weight PFSA membrane (fumapem® F-1850) and (2) the hydrocarbon membrane based on sPEEK (fumapem® E-730). Both approaches have been considered for optimization in terms of thickness variation, production process and activation procedure (Figure III–1). Furthermore, one approach using ZrP / sPEEK composite has been considered for an additional assessment for high temperature DMFC application.

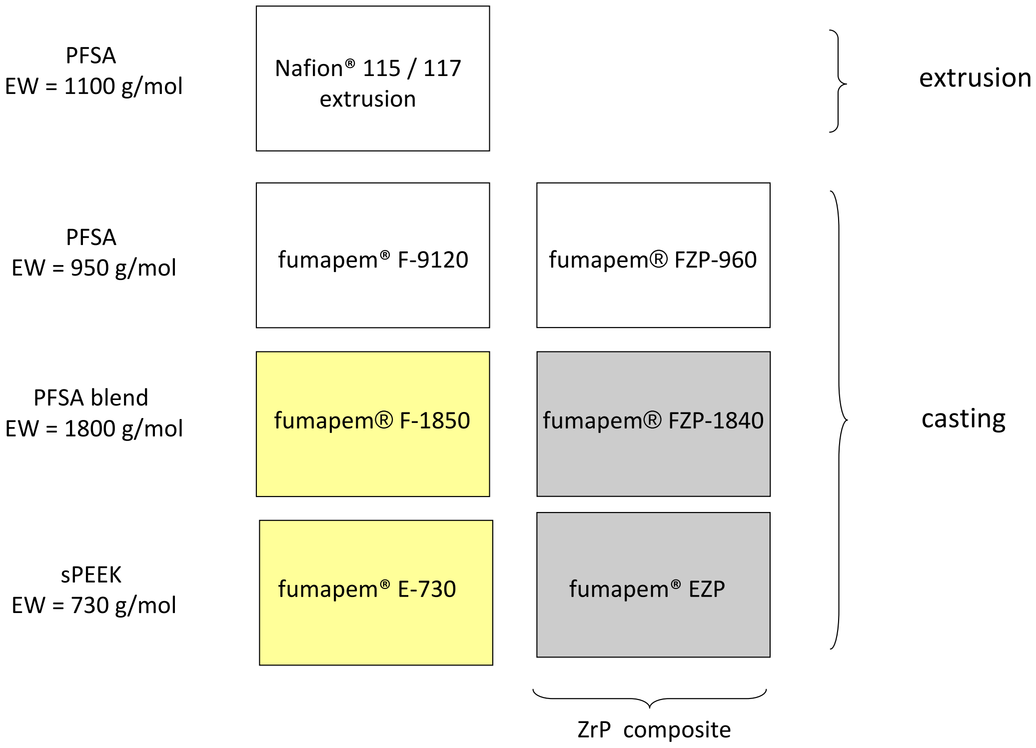


Figure III–1: **Down selection of membranes from FUMATECH: Yellow = Down-selected membranes, grey = composite membranes yet under consideration, in particular the fumapem® EZP membrane.**

Key features of fumapem® 1850 are the reduced area resistance while maintaining methanol permeation low (close to Nafion® 115) – resulting in comparable or even better DMFC performance than for Nafion® 115. However, most important is the fact that fumapem® F-1850 has the potential to reduce material cost by a factor of 4 compared to Nafion® 115. In total, more than 200 linear meter (width 50 cm, > 100 m^2) was produced, some sqm of Fumapem® F-1850 have been delivered to project partners, in particular to IRD for MEA fabrication and stack testing (Figure III–2).

Figure III–2**:** ***Membrane roll of fumapem® F-1850 (length 38 m, width 50 cm, Lot No M24731312) on white PET foil as backing.***

The assessment of the production reproducibility and membrane quality has been carried out in terms of thickness variations and other properties such as conductivity, swelling and mechanical properties. Different polymer batches have been used and production parameters have been optimized. Different activation times and conditions as well as storage conditions have been assessed.

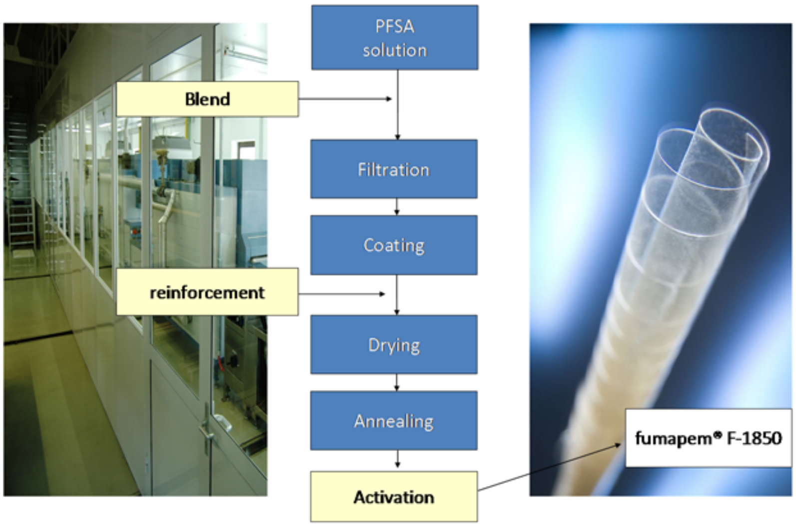


Figure III–3: Membrane production scale-up process at Fumatech

Sulfonated PEEK-ZrP composite membranes for lower cost and reduced methanol cross-over were selected for high temperature application (CNRS). Furthermore sPEEK-ZrP are low cost membranes compared to PFSA obtained by a facile and reproducible preparation method and appropriate for scale up.

Hybrid (composite) membranes based on sulfonated PEEK (sPEEK) have been developed at CNRS using sPEEK of IEC 1.35 meq/g provided by FuMA-Tech. The method followed was that of membrane casting from a multicomponent solution of sPEEK and an appropriate zirconium precursor (zirconyl propionate), followed by phosphoric acid treatment of the cast membrane. sPEEK-ZrP membranes were prepared according to the following procedure developed at CNRS:

- sPEEK polymer of IEC 1.35 meq/g was converted to the Na form by immersing it in 0.5 M NaCl for 24 h.
- The sPEEK-Na was dissolved in DMAc at 80 ° C for 2 h.
- Separately, zirconyl propionate powder was dissolved in DMAc at room temperature for 2 h
- Afterward, the two solutions were mixed and kept under stirring at 80 ° C for 2 h.
- The mixed solution was then concentrated (to 15 wt%) and cast on a glass plate using doctor blading. The cast membrane was allowed to dry in the oven overnight at 80 °C.
- The membrane was removed from the glass plate and immersed directly in 1M H_3PO_4 at 80 ° C for 15h. The phosphoric acid reacts with the zirconium hydroxyoxide in the membrane to form zirconium hydrogen phosphate (ZrP).
- The membrane was washed using deionized water to eliminate unreacted phosphoric acid.
- Figure III–4 is a schematic diagram of the typical fabrication process leading to sPEEK-ZrP membranes (CNRS).

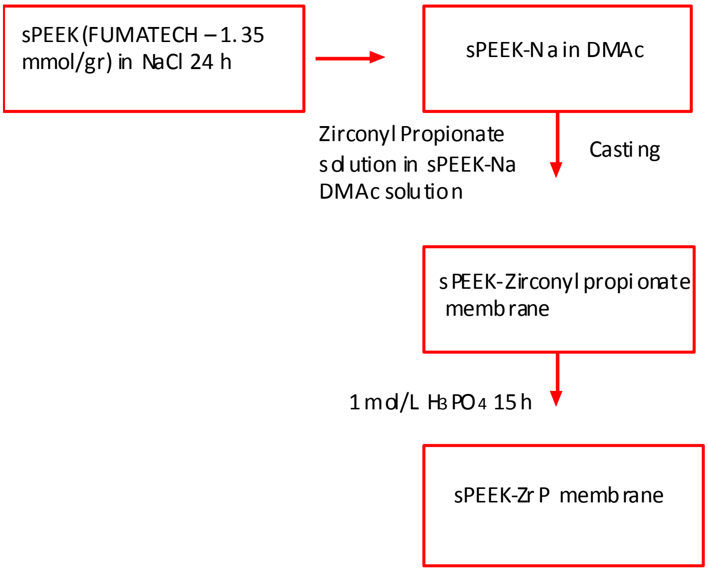


***Figure III–4*: sPEEK-ZrP membrane preparation method developed at CNRS**

The conductivity of sPEEK-ZrP membrane at 120 °C and 95 % RH is 43 mS/cm which is comparable to the target of the 50 mS/ cm at 120 °C (Table III–1)

***Table III–1*: *Proton conductivity of sPEEK-ZrP at 95 % RH*.**

Parameter	Units	sPEEK-ZrP
Proton conductivity	mS/cm @ 80 ° C	25
Proton conductivity	mS/cm @90° C	32
Proton conductivity	mS/cm @100° C	36
Proton conductivity	mS/cm @120° C	43

CNRS has produced thirteen sPEEK-ZrP membranes with the above properties with average dimension 12 x 12 cm^2. The membranes were delivered to IRD Fuel Cells for MEA fabrication.

Figure III–5 includes a comparison of methanol cross-over values among the membranes developed within the DURAMET project and the commercial Nafion 115. The cross-over increased in the order SPSf < E-730 < sPEEK-ZrP < F-1850 < Nafion-115.

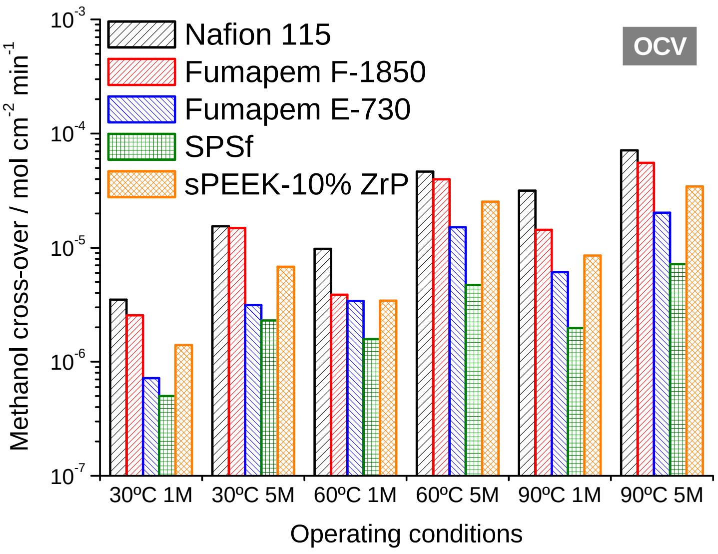
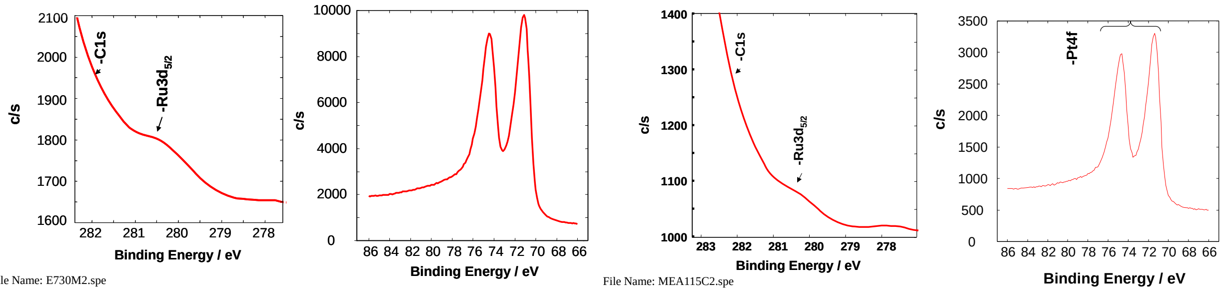


***Figure III–5**: Cross-over of methanol: chart comparison of a selection of membranes in the DURAMET project under different operating conditions and at open circuit voltage (OCV).*

Regarding the reduced Ru ions cross-over, a Ru ions permeation rate for a Duramet membrane lower than a benchmark membrane was registered. The method consisted in an XPS analysis of the cathode surface. The down-selected FUMATECH E730 membrane was assessed against Nafion 115 (benchmark). The electrochemical test was carried out as follows: the anode was fed with MeOH 2 M and operated at 0.5 V RHE for 24 hrs; the cathode was fed with H_2 (counter, ref. Electrode; reduction of Ru ions which have crossed the membrane on the cathode). The cathode/membrane interface was scraped from the MEA and the surface analysed by XPS. Estimation of Ru ions permeation was made from the surface Pt/Ru atomic ratio at the cathode (XPS) (Figure III–6).



File Name: E730M2.spe

File Type: XPS SPECTRUM; Pt cathode - E730

Atomic Concentration Table

Ru3d	Pt4f
[4.529]	[6.080]
0.20	99.80

For E730 FUMATECH
Atomic ratio (Ru ion cross-over)
Ru/Pt=2 10^{-3}

File Name: MEA115C2.spe

File Type: XPS SPECTRUM; Pt cathode - Nafion 115

Atomic Concentration Table

Ru3d	Pt4f
[4.529]	[6.080]
0.30	99.70

For Nafion 115
Atomic ratio (Ru ion cross-over)
Ru/Pt=3 10^{-3}

***Figure III–6**: Ru ions cross-over studies at CNR-ITAE*

Both the milestone regarding membrane conductivity at low (60 °C) and high temperature (120 °C) better than 50 mS cm^{-1} for DMFC applications in portable and APU systems and the milestone dealing with a reduced Ru ion cross-over have been fully achieved (E730 FUMATECH provided a reduction in Ru ions permeation of 33% compared to a Nafion 115 membrane of similar thickness). Whereas, the milestone dealing with reduced methanol cross-over was partially achieved. Room temperature conductivity of the scaled-up F-1850 membrane (a roll of 200 m length) was 58 mS cm^{-1}, the sPEEK-ZrP membrane at 120 °C and 95 % RH showed 43 mS/cm. Mixed functionality membranes based on PFSA polymer (sulfonic acid polymer-bound) and molecular bound phosphonic acids provided~40 mS cm^{-1} at 120 °C at 50% R.H. (AC879). The lowest methanol cross-over rates were registered for the sPEEK E730 and sulphonated polysulfone membrane membranes with 1 M methanol at 30°C i.e. 5-7.x10^{-7} mol cm^{-2} min^{-1} comparable to the target. The cross-over of the down-selected E-730, sPEEK-ZrP was 5-7.x10^{-7} mol cm^{-2} min^{-1} under same conditions. The down-selected membranes were characterised, beside suitable conductivity and low-cross-over characteristics by suitable processability for scaling up.

Summary output from WP3

The general scale-up capability for the production of the down-selected membranes has been demonstrated. Several membrane productions of fumapem® F-1850 and E-730 have been conducted in order to assess reproducibility scale-up capability and quality. In total more than 200 linear meter (width 50 cm, > 100 m^2) have been produced. Production parameters have been optimized and some sqm of fumapem® F-1850 and E-730 have been delivered to project partners for MEA fabrication and stack testing. Furthermore, since suitable performance and low cross-over rate were also obtained with the composite sPEEK-ZrP membranes, these have been scaled-up at CNRS and provided to IRD for MEA fabrication. For high temperature operation, the fumapem® F-1850 and composite sPEEK-ZrP were selected. Significantly lower polymer cost than Nafion for cheap hydrocarbon membranes (PEEK) was achieved; a lower cost for F1850 than Nafion 115 is associated to the significantly lower amount of polymer used in the cell due to the lower thickness. Both Fumatech membrane F-1850 and CNRS sPEEK-ZrP also showed good potentialities to cover a wider range of operating temperatures (up to 120-130 °C). The scaled-up membranes were provided for membrane-electrode assembly manufacturing and integrated in bipolar and monopolare DMFC stacks.

E730 FUMATECH provides a reduction in Ru ions permeation of 33% compared to a Nafion 115 membrane of similar thickness.

The successful scale-up of Fumatech F-1850 and CNRS sPEEK-ZrP membranes reaching proper conductivity has contributed to enabling IRD to produce MEAs with DURAMET membranes. The MEAs containing F-1850 and sPEEK-ZrP membranes have been assembled into stacks at CNR-ITAE and the stacks successfully tested at high temperature at CNRS.

IV. WP4 ENHANCED DURABILITY ELECTRO-CATALYSTS – WPL: CNR-ITAE

The activity carried out in Work Package 4 of Duramet project aimed at enhancing the stability, reduce the cost and increase the performance of DMFC electro-catalysts. New catalytic formulations as well as modified conventional electro-catalysts were developed to find appropriate synergisms for enhancing the catalytic activity, improve methanol tolerance and address cost-effectiveness by reducing Pt loading or developing non noble metal formulations. WP4 thus aimed essentially at enhancing the reaction rates with respect to the state of the art catalyst/ionomer assemblies at relevant operating conditions suitable for DMFC application in portable power sources and for auxiliary power units (APU).

The following main research directions have been investigated:

- Stable carbonaceous and non-carbonaceous supports
- Development of noble metal-based Pt and PtRu catalyst formulations, for cathode and anode, respectively, with appropriate structure, particle size and morphology.
- Modification of the above formulations by alloying with non-noble metals (e.g. Co for the cathode) or forming composites with oxide promoters (e.g. PtRu-TiO_2, Pt-WO_3, Pt-IrO_2, Pt-SnO_2) for the anode.
- Development of cost-effective Pd-based electro-catalysts both Pd/C and Pd-alloys decorated with Pt on the surface such as 50% [5% Pt-Pd_3Co_1]/C.

- Assessment of the methanol tolerance for cathode formulations and the capability of the anode electro-catalysts to operate with different methanol concentrations.
- Assessing the oxygen electro-reduction activity in acidic environment of stable non noble metal oxides (e.g. ZrOx/C) and their tolerance to methanol. Interesting alternative catalyst supports such as Ti, Ta, Nb oxides, graphene and tungsten oxide have been tested.
- Establishing baseline components against which progress is assessed.
- Use of computational studies to progress in the knowledge of the physico-chemical properties of the investigated formulations and to support the interpretation of the electrochemical results. Ab-initio density functional (DFT) and classical molecular dynamics were applied to model the structural and electronic properties for cathodic materials such as PtCo and valve metal oxides (Ta_2O_5).

Enhanced cathode reaction rate at low temperature in the presence of methanol cross-over has been fully achieved using carbon supported PtCo alloy formulations with 3 nm particle size and specific Pt enrichment on the surface. At 0.125 A cm^{-2}, 60 °C, a potential of 870 mV vs. RHE corresponding to a total overpotential of 330 mV was recorded for the cathode, in the presence of 2 M methanol fed to the anode causing relevant cross-over (Figure IV–1).

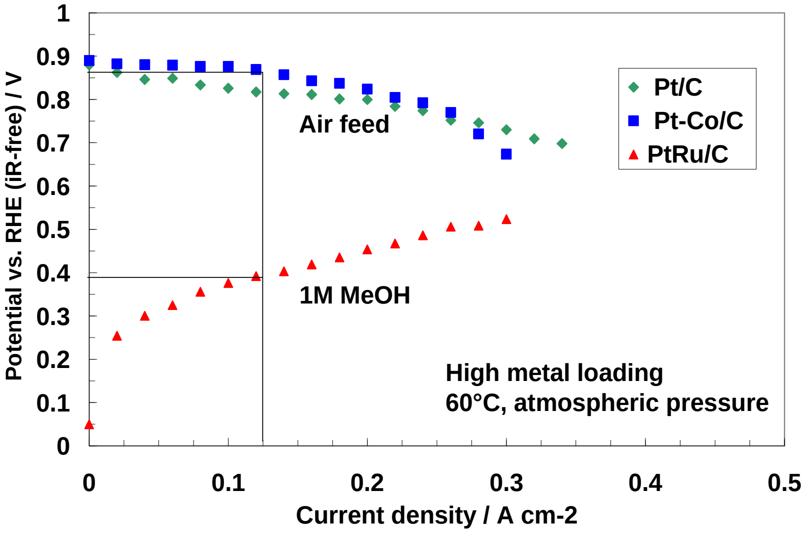


***Figure IV–1**: In situ cathode and anode DMFC polarisation curves (CNR-ITAE)*

Since the aim of the project is to reduce the noble metal loading and catalyst cost, half cell cathode polarisation curves are reported for MEAs with a low catalyst loading i.e. 1 mg cm^{-2} Pt. Specifically, it is compared the performance of the low noble metal loading Pt electrode with that of the Palladium-based electrode (Figure IV–2). In the latter case, the Pt content in the catalyst was 5% wt. corresponding to a content in the electrode of only 50 µg cm^{-2} whereas the Pd content was less than 1 mg cm^{-2} (CNR-ITAE).

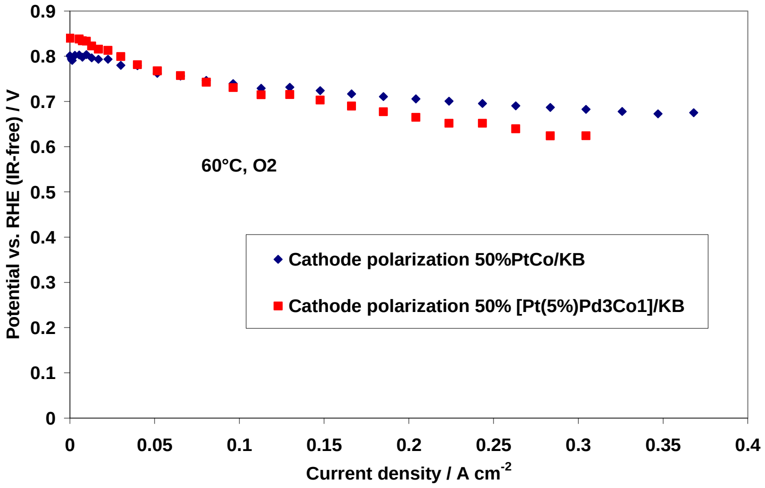


***Figure IV–2**: In situ cathode DMFC polarisation curves at low noble metal loading (1 mg Pt+Pd cm^{-2}). (CNR-ITAE)*

Pd-based catalyst cathode is more tolerant than the Pt-based catalyst to methanol at low current densities. However, when the current density increases and the potential is lower, the capability of the PtCo to interact with methanol is less favoured and oxygen reduction occurs at a higher rate compared to the Pd catalyst. Thus, at high current densities or higher over-potentials PtCo is surpassing in performance the Pd-based catalysts.

An enhanced anode reaction rate at low temperature was achieved using ternary system made of a composite between Pt-Ru alloy (2 nm particle size) supported on carbon and nanosized TiO_2 (280 m^2 g^{-1}). At 0.125 A cm^{-2}, 60 °C, a potential of 370 mV vs. RHE corresponding to a total overpotential of 350 mV was recorded with 2 M methanol (Figure IV–3). At the same current density, a significantly larger noble metal loading was necessary to reach the same performance for the baseline PtRu anode catalyst. The better performance shown by the $PtRu-TiO_2$ appears due to an enhanced interfacial surface area and a promoting effect of the hydrophilic TiO_2 for the activation of the water discharging process, which is one of the rate determining steps for methanol oxidation.

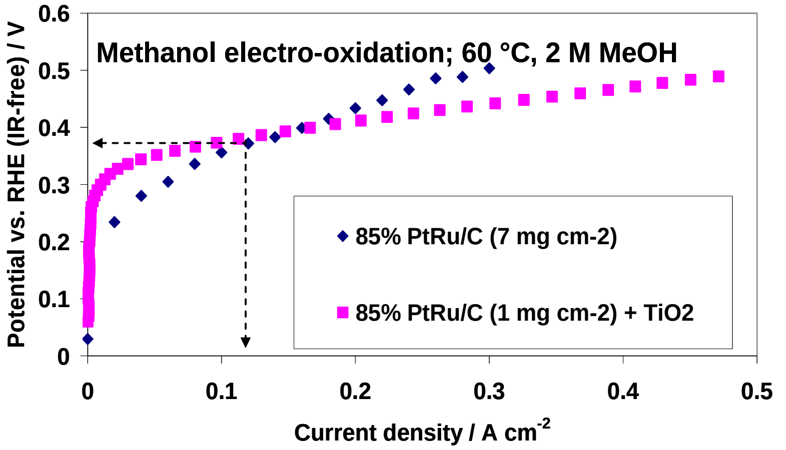


***Figure IV–3**: In situ DMFC anode polarisation curves with low ($PtRu-TiO_2$, 1 mg Pt+Ru cm^{-2}) and high (baseline PtRu, 7 mg Pt+Ru cm^{-2}) noble metal loading. (CNR-ITAE)*

At high currents, due to the mass transport constraints caused by the large thickness of the baseline electrode, the $PtRu-TiO_2$ containing just 1 mg cm^{-2} noble metal loading provided a superior performance.

Regarding the high temperature performance, the single cell polarization curves together with anodic and cathodic contributions (half-cell curves) at 130°C for the down-selected catalysts are reported in Figure IV–4. An oxygen reduction overpotential at 0.5 A cm^{-2} < 0.4 V IR-free, at 2 atm rel., in the presence of methanol cross-over (η ~ 350 mV) was recorded at 130 °C using a PtCo/C electrocatalyst. The anodic polarization curves at 130°C and 2 M methanol, at 2 atm rel show an overpotential for methanol oxidation at the 85% PtRu/C catalyst of about 280 mV (IR-free).

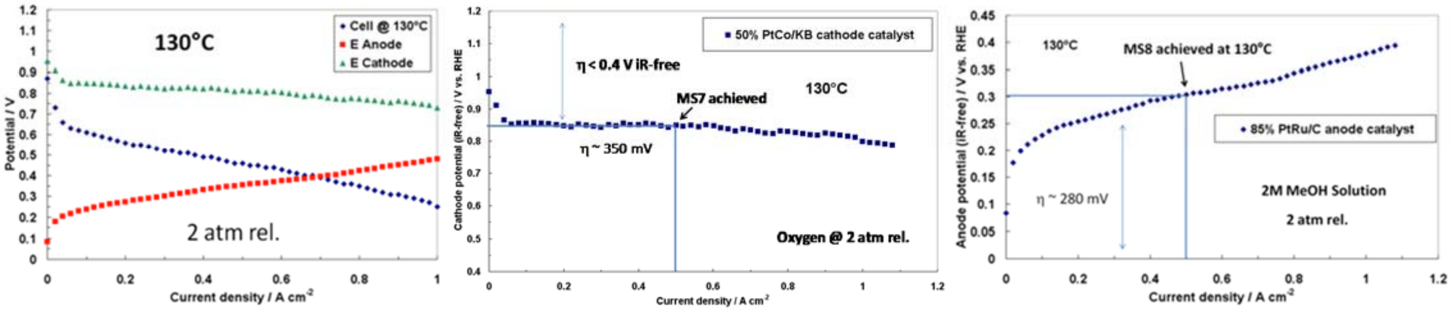


***Figure IV–4**: Half-cell (raw and IR-free) and complete cell polarization curves (anode: 85% PtRu/C; cathode: 50% PtCo/C). (CNR-ITAE)*

Accelerated degradation tests (ADTs), i.e. 10^4 step cycles (steps 0.6-0.9 V, H_2-O_2), were carried out for the cathode at high temperature, i.e. 110 °C, and 33% relative humidity. The anode fed with hydrogen was assumed as a reference electrode and all potential losses were attributed to the cathode that sustained the cycled operation. After the degradation test of 10^4 cycles at 110 °C and 33% R.H., polarization curves were carried out, (Figure IV–5). At 1 A cm^{-2}, the MEA polarization showed a voltage loss of about 30 mV at high temperature when operating at a potential of 0.67 V. The percentage of decay (4.5%) is thus within the 5% loss target.

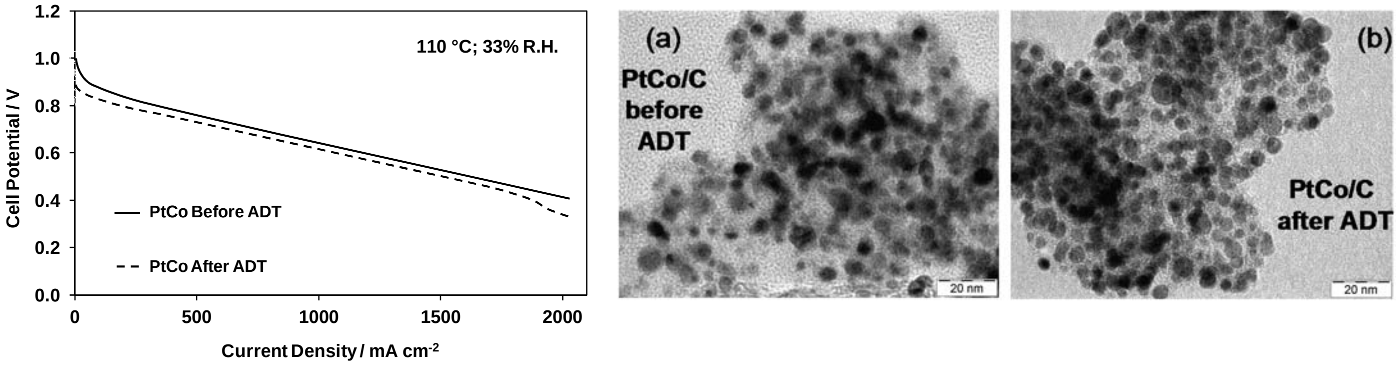


***Figure IV–5**: Comparison of the polarization behaviour before and after ADTs for the carbon-supported 50%PtCo/C electrocatalyst, at 110 °C and 33% RH (H_2-O_2) and TEM related analysis. (CNR-ITAE)*

A comparison of TEM micrographs for the Pt-Co catalyst before and after the accelerated degradation test (with catalysts scraped from the electrodes) is shown in Fig. 12. No significant morphological changes were observed after the ADT. Besides, the mean particle size of the Pt-Co catalyst essentially remained the same as before the ADT.

Also anode stability was demonstrated for the down-selected formulation. Anode Ru ions loss was lower than 5% after 24 hrs potential hold at 0.5 V vs. RHE. Elemental analysis before and after an accelerated electrochemical test at 0.5 V vs. RHE showed a loss of Ru of 0.85 ± 0.1 at. % that is well below the limit of 5 at. % loss planned as target.

For what concerns non noble metal formulations, both ZrOx/C and TaOx/graphene showed promising properties for the oxygen reduction in the presence of methanol and transition metal silicides were explored as anodes (TUM). All these formulations showed excellent stability. In the first phase, most of the focus was addressed to the optimization of non-noble metal ZrO_2/KB catalyst in correlation with its structural-morphological properties (ranging from 3 to 15 nm in particle size). RDE measurements showed a drastically increased catalytic activity towards the ORR at 20°C compared to baseline TaC non-noble-metal catalyst. The best formulation i.e. 12 wt.% ZrO_2/KB showed good activity for the oxygen reduction at 650 mV vs. RHE and spanning a gap of 450 mV at 1 $A/g_{Zr/Pt}$ catalyst when compared to 20 %wt Pt/Vu (Tanaka) (***Figure IV–6***). Afterwards, the aim at TUM was to improve the understanding of the active sites in these valve metal oxide catalysts.

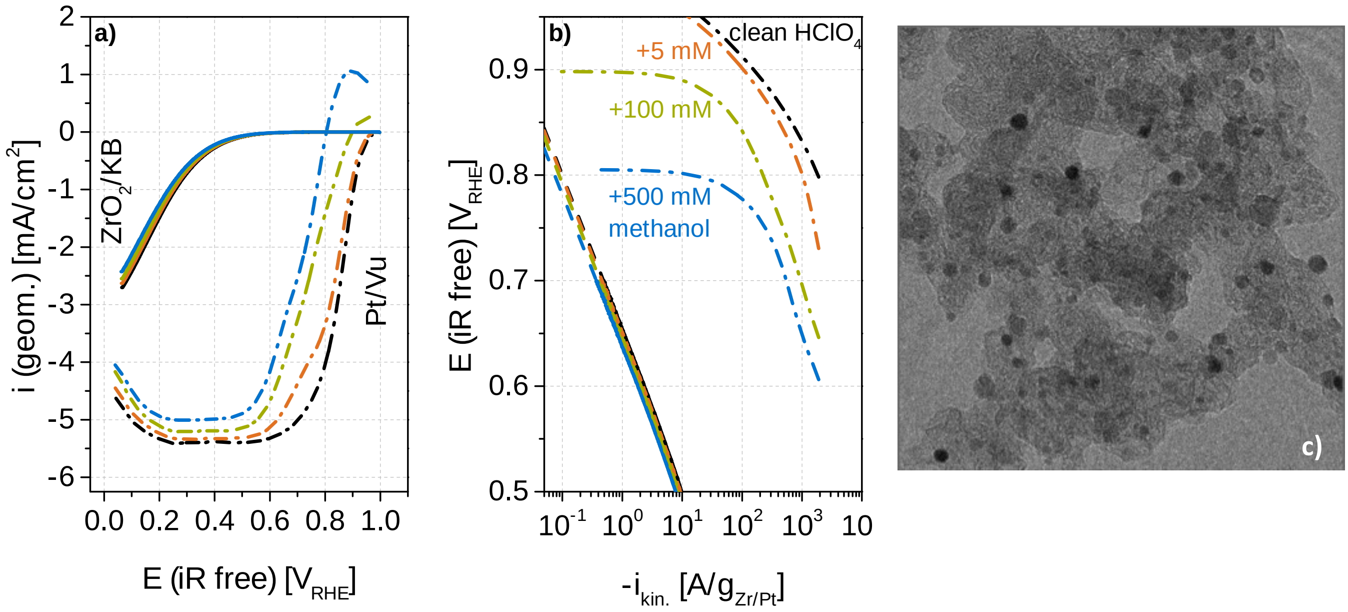


Figure IV–6: RDE measurements of 20 %wt Pt/Vu (TKK) and ZrOPc/KB oxidized at 1000 °C in absence and presence of dilute methanol. a) raw data, b) iR-free potential as a function of the mass-specific kinetic current c) TEM micrograph of a KB-supported, nanometric ZrO_2 heat-treated at 1000°C. (TUM).

In the second phase, a new ORR catalyst formulation based on a sub-stoichiometric sodium tantalate ($Na_2Ta_8O_{21-x}$) characterized by high crystallinity and supported on high surface area (450 m^2 g^{-1}) graphene (50 wt% $Na_2Ta_8O_{21-x}$/graphene) was prepared. This novel formulation is active for the ORR in acid medium, has a remarkably high tolerance to the presence of methanol and good chemical stability with no degradation during potential cycling. Transmission electron microscopy (TEM) images of the graphene-supported tantalate-based catalyst (referred to as TaOx/G900) are reported in Figure *IV–7*.

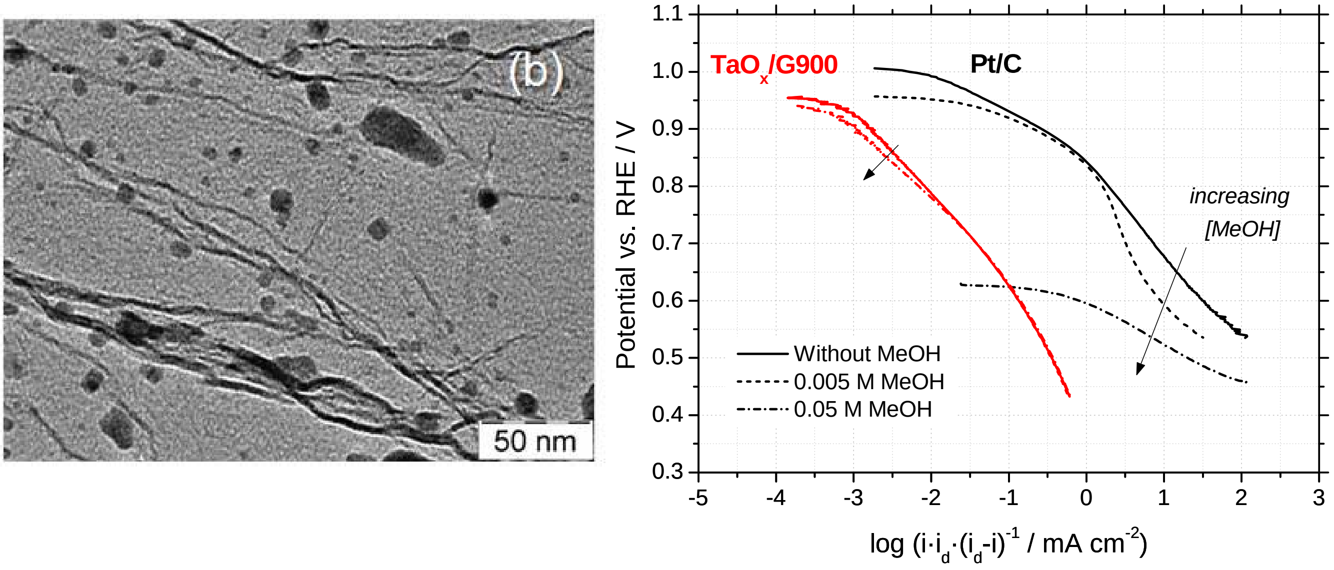


Figure IV–7: TEM micrographs of the TaOx/G900 catalyst; Tafel plot of TaOx/G900 and Pt/C catalysts without and with 0.005 M and 0.05 M methanol (MeOH) at room temperature, 0.5 M H_2SO_4, 50 µg cm^{-2} total catalyst. (CNR-ITAE)

A theoretical increase of catalyst loading for this non-noble metal catalyst up to reach a reasonable electrode thickness (*e.g.* 10 mg cm^{-2} corresponding to 10-20 µm thick catalytic layer) may lead to comparable or even better performance than an ultra-low loading Pt electrode. The latter is required to make low temperature fuel cell as cost-effective power sources. The Ta-based cathode catalyst is not affected at all by the presence of methanol. However, in the presence of the novel Fumatech membranes characterised by much lower cross-over compared to Nafion or in the case of thick Nafion membranes (e.g. Nafion 115 and Nafion 117), Pt-based cathode catalysts are still superior than non-noble metal formulations; for this reason, these Pt-based catalysts were down-selected for large area MEAs and for stack assembling and testing.

Regarding the non noble metal anode performance target, this was not achieved for the metal silicides. In this regard, significant progress is still necessary to approach Pt performance.

Modelling studies regarding specific catalyst structures of oxides and Pt alloys have been made to provide a tool for the interpretation of the electrocatalytic activity at a fundamental level. Atomistic simulations on promising catalysts and supports was carried out by CRF. CRF applied both ab-initio density functional (DFT) and classical molecular dynamics to model the structural and electronic properties for cathodic materials such as PtCo and valve metal oxides (Ta_2O_5). A wide applied open-source simulation code was adopted (e.g. ABINIT, OPENMX and GROMACS). This method contributed to a better understanding of the activity and stability. This approach was used for the non noble metal catalysts and noble metal formulations. The aim of this study was to aid for a rational catalyst design in both cases.

The down-selected cathode formulations for MEA development concerned with nanosized carbon supported Pt and Pd-based alloys, whereas, regarding the anode, enhanced PtRu catalysts containing catalytic enhancers such as TiO_2, IrO_2 were selected. These were produced in amount appropriate for MEAs manufacturing.

Summary output from WP4

Several cathode and anode formulations have been investigated and a down-selection of the most active components has been made. An analysis of the cathode electrocatalyst formulations indicates suitable activity for PtCo alloys supported on carbon. These are promising in terms of performance whereas a Pt-decorated PdCo alloy appears to provide a good compromise in terms of cost-effectiveness, methanol tolerance and catalytic activity. Accelerated stress tests indicated suitable electrochemical stability for the down selected formulations. Regarding the anode, a similar comparative analysis has indicated the TiO_2 modified PtRu catalyst supported on carbon as one of the most appropriate formulations. Possibly, another ternary system Pt-Ru-Ir can also provide relevant results.

An explorative study has been undertaken for non-noble metal cathode catalysts and promising results have been obtained for ZrO_2/KB and TaOx/graphene. The zirconia-based formulation i.e. 12 wt.% ZrO2/KB showed good activity for the oxygen reduction at 600 mV vs.RHE and spanning a gap <500 mV at 1 A/g catalyst when compared to Pt-Black catalyst. TaOx/graphene appeared also very promising especially in terms of methanol tolerance.

Some interesting alternative catalyst supports such as Ti, Ta, Nb oxides, graphene and tungsten oxide have been tested. Oxide materials showed excellent resislience to electrochemical corrosion, however BET surface area and conductivity is not yet approaching the levels obtained for carbon blacks. Pt dispersed on doped Ti-oxide used as cathode provided a modest performance.

Modelling studies regarding specific catalyst structures of oxides and Pt alloys have been made to provide a tool for the interpretation of the electrocatalytic activity at a fundamental level.

V. WP5 VALIDATION OF MEMBRANES AND CATALYSTS IN MEAS - WPL: IRD

The aim of WP5 regarded the validation in terms of stability and performance of the novel membranes in combination with the enhanced durability catalysts in practical MEAs with conventional and reduced noble metal loading. The final objectives concerned with a reduced fuel cell degradation compared to benchmark MEA while maintaining or improving the present levels of power density. MEAs were designed for two applications i.e., portable and APU uses and operating at corresponding targeted temperatures (room temperature up to 60 °C; 100-130 °C). The testing has been focused on MEAs ranging from 4-180 cm^2 active area since different size requirements are due for portable and APU applications.

MEAs based on reference and down selected materials were manufactured by IRD and supplied for stacks using two different configurations 5-layer and 7-layer types. Initially lamination and activation procedures based on a GDE approach were developed at IRD based on the developed membranes; subsequently the CCM approach was used. For an easy handling of the MEAs both during production and stack assembly, it was useful to manufacture the MEA as a 7-layer where a sub gasket is an integrated part of the MEA configuration. The addition of the sub gasket both stabilized the MEA making easier the stack assembling and in addition it served to protect the membrane from mechanical damage from for instance at the edges of the gas diffusion layer (Figure V–1).

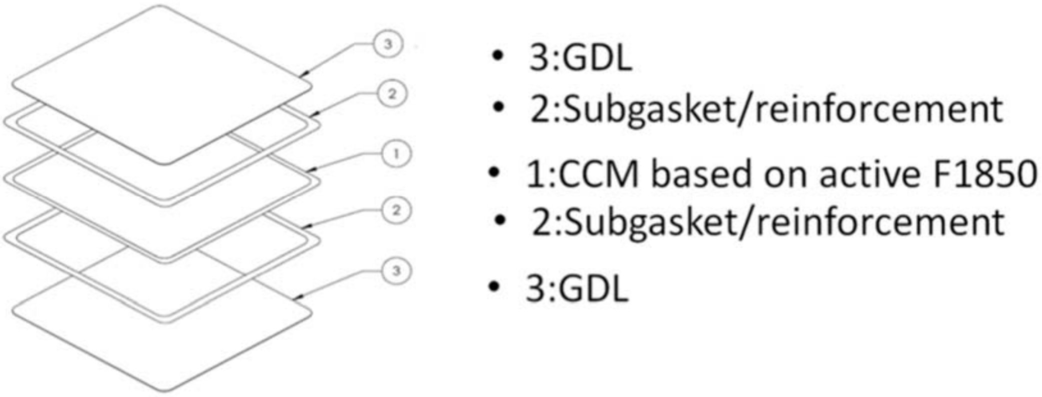


Figure V–1*: *Overview of a typical IRD 7 layer MEA design, based on a catalyst coated membrane, sub-gaskets and GDL's.

Figure V–2*: *Picture of the scaled up IRD 180 cm^2 7-layer DMFC, based on F1850.

MEAs for mini-stack have been prepared at CNR-ITAE using the down selected catalyst and membrane components discussed above. A picture of monopolar MEA configuration and assembling is shown in Figure V–3.

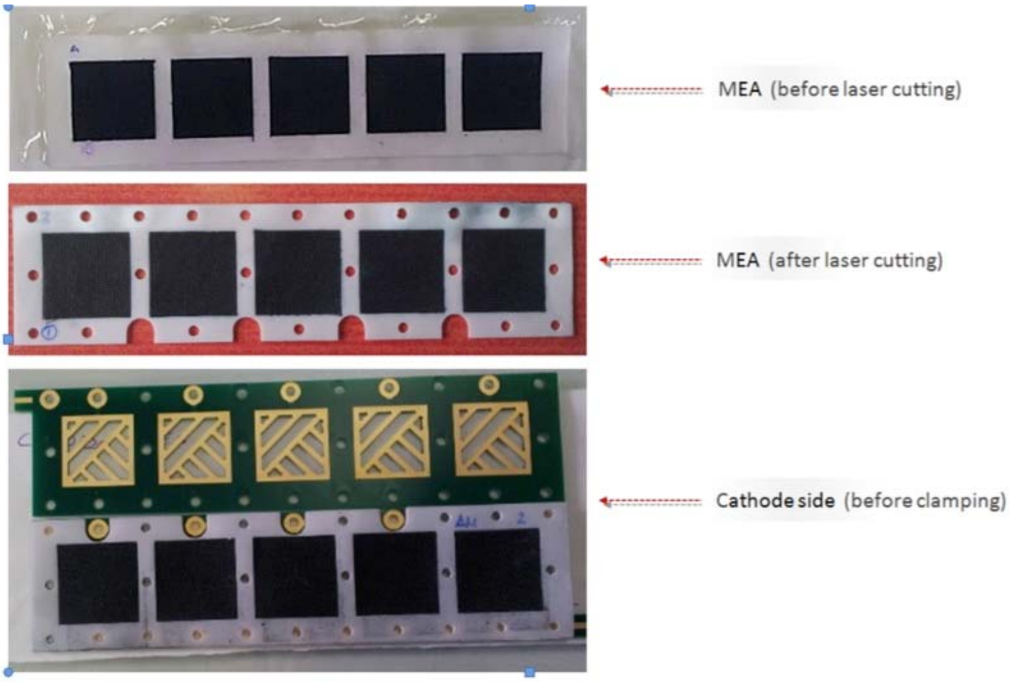


Figure V–3*: *Monopolar MEA configuration and assembling (CNR-ITAE).

To assess the membranes developed in Duramet in MEAs, single cells have assembled at the CNR-ITAE to be investigated at low (60°C) temperature and compared to the benchmark Nafion 115 membrane (Table V–1, Figure V–4).

Table V–1*: *Electrochemical characteristics of the FUMATECH membranes tested at CNR-ITAE

Parameter	**Units**	**E-730**	**E-750**	**F-1850**	**F-18120**	**F-2350**	**FZP-960***	**FZP-990**	**FZP-9110**	**FX-7050**	**sPSf****	**Nafion 115**
Max. Power density	mWcm^{-2} @60°C	77	17	74	36	50	41	32	35	42	65	64
R_s (EIS)	Ωcm^2 @ 60°C	0.2	0.62	0.2	0.50	0.31	0.07	0.29	0.33	0.13	0.18	0.20
Cross-over current	mAcm^{-2} @ 60°C	47.6	185	47	100	88	128	135	208	186	30	120

Thin membranes, both bare and composite ones, were performing better than thicker ones in the same series despite the larger methanol cross-over. The membrane based on s-PEEK, 30 µm in thickness (E-730), presented higher performance and moderate methanol cross-over than the membrane based on the same polymer with 50 µm in thickness (E-750), due to a larger cell resistance. The same behavior was recorded with the membrane based on a novel PSFA (F-1850) compared to the thicker F-18120. Also polysulfone membrane provided promising results in terms of performance at low temperature and especially low cross-over. The MEAs based on s-PEEK (E-730) and the F-1850 were the most performing for operation in the low range. Sulfonated polysulfone appears also good for low temperature operation but less performing than sPEEK. It is shown here that at 60 °C, there are at least two Fumatech membranes performing better than Nafion.

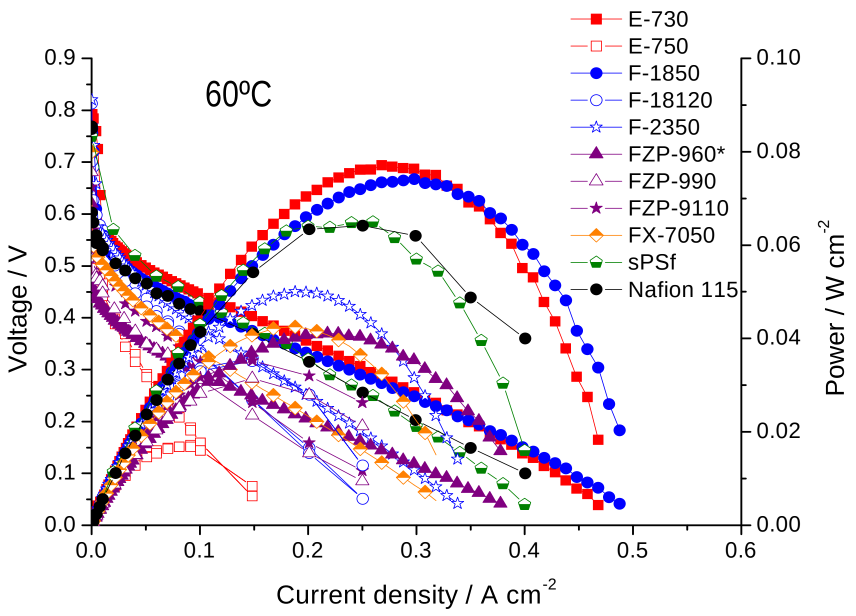


Figure V–4: ME Screening results obtained at CNR-ITAE at 60 °C for the low temperature membranes.

A comparison of the recorded MEA performances at high temperatures for several membranes is provided below. These results allowed the selection of two high temperature membranes: sPEEK-ZrP and F-1850. Further development was instead considered necessary on the mixed functionality membrane based on sulfonic (PFSA) and phosphonic acids for what concerns the stability in the presence of liquid methanol feed. This showed an excellent performance of 344 mW cm^{-2} but was not characterised by sufficient stability (Table V–2).

Table V–2: Electrochemical characteristics at 120 °C of selected MEAs tested at CNRS

Parameter	**Units**	**F-1850**	**F-18120**	**F-2350**	**FX-7050**	**F900/P002**	**sPEEK-ZrP**
Thickness	µm	50	120	50	50	20	30
Max. Power density/ air	mW/cm^2 @120°C	214	110	164	151	98	155
Max. Power density/ O_2	mW/cm^2 @120°C	357		226	231	344	266

The maximum power density achieved with FUMATECH F-1850 was 255 mW/cm^2 whereas for the CNRS sPEEK-ZrP composite membrane this was 266 mW/cm^2. Representative polarisation results obtained at CNRS and CNR-ITAE are shown below (Table V–3, Figure V–5).

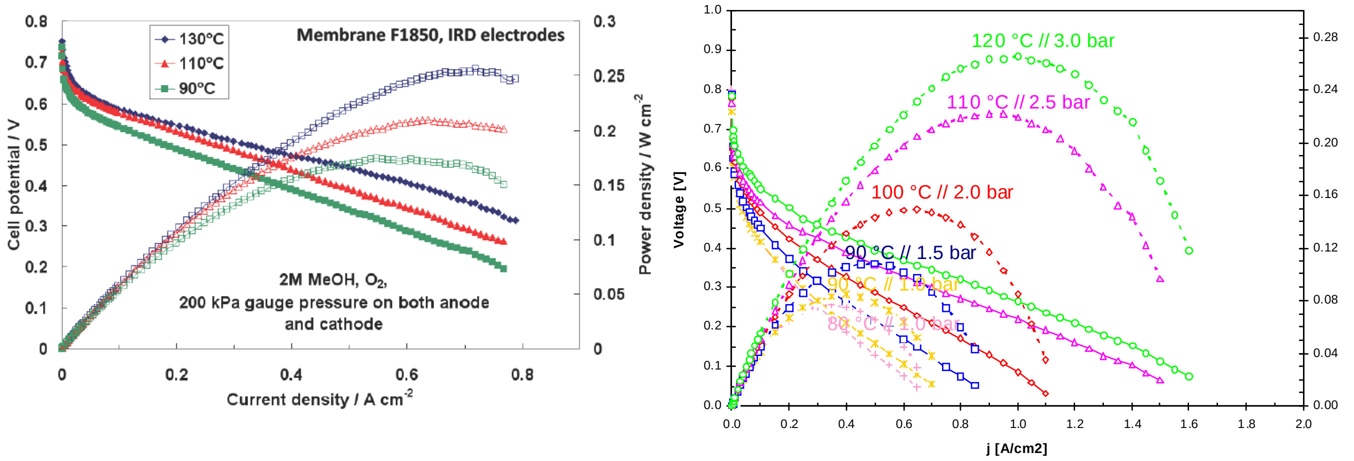


Figure V–5: DMFC performance at high temperature of sPEEK-ZrP (30 µm, 20 wt% ZrP) membrane (right, CNRS) and, Fumatech 1850- (left, CNR-ITAE)

Table V–3: MEA results at High Temperature on the down-selected DURAMET membranes

Membrane	Anode electrode	Cathode electrode	Anode conditions	Cathode conditions	Cell Temperature	**Maximum power density**	Open circuit potential
F-1850	PtRu (1.8 mg cm^{-2}) IRD electrode	Pt (1.2 mg$_{Pt}$cm^{-2}) IRD electrode	2M MeOH, 2 cc min^{-1} 2 bar(g) 5 cm^2 cell	2 bar(g) O_2, 100 cc min^{-1} 5 cm^2 cell	130 °C	**255 mW cm^{-2}**	0.75 V
sPEEK ZrP	PtRu (3 mg cm^{-2})	Pt (3 mg$_{Pt}$ cm^{-2})	1M MeOH, 50 cc min^{-1} 2 bar(g) 25 cm^2 cell	2 bar(g) O_2, 400 cc min^{-1} 25 cm^2 cell	120 °C	**270 mW cm^{-2}**	0.78 V

With reference to tests performed at the CNR-ITAE for low temperature applications, MEAs based on the F-1850 membranes with electrodes from CNR-ITAE were tested in passive mode operation, at room temperature, 5 M MeOH concentration. The cell was equipped with CNR-ITAE electrodes based on low-loading (1 mg cm^{-2}) Pt and PtRu type catalysts. The main results obtained are shown in Figure V–6. Under passive mode operation, the maximum power density reached 34 mW/cm^2.

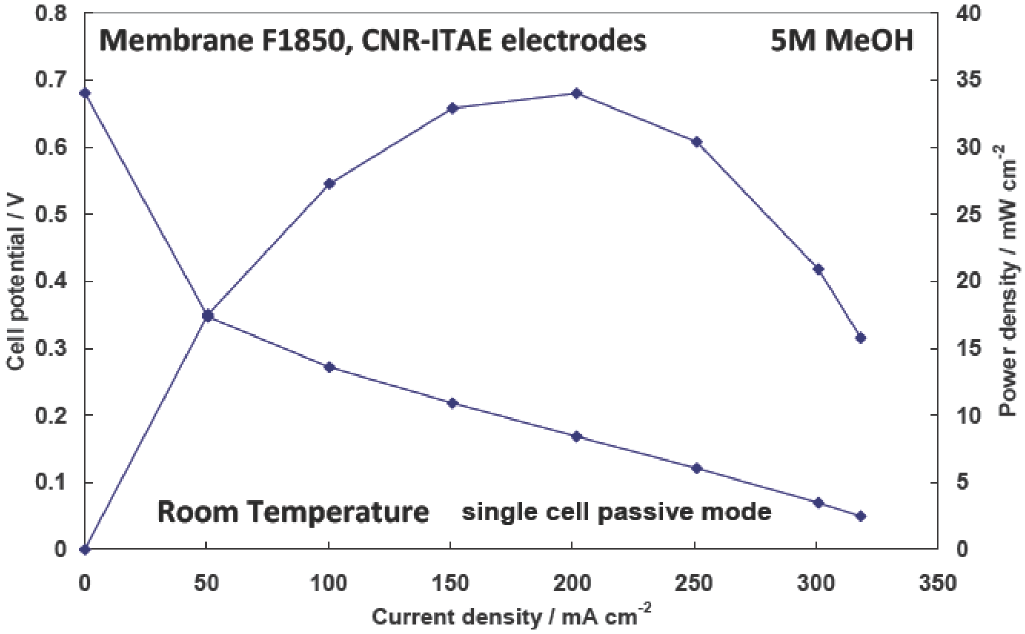


***Figure V–6**: CNR-ITAE tests on single cell passive mode MEA realized with F-1850 membrane and electrodes from CNR-ITAE, tested at room temperature and 5 M MeOH concentration.*

The best performance achieved at intermediate temperature 75 °C, was recorded for the IRD MEAs based on the FUMATECH F-1850 membrane under active mode operation with 1 M MeOH feed. This was 120 mW cm^{-2} with low air stoichiometry (λ=3). Moreover IRD tests showed excellent stability with almost no degradation for the entire polarization curve after 130 hrs (Figure V–7).

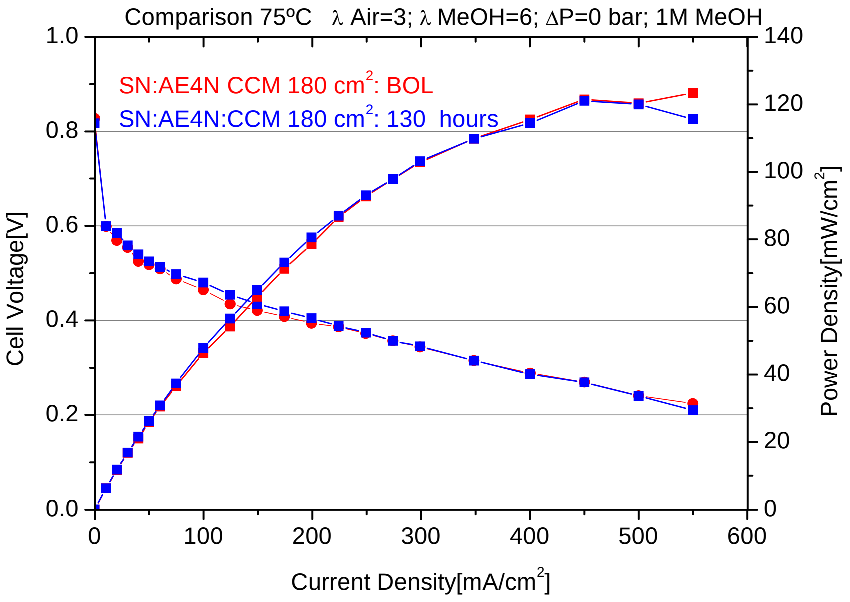


***Figure V–7**: Performance and durability of an IRD single cell active mode MEA based on the F-1850 membrane at 75 °C and 1 M MeOH concentration.*

To summarise, the most relevant MEA performance characteristics at different operating conditions are listed in Table V–4.

***Table V–4**: Most relevant MEA results obtained at different operating conditions for the down-selected DURAMET membranes (R.T.: room temperature).*

DMFC Membrane	Operating mode	Operating temperature	Pt and PtRu loadings	Best performance: power density
F-1850	passive	R.T.	1.2-1.8 mg cm^{-2}	34 mW cm^{-2}
F-1850	active	75°C	1.2-1.8 mg cm^{-2}	120 mW cm^{-2}
F-1850	active	130 °C	1.2-1.8 mg cm^{-2}	255 mW cm^{-2}
sPEEK-ZrP	active	120 °C	1.2-1.8 mg cm^{-2}	181 mW cm^{-2}
sPEEK-ZrP	active	120 °C	3.0-3.0 mg cm^{-2}	270 mW cm^{-2}

Large area MEAs were validated in term of stability in a 10 cell stack with 5 CCM based F1850 and 5 GDE based MEA's, same batch of Ink and membrane (Fumatech F-1850 membrane) where used. The stack was was tested at IRD inside a DMFC system. This test would allow for a direct comparison between the intitial GDE based MEA's and the CCM based MEA's that where developed for an industrial scale up. The system was operated in a stress test operation mode with max system power output and without stops. The typical stack operation temperature was 73 °C, the current density 0.25A/cm^2 and the stack pressure was ~40 mbar above ambient. The recorded average degradation rate during 723 hrs was: 24 µV/h/cell for the GDE (catalyst coated gas diffusion electrode) and 16 µV/h/cell for the CCM (catalyst coated membrane) (Figure V–8).

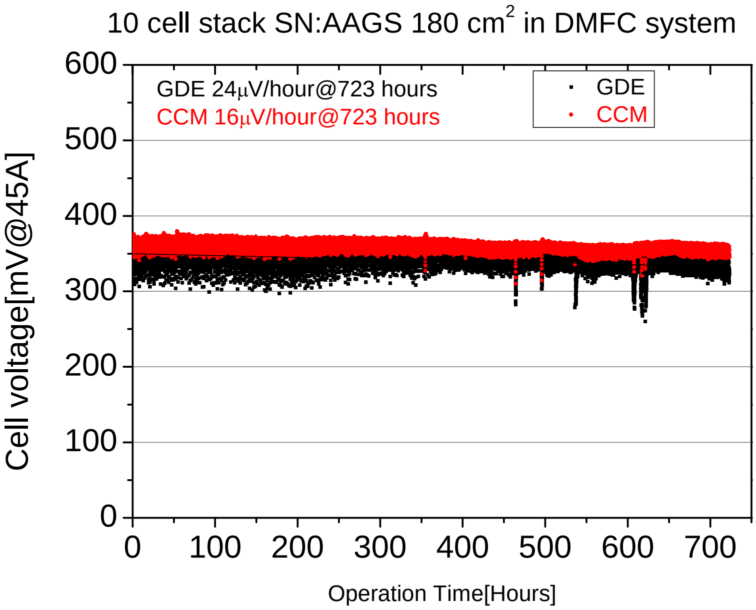


***Figure V–8*: *Performance of a 10 cell stack with F1850 based MEA's 5 cells where GDE based and 5 cells were CCM based (IRD). The stack was operated in a DMFC system*.**

The observed degradation was significantly lower than a reference MEA (>60-100 µV/h/cell). Similar decay rate was recorded for the bipolar stack assembled at CNR-ITAE and based on such MEAs after 500 hrs operation confirming the good stability of these components.

POLITO carried out a modeling task using the software COMSOL® Multiphysics. The modeling task consisted of three parts: the first one related to the definition of geometry and input values, the second related to the mathematical models used to describe the operation of the cell (mass transfer, thermal and electrochemical model) and finally the multiphysic analysis of the system. The model reproduced quite well the experimental data. In terms of polarization curve fitting, the differences between the trends of voltage and power were almost absent at low current density, and slightly more pronounced at high current density. The difference between experimental data and calculated values increased with the current density and decreased when the working temperature increased. A typical example of model applications for the components developed in the project is reported in Figure V–9.

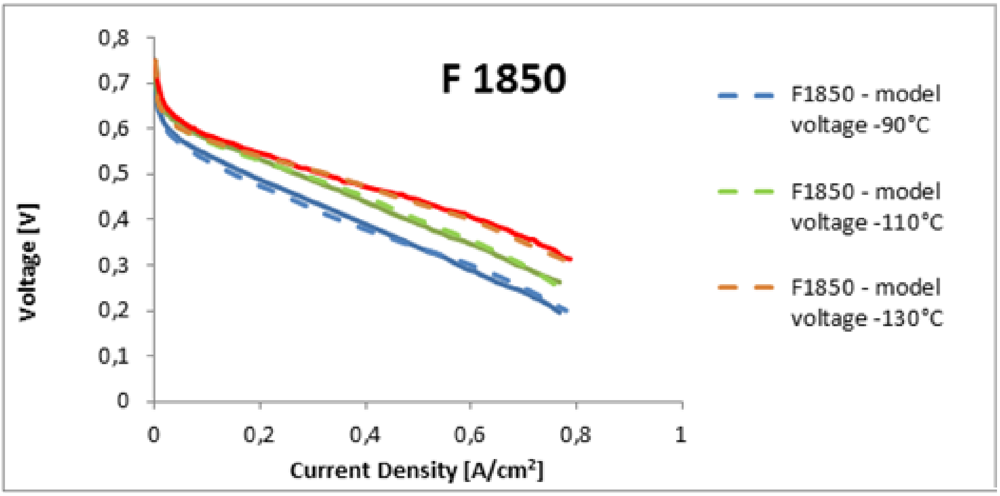


Figure V–9*: *Trend comparison between simulated data at POLITO from the Comsol® model and FUMAPEM F-1850 MEA experimental data from CNR-ITAE (solid lines: experimental data/ dash lines: model computations).

Some simulations were carried out at POLITO to verify the methanol crossover model. Also in this case the simulated trends were close to the experimental data.

The model on Comsol® was able to draw out 1D, 2D and 3D and iso-surface trends for all of the variables of interest. It was possible to obtain the mass flows trends and concentrations of methanol, water and carbon dioxide concentration at the anode (in which the molar flux through the anode as a function of the assumed membrane anode-side methanol concentration was described), oxygen and water concentration at the cathode, the fluid-dynamic variables trend and diffusivity coefficients trends.

Summary output from WP5

During the first period, MEAs with optimized production procedures and with precursor materials from WP3 and WP4 have been produced in the range of 5-180 cm^2 and tested by the different partners. The MEAs were tested in different test stations under different temperatures (-21 °C to 120 °C) and pressures (ambient to 3.0 bar). Different catalyst loadings have also been investigated. The most important result of the first phase was the pre-screening of MEA materials where the overall trend in membrane performance was validated at different laboratories; the results were consistent enough to down-select membranes and catalysts for high and low temperature operation. Optimization of production parameters has also been carried out. Further development of down-selected MEAs, testing of the MEAs under conditions relevant to the applications and the supply of the MEAs in appropriate amounts for stack testing was carried out in the second phase. Target performances were achieved for operation at both low and high temperature. Methanol crossover remains a challenge to be specifically addressed in future work. The approach of using composite membranes incorporating inorganic particles is validated, but to go further this approach needs to be combined with methods leading to engineered membrane architectures that block methanol crossover effectively. A 3D multi-physics, multi-phase, multi-component and non iso-thermal model has been developed to analyse the effects of catalyst structures, cell design and MEA components on the performance of a DMFC. The model has been validated against experimental data from CNR-ITAE and CNRS, showing congruent and convergent data for three different membranes (Nafion® 112, Fumatech E-730 and Fumatech F-1850) and six catalysts tested at different temperatures, pressures, and inlet concentrations, confirming the accuracy of the model and the equations applied.

VI. WP6 STACK DEVELOPMENT AND TESTING - WPL: CRF

The aim of the WP6 was to provide an assessment of the new developed components in verification units for testing under realistic operating conditions and validation with respect to the project objectives. Two prototypes of DMFC stack have been designed for this activity. The first was a bipolar stack configuration made of 5-10 cells assembled in series, with an active area of 100 cm^2. This was selected for high temperature operation in active mode; the target was regarding the application in auxiliary power units (APU). The second prototype was a stack designed as monopolar configuration, 2 strings of 5 cells connected in parallel (cells are connected in series inside each string), for operation at low temperature under passive mode. Two printed circuit boards were used to clamp and support the MEAs and to electrically connect the electrodes. The monopolar stack consisted of 10 cells with 4.85 cm^2 active cell area. This monopolar stack was developed as proof-of-concept for portable applications. The two prototypes were investigated in terms of performance and durability under several conditions. The aim was to validate the MEA and the other components under practical operating conditions. The analysis of stack characteristics and modularity was used for a scale-up study, in order to evaluate the impact of single components developed and to estimate costs for mass production of DMFC stacks. The manufactured bipolar stack, was initially assembled with 5 cells and subsequently with 10 cells, the device ready for testing is shown in Figure VI–1, where the current collectors, the graphite and the clamping plates can be observed (CNR-ITAE).

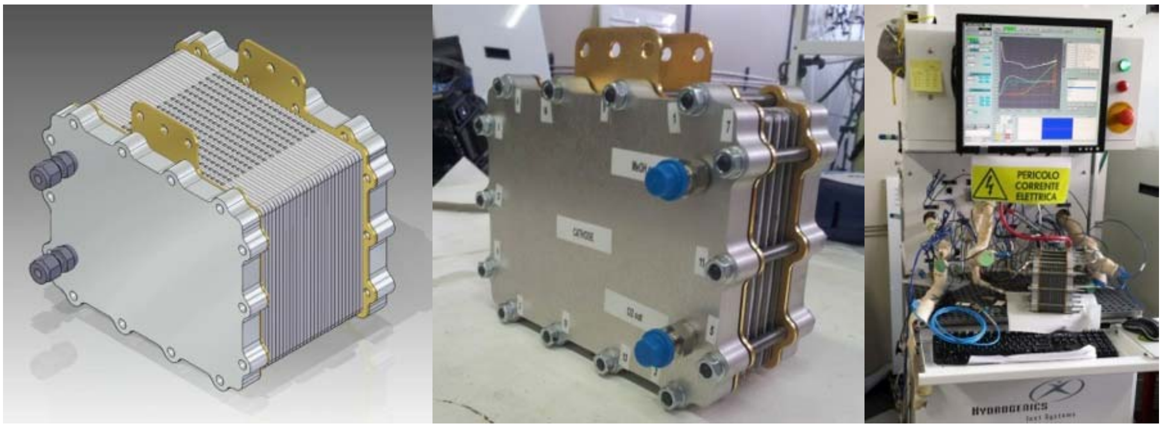


***Figure VI–1**: Bipolar stack 5- 10 cell design, assembling, operation (CNR-ITAE).*

Tests at higher temperatures, carried out at CNRS showed that the temperature of the stack (measured at the stack outlet of the methanol/water mixture) increased to around 100 °C under current (most likely the internal temperature of the stack was approaching 110°C). A maximum power of 195 W was achieved with 5 M methanol feed at the anode. The stack durability was first tested under mild conditions (20 A, 60°C and 1 atm rel pressure at the cathode) at CNR-ITAE. A stable behavior of the stack voltage with time voltage loss of 12 µV/h/cell was recorded. The voltage decay under these conditions was lower than maximum degradation limit fixed in the project (40 µV/h/cell). Using the sPEEK-ZrP membranes and by decreasing the concentration of methanol (2M instead of 5M used for stack 1), a maximum power of 210 W was achieved for a temperature 110-120 °C, which largely surpasses the project target (which was to achieve 150 W at 110-130 °C). Thus, for the bipolar stack tested at high temperature operating conditions i.e. (100-110 °C) a maximum power of 195 W was achieved with 5 M methanol feed at the anode and 205 W with 2 M (Figure VI–2).

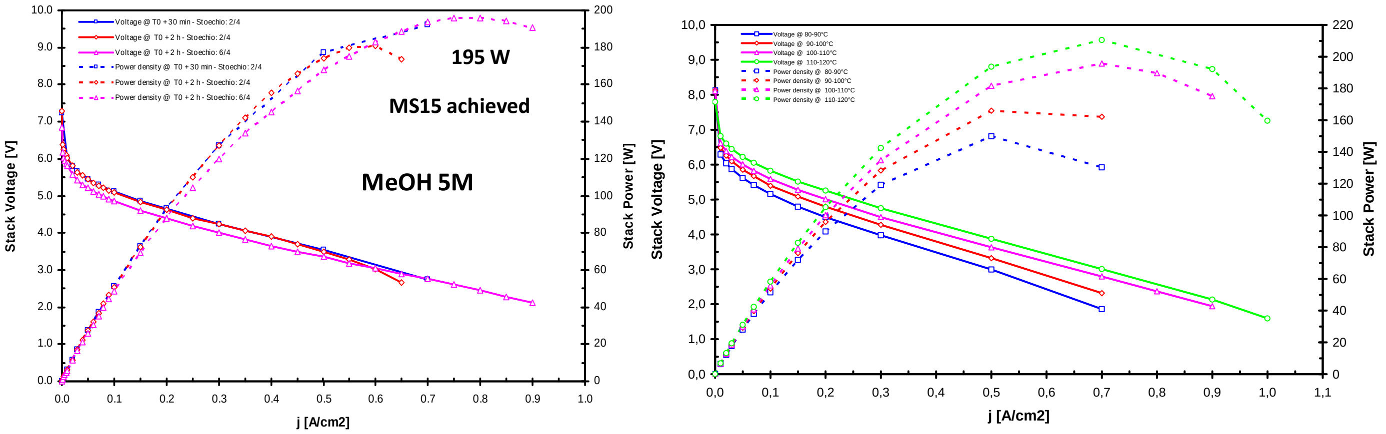


***Figure VI–2**: 5M MeOH F1850 - (left) and 2M MeOH sPEEK-ZrP membrane-based 10-cell stacks polarization and power curves at T>100°C (CNRS).*

The bipolar stack made of 8-cells with 5-layer MEA configuration was also provided to JRC-IET for testing under mild conditions.

A direct methanol fuel cell mini-stack for portable applications was designed with two strings composed of 5 cells connected in series, whereas, the two strings were connected in parallel, the single cell area was 4.85 cm^2 and the operating conditions were ambient pressure and temperature (CNR-ITAE, CRF).

The design and assembling of the planar ministack is shown in Figure VI–3.

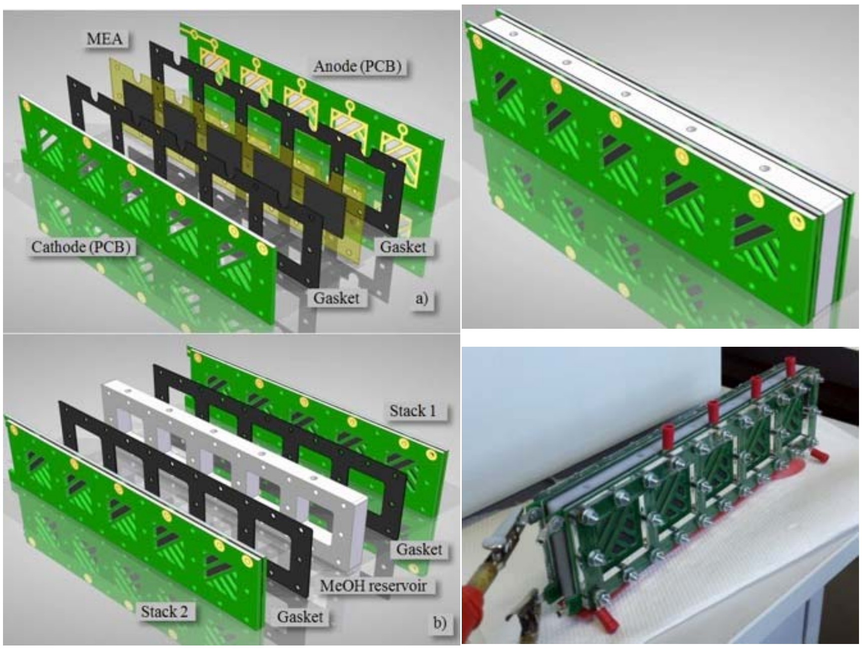


***Figure VI–3**: Assembling concept of a string (a) and of the two strings with the reservoir (b) view of the assembled modular stack (CNR-ITAE, CRF).*

For the performance tests of the monopolar ministack operating under passive mode, the methanol reservoir inside the ministack was filled with 10 cc of 5M methanol solution and the cathode side was exposed to the ambient. The total series resistance for this stack was about 278 mΩ, this value, normalised by the geometric surface area of the electrodes, corresponds to 0.54 Ω cm^2 at room temperature. The DMFC monopolar stack achieved a maximum power of 1.2 W at 1.2 A under passive mode at room temperature (CNR-ITAE, CRF), Figure VI–4.

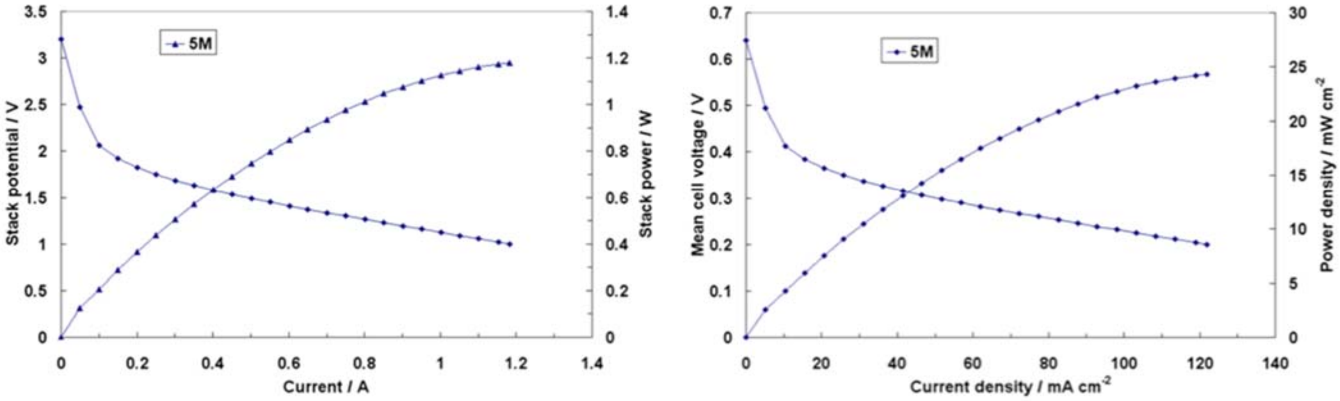


***Figure VI–4**: Polarization and power curves for the monopolar stack under passive mode operation (room temperature, air breathing, MeOH natural convection) (CNR-ITAE, CRF).*

For the bipolar stack prototype developed in Duramet, a cost analysis and a scale-up study were made in order to evaluate how the improvements in materials can have effect on a mass production of fuel cell stacks (CRF). A significant reduction in cost can be achieved for the plates, Al, Cu and graphite. This is mainly due to the fact that, for industrial production, the components cost is near to the market cost of raw materials. Regarding the MEA, at scaled-up level, the situation is also significantly different. Looking at the single unit, the catalysts represent the largest part of the MEA cost. This is essentially due to the high cost of the noble metals. However, for series production, the cost is near to the market cost of raw materials and a significant cost saving can be achieved for mass production. Same situation appears for the membrane. Overall a cost reduction of more than 50% can be achieved for series production by using the Duramet components as compared to the present commercial components.

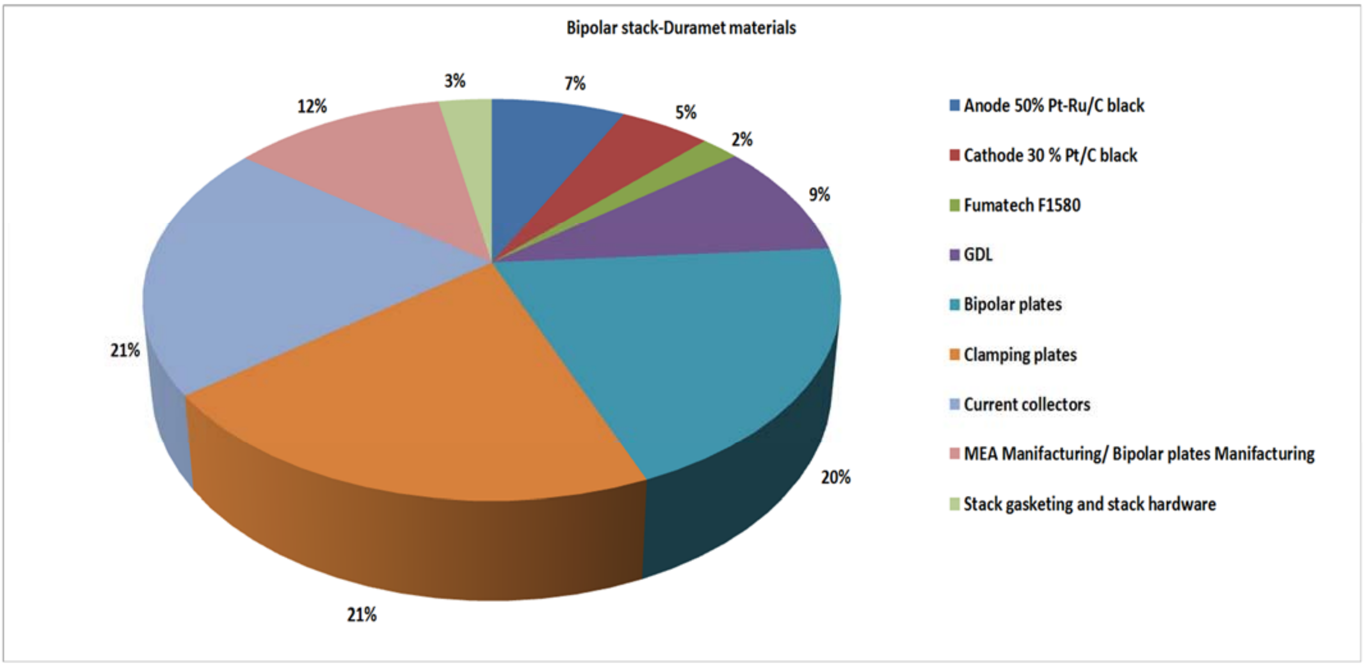


***Figure VI–5**: Costs distribution for the scaled-up stack prototype (CRF)*

Summary output from WP6

The fuel cell ministack stack achieved a maximum power of 1.2 W at 1.2 A, operating under passive mode, room temperature, air breathing, natural convection, with 5 M methanol. This performance is matching the target of the project. Several bipolar DMFC stacks designed for APU applications were assembled with the novel components developed in the project and tested in different laboratories. These fuel cell bipolar stacks were designed for APU applications and operated at both intermediate (60-70°C) and high (~100°C) temperatures. It was observed that the 7-layers MEA is both more stable and better performing than the 5-layer configuration. A maximum power of 195 W at T>100 °C, was achieved for the designed 10 cell stack with 100 cm^2 active area under operation with 5 M methanol. This corresponds to 195 mW cm^{-2} cell normalised performance. This value recorded for the stack is quite good and in line with the single cell target of 250 mW cm^{-2} at 110-130 °C that was effectively achieved in the project in a small single cell at 130 °C. Durability with F1850 membrane developed in the project exceeded 500 h with moderate voltage decay (12 µV/h/cell) under mild operating conditions. Demonstration of long-term durability at high temperature (>100 °C) still remains an aspect that deserves of further studies. Stack power exceeding 210 W was achieved for the stack based on composite CNRS membranes but operating on 2 M MeOH, at a stack operating temperature of 110-120 °C. Regarding scaling-up analysis, automated manufacturing processes, continuous or semi-continuous, can save time and then cost of energy and labour for every single unit produced. This will cause also the reduction of the waste materials produced in every single step of production and assembling. A study dealing with mass production estimates was carried out. Real volume production costs have been estimated. Future studies may concerns with market requests, fuel distribution, life cycle analysis and recycling fuel cell components.

VII. WP7 DISSEMINATION, OUTREACH, EXPLOITATION - WPL: PRETEXO

Regarding the dissemination and exploitation activities, these were mainly concerning with dissemination of project information achieved through various ways depending on the audience:

- Implementation of a dedicated project website
- Journal publications (14 published articles and several articles planned to be submitted after the end of the project)
- Conference presentations (25 contributions)
- Edition of a brochure
- Workshop

The coordinator has represented the project at international conferences, in particular at the FCH-JU review days 2012, 2013, 2014. A deliverable on "State of the art on high temperature DMFCs and portable applications DMFCs" has been released and published in the Duramet website. This represents the first step for the task on "Exploitation and use". Fourteen papers have been published on international peer-reviewed journals.

A DURAMET workshop was organized on 19th June 2014 during the CIMTEC 2014 - 6th Forum on new materials (Materials Solutions for Sustainable Energy) within the symposium on "Fuel Cells: Materials and Technology Challenges (website link)" - June 15-20 2014 Montecatini (Tuscany).

During the "**FA-4 DURAMET Workshop on Direct Alcohol Fuel Cells (DAFCs)**" 85 participants were registered and 20 presentations given.

To focus more on dissemination towards academic and industrial specialists, a leaflet presenting DURAMET objectives, consortium and output has been prepared prepared during the first 18 month period. It has been printed again and distributed during conferences, workshops etc. This brochure is also available for download from the DURAMET public web site: http://www.DURAMET.eu/brochure.html.

Regarding exploitation, key objectives for the period were regarding an assessment of the industrial scalability for down-selected components and fabrication processes as further analysis of the scaling up and cost analysis studies made in WP2 and WP6. Further objectives were dealing with the individuation by the industrial partners of appropriate exploitation routes for the components and results achieved in DURAMET.

As reported in the technical WPs, the materials developed in DURAMET appear appropriate for applications in advanced DMFC systems. The further steps needed to bring such impact is the introduction of the novel materials into the next generation DMFC systems that are commercialised by the IRD partner for portable and distributed energy markets (including back-up power systems for telecommunications etc.) and the validation of the APU DMFC systems on board for transportation applications by the CRF end user. Whereas, FUMATECH as a chemical company has already started deployment of project results by including the new membrane products in their catalogue.

A.4. POTENTIAL IMPACT, DISSEMINATION ACTIVITIES AND EXPLOITATION OF RESULTS

I. POTENTIAL IMPACT

The market segments for DMFCs concern with portable generators, UPS, back-up power systems and portable micro-fuel cells for specialist products. They are considered to be financially attractive for an emerging Fuel Cells European industry in the short term while being technically representative of power ranges and application requirements for which fuel cells can be used in other early-market applications. Direct methanol fuel cells are indeed particularly suited for auxiliary-power-units (APU) and for portable applications. Cars and other vehicles, from trucks to airplanes, have power requirements beyond those for propulsion. Auxiliary-power requirements are likely to grow significantly as developers incorporate additional electronics into vehicles. The power range of some hundreds Watts is suitable for devices such as weather stations, medical devices, signal units, APU's, gas sensors and security cameras. DMFCs can take care for much longer power autonomy and can make possible to expand the use of different devices even in remote areas. Not only do they provide the potential to reduce pollution, energy use, and greenhouse gases, but they also provide the potential to reduce costs and to increase comfort since vibration and noise are reduced in several applications. They have been postulated as suitable systems for power generation in the field of portable power sources, remote and micro-distributed energy generation as well as for auxiliary power units (APU) in stationary and mobile applications. DMFCs utilize a liquid fuel to deliver continuous power and they have low fuel storage and handling constraints than hydrogen fuelled fuel cells.

A cost analysis for the developed DMFC stacks was carried out. A first study was dealing just with prototype costs and not including considerations on mass production. This already indicated a total cost saving for the Duramet APU stack prototype of 37% and 22% for the passive mode operation monopolar stack used in portable applications compared to analogous stacks consisting of commercial state-of-the-art products. Such cost savings are almost entirely due to the catalysts and membranes. These components represent a consistent part of the total cost of the stack. The impact of the MEA on the overall cost is lower for the passive mode operation ministack than the APU bipolar stack. An analysis of the stack scaling-up production was carried out to estimate costs for mass production of DMFC devices. It is estimated that an overall cost reduction of more than 50% can be achieved for mass production by using the Duramet components as compared to the present commercial components.

Regarding environmental aspects, direct methanol fuel cells present a high potential for environmentally benign energy production mainly due to their high energetic efficiency compared to current power sources (mainly batteries or ICE small generators). The overall efficiency depends on the characteristics of the many steps and chains involved, which include production, distribution and conversion of the chemical energy of methanol into electrical energy. Adequate evaluation of environmental impact, materials and energy consumption throughout the overall methanol production and utilization life cycle (from ‘cradle-to-grave’) is important for making proper strategic decisions about its competitiveness in the future. Methanol can be produced from a wide variety of resources, including fossil fuels, such as natural gas or coal, or renewable sources. Nowadays methanol is produced by natural gas steam reforming in large quantities for industry applications. The reforming process is not a highly efficient method and results in energy losses of more than 30%. This fact makes methanol production from fossil fuels of great importance for the overall impact, especially for the primary energy demand and greenhouse gas (GHG) emissions. However, methanol can also be produced using biogen synthesis gases, such as from the gasification of wood or bio waste, anaerobic digestion, or absorption of CO_2 produced in cement plants or other industrial plants. Technical data of these supply paths is scarce: efficiency numbers are often in the range of 40% for biomass gasification, but in these cases, GHG emissions as well as the primary energy demand are very low. On the other hand, methanol is a high energy-dense liquid under normal conditions, which allows it to be easily stored, transported and dispensed (much like gasoline). This means that no significantly high-energy demands are required in pumping or compressing as in the case of gas fuels.

The emphasis is thus addressed to fuel cell hardware and materials recovery, including component reuse, remanufacturing, materials recycling and energy recovery for fuel cell maintenance and retirement processes. The production of fuel cell stacks leads to environmental impacts mainly associated to the platinum group metal (PGM) materials for the catalysts and, to a lesser extent, the materials and energy for the flow field plates. Recycling of the PGM is, therefore, a major requirement for future stack generations, not only an economic requirement. PGMs such as Pt, Pd and Rh are successfully recycled from today's vehicles, principally from catalytic converters – modern vehicles may contain around 1 g of Pt for gasoline and around 8 g of Pt for diesel – and the technologies can be adopted to recycle Pt from fuel cell systems. Recycling in the fuel cell manufacturing industry will become paramount for mass-produced systems in which environmental considerations will have to be taken into account (for example, collection/separation systems, recycling processes, component reuse, re-manufacturability and energy recovery).

Regarding the application of DMFCs to portable systems there are great environmental benefits. Portable systems usually compete with rechargeable batteries to power laptops, telecommunication devices and other small portable electronic devices or with gasoline or diesel power generators. Batteries contain critical materials such as cadmium, lead or mercury. In many countries, the disposal of batteries is the main source of heavy metal contamination of waste disposal sites. Additionally, the production of batteries consumes up to 500 times the energy contained in the battery itself. In the life cycle of DMFC system, the production supply will play a less important role than the substitution of batteries. As DMFC systems will have much longer lifetimes and offer the potential of catalyst recycling, the net effect will be clearly positive. The main regard about DMFC operation is the production of CO_2. In this case, the selection of the resource used in the production of methanol, i.e. from fossil fuels or from renewable sources, plays a fundamental role in balancing GHG emissions in the overall process. APU units based on DMFC also compete with gasoline/diesel generators. These small systems have an efficiency of typically 10% compared to fuel cells of a similar size with efficiencies typically higher than 20-40% depending on the load factor. Moreover, reduction in the noise level is a clear advantage of DMFC systems. Two additional benefits of the DMFC compared to a diesel generator are:

1) Longer service intervals
2) No particulate emissions for DMFC systems.

II. EXPLOITATION

The consortium covers the manufacturers of DMFC basic materials, MEA, stack, system as well as an end-user. Exploitation and use of the project results are essentially addressed by the industrial partners. A narrow collaboration between research organizations and industry makes possible a rapid exploitation of the new components and their integration into practical systems. Thus exploitation of the project results is first carried out inside the consortium. In this regard, the exploitation manager in this matter assists the coordinator. The role of exploitation manager for this project is covered by IRD that already commercialise DMFC systems. Whereas the need for the applications of DMFC power units in vehicles is addressed by an automaker partner CRF (FIAT).

Both coordinator and exploitation manager were responsible for co-ordination of key-issues such as licenses and dissemination of the intellectual property arising from the project. They will be involved in coordination of negotiations between the Consortium and external parties concerning exploitation issues. However, in addition to the activity of the exploitation manager, the project steering committee also considers and evaluates the commercial significance of the results, and assists the exploitation manager with regard to the question of patent/copyright protection.

Several promising materials showing enhanced performance with respect to the corresponding benchmarks are actively evaluated by the industrial partner commercialising DMFC systems and are taken under consideration for their future system developments. Similarly, the end-user is also analysing the characteristics of the DMFC devises for specific applications.

The fact that this project team comprises a strong participation of companies with established development, manufacturing and commercial activities facilitate the exploitation of results, since the industrial partners can immediately explore any new successful development. In general, the industrial partners of the Consortium have significant experience on the exploitation of this technology. Thus, any successful new product development will add to the value of their product portfolios. The industrial partners will also seek after the termination of the project to inform potential customers of positive results arising from the project in accordance to the IPR considerations. According, these extensive contacts and relationships may have a positive impact to extend largely the results beyond the project partnership.

Regarding the time-scale for the exploitation of the materials developed within the project, this can be reasonably identified in a few years after project termination to properly assess also in terms of scaling-up, cost-effectiveness and durability the new components and related devices.

Further RTD on DMFCs as well as related demonstration activities after the termination of the project could strongly contribute to increase the commercial impact of these devices.

The exploitation plan for the main industrial partners involved in the project is summarised as follows:

- **CRF-FIAT**

The technology developed in the project allows decreasing the cost and improving the durability of direct methanol fuel cell stacks. This can enable the construction of reliable and affordable auxiliary power units to be installed on special vehicles and trucks. The possible impact is related to the installation of 1-5 kWh APU on commercial vehicles and caravans. The yearly production volume can be estimated to be 10000 units.

- **IRD**

The gained knowledge about MEA’s based on both novel membranes and novel catalyst will be used for further development of both DMFC MEAs and systems based on these MEAs. On the short term the novel membranes developed will be further tested for durability and stability in IRD’s DMFC systems. The novel membranes have a promising cost potential that will make the IRD DMFC systems more competitive with respect to competing technologies like small diesel generator based APU’s

- **FUMATECH**

In the DURAMET project, FUMATECH has developed a cost-effective membrane for DMFC applications. This membrane was successfully produced on the FUMATECH continuous production line with the aim to obtain high-quality and highly reproducible membranes for MEA development evaluation and sampling. The process of the pilot-scale production of the novel DMFC membrane is fully compatible with the standard large-scale membrane production enabling the rapid transfer and integration of the new technology into the standard operation of manufacturing processes; this allows the subsequent commercialisation of project results. The potential impact for FUMATECH is related to a yearly membrane production of around 2000 m^2 for 10000 units.

An evaluation has been made of the down-selected approaches to membrane, catalyst, and MEAs developments to assess all potentialities for industrial scale-up in a cost effective way. The most relevant areas for early market applications such as portable power sources and assisted power units were considered.

An assessment related to the industrial scalability of down-selected components and fabrication processes has been made in the project. The analysis essentially focused on the MEAs production processes and their relevant characteristics. In particular, the pros and cons of the 7-layer MEA fabrication process that was the final procedure selected for the DURAMET MEAs were discussed. The analysis also includes cost and environmental considerations. In particular, the study of the industrial scale up (10^4 units) has individuated some important aspects for the MEAs:

- A cost saving for components; this is due to scale numbers where the cost is dominated by raw materials cost and not production cost e.g. the price of catalyst will approach the raw noble metals price.
- Significantly lower loss of materials during production.
- Less machine and labour time due to more efficient production processes.
- A perspective cost of 30 Euro/180 cm^2 DMFC MEA has been individuated for the novel materials.

Scalability, reliability and cost-savings appear as relevant aspects to favour the large-scale diffusion of the DMFC technology. According to the analysis carried out in the project, series production causes a decrease of the MEA cost of more than one order of magnitude. This evidence is related to several aspects. An increase in the efficiency of energy usage, a reduction in the amount of waste materials but, especially the reduction of labour costs due to the automation. Thus, on a large scale, the final costs are essentially the costs of the raw materials e.g. noble metal catalysts and membranes. The final MEA costs estimated for series production appear in line with the market requirements for portable and APU applications. In portable applications, the cost has minor relevance with respect to performance and high energy density since the main competitors in this field are Li batteries.

Six exploitable foregrounds, allowing several partners to promote and exploit DURAMET research results, have been identified.

III. DISSEMINATION

The main objective of the dissemination and outreach activities for this second period was to guarantee proper diffusion of knowledge and project results according to an agreed strategy aimed to secure maximum impact with respect to the Intellectual Property Rights.

Dissemination and outreach activities arising from the DURAMET project have been carried out and are listed below:

- Research publications in peer-reviewed journals,
- Meetings, conferences,
- Website,
- Outreach activities
- Brochure
- International workshop
- The DURAMET public website (http://www.duramet.eu/) fully operational since 18th March 2011 has been updated on a regular basis with information on project activities (news, meetings, publications…) and project resources (links, related events…).
- Over the last 18 months, the public website has been consulted on a regular basis with an average of 77 unique visits per month showing also a regular increase over the last 18 month period.

Further analysis of this traffic shows that, even more than during the first reporting period, 80% of the visits arise from new visitors (using “DURAMET” as a main search key word generally associated with FP7 or fuel cells) who are mainly looking for information on the DURAMET project, its partners and results. This information reveals that dissemination activities of the consortium remain efficient, attracting new visitors.

The consortium has attended prominent international conferences, workshops and symposia. All presentations have followed the dissemination protocol to protect IPR.

LIST OF CONFERENCE PRESENTATIONS

1. **HYCELTEC 2013, June 26-28 2013, Estoril, Portugal**
   - **Oral presentation:** Investigation of PtCo catalysts in direct methanol fuel cells, V. Baglio, A. Stassi, C. D'Urso, A.S. Aricò, CNR-ITAE
2. **4th European PEFC & H_2 Forum 2013, July 3-5 2013, Lucerne, Switzerland**
   - **Poster presentation:** Valve Metal Oxide Based Catalysts for the Oxygen Reduction Reaction in Acidic DMFCs, T. Mittermeier, P. Madkikar, X. Wang, H. A. Gasteiger, M. Piana, TUM
3. **CSE 2013, 5-9 July 2013, Guangzhou, China**
   - **Invited oral presentation**: Improved durability and cost-effective components for new generation solid polymer electrolyte direct methanol fuel cells, Stefania Specchia, Antonino A. Aricò, Deborah Jones, Michael Schuster, Mauro F. Sgroi, Hubert Gasteiger, Jacob L. Bonde, Nathalie Cros, Georgios Tsotridis
4. **GEI 2013, 22-27 September 2013, Pavia, Italy**
   - **Poster presentation**: Development of Durable and Cost-effective Cathode Electrocatalysts for Direct Methanol Fuel Cells, V. Baglio, C. D'Urso, D. Sebastián, A. Stassi, A. S. Aricò, CNR-ITAE
5. **SFGP, 8-10 October 2013, Lyon, France**
   - **Poster presentation**: Improved Durability and Cost-effective Components for New Generation Solid Polymer - DURAMET Project, S. Specchia, POLITO
6. **ECS-fall-meeting, 27 October–1 November 2013, San Francisco**
   - **Oral presentation**: Temperature Study on Zr-Oxides for the ORR in DMFCs, T. Mittermeier, P. Madkikar, X. Wang, M. Piana, H. A. Gasteiger, TUM
7. **FCH-JU review days, 11-12 November 2013, Brussels, Belgium**
   - **Oral and poster presentation:** DURAMET project, A. S. Aricò, CNR-ITAE, Messina, Italy
8. **Fuel Cells 2014 – Science and Technology conference that will be held in Amsterdam, the Netherlands from 3 - 4 April 2014.**
   - **Oral presentation:** Pd-based electrocatalysts for direct methanol fuel cells, *A. Stassi, V. Baglio, C. D'Urso, D. Sebastián, A. S. Aricò, CNR-ITAE*
9. **225th ECS Meeting, Orlando FL (USA), May 11th-15th 2014**
   - **Oral presentation**: Catalysts Based on Trimetallic Formulations for the Electro-Oxidation of Methanol, D. Sebastián, V. Baglio, C. D'Urso, A. Stassi, A.S. Aricò, CNR-ITAE
10. **Symposium on "Fuel Cells: Materials and Technology Challenges" Special session FA-4 DURAMET, CIMTEC conference, CIMTEC 2014 - 6th Forum on new materials, 15-20 June 2014, Montecatini Terme, Italy**
    - **Poster presentation**: Improved Durability and Cost-effective Components for New Generation Solid Polymer- DURAMET Project, A.S. Aricò, CNR-ITAE
    - **Oral presentation**: Composite Anode Catalysts based on PtRu and Metal Oxides for DMFCs, D. Sebastián, V. Baglio, C. D'Urso, A. Stassi, A.S. Aricò, CNR-ITAE
    - **Oral presentation**: Pd-based electrocatalysts as cost-effective cathodes for direct methanol fuel cells, V. Baglio, C. D'Urso, D. Sebastián, A. Stassi, A. S. Aricò, CNR-ITAE

- **Oral presentation**: Direct Methanol Fuel Cell Stack Design and Test in the framework of DURAMET Project, O. Barbera, A. Stassi, V. Baglio, D. Sebastian, A.S. Aricò, CNR - ITAE,
- **Oral presentation**: Membranes for Direct Methanol Fuel Cells, Deborah Jones, CNRS
- **Oral presentation**: DMFC degradation and lifetime studies, Jacob L. Bonde, IRD
- **Oral presentation**: 3D Direct Methanol Fuel Cell (DMFC) validation model for analysing new materials and components, N. S. Vasile, A. H.A. Monteverde Videla, S. Specchia, POLITO
- **Oral presentation:** Synthesis and Characterization of ZrO_2 Nanoparticles from an Organometallic Precursor as ORR-Selective Catalysts for DMFCs, P. Madkikar, T. Mittermeier, C. Denk, X. Wang, M. Piana, A.H.A. Monteverde Videla, S. Specchia, H. A. Gasteiger, TUM
- **Oral presentation**: Impact of N/Zr atomic ratio on the oxygen reduction reaction activity of heat-treated carbon-supported Zr-oxyphthalocyanine, T. Mittermeier, C. Denk, X. Wang, H. Beyer, P. Madkikar, M. Piana, H. A. Gasteiger, TUM
- **Poster presentation**: Nobel-metal-free anode catalysts for direct methanol fuel cells X. Wang, P. Madkikar, T. Mittermeier, M. Piana, H.A. Gasteiger, TUM
- **Poster presentation:** Ab-initio simulation of beta-Ta2O5 as a catalyst for oxygen reduction reaction, M. F. Sgroi and V. Dellacà, CRF

11. **EEST2014 congress, Shanghai, P.R. China**
    - **Oral presentation**: Varying the morphology of FeTMPPCl electrocatalysts by using different SiO_2 template promoting the Oxygen Reduction Reaction, A.H.A. Monteverde Videla, L. Osmieri, S. Specchia, POLITO
12. **EHEC 2014, 12-14 March 2014, Seville, Spain**
    - **Oral presentation**: Noble metal oxide and valve metal oxide promoters of Pt for methanol oxidation, V. Baglio, R.S. Amin, K.M. El-Khatib, S. Siracusano, A. Stassi, D. Sebastián, A.S. Aricò, CNR-ITAE
13. **UECT 2014, 23-26 June, Ulm, Germany**
    - **Poster presentation**: 3D Multi-physics modelling and validation of a Direct Methanol Fuel Cell for analyzing internal phenomena and the influence of new materials in performance optimization, N. S. Vasile, Alessandro H.A. Monteverde Videla, V. Baglio, A. S. Aricò, S. Specchia, CNR-ITAE, POLITO
14. **FCH-JU review days, 10-11 November 2014, Brussels, Belgium**
    - **Poster presentation:** DURAMET project, A. S. Aricò, CNR-ITAE, Messina, Italy

DURAMET JOURNAL PUBLICATIONS

The Consortium has published, and will continue to submit for publication, a number of individual or joint publications to scientific journals. As for participation in international events, each publication has followed the DURAMET dissemination protocol.

1. **Hybrid ordered mesoporous carbons doped with tungsten trioxide as supports for Pt electrocatalysts for methanol oxidation reaction** J. Zeng, C. Francia, C. Gerbaldi, V. Baglio, S. Specchia, P. Spinelli, A. S. Aricò, *Electrochimica Acta*, Volume 94, 1 April 2013, Pages 80–91 *http://dx.doi.org/10.1016/j.electacta.2013.01.139.*
2. **Composite anode electrocatalyst for direct methanol fuel cells,** V. Baglio, S. C. Zignani, S. Siracusano, A. Stassi, C. D'Urso, A. S. Aricò, *Electrocatalysis – December 2013, Volume 4, Issue 4, pp 235-240, (http://www.doi.org/:DOI 10.1007/s12678-013-0139-0).*
3. **Preparation and characterisation of Ti oxide based catalyst supports for low temperature fuel cells**, S. Siracusano, A. Stassi, E. Modica, V. Baglio, A.S. Arico', *International Journal of Hydrogen Energy - Volume 38, Issue 26, 30 August 2013, Pages 11600–11608 (http://dx.doi.org/10.1016/j.ijhydene.2013.04.161).*

4. **Performance analysis of polymer electrolyte membranes for direct methanol fuel cell**, F. Lufrano, V. Baglio, P. Staiti, V. Antonucci, A.S. Aricò, *Journal of Power Sources - Volume 243, 1 December 2013, Pages 519–534 (http://dx.doi.org/10.1016/j.jpowsour.2013.05.180)*
5. **Improved Pd electro-catalysis for oxygen reduction reaction in Direct Methanol Fuel Cell by reduced graphene oxide**, R. Carrera-Cerritosa, V. Baglio, A. S. Aricò, J. Ledesma-García, M. F. Sgroi, D. Pullini, A. J. Pruna, D. Busquets Mataix, R. Fuentes-Ramírez, L. G. Arriaga, *Applied Catalysis B: Environment – Volume 144, January 2014, Pages 554–560, (http://dx.doi.org/10.1016/j.apcatb.2013.07.057)*
6. **AC Impedance Spectroscopy Investigation of Carbon Supported Pt3Co and Pt Cathode Catalysts in Direct Methanol Fuel Cell**, F. Capitanio, S. Siracusano, A. Stassi, V. Baglio, A.S. Arico, A.C. Tavares, *Int. Journal of Hydrogen Energy, Volume 39, Issue 15, 15 May 2014*, Pages 8026–8033, DOI: 10.1016/j.ijhydene.2014.03.080
7. **Composite anode electrode based on iridium oxide promoter for direct methanol fuel cells,** V. Baglio, D. Sebastián, C. D'Urso, A. Stassi, R.S. Amin, K.M. El-Khatib, A.S. Aricò, *Electrochimica Acta, Volume 128, 10 May 2014, Pages 304–310*, DOI: 10.1016/j.electacta.2013.10.141
8. **PtCo catalyst with modulated surface characteristics for the cathode of direct methanol fuel cells,** V. Baglio, C. D'Urso, D. Sebastián, A. Stassi, A.S. Aricò, *Int. Journal of Hydrogen Energy, Volume 39, Issue 10, 26 March 2014, Pages 5399–5405*, DOI: 10.1016/j.ijhydene.2013.12.015
9. **IrO2 as promoter of Pt-Ru for methanol electro-oxidation,** V. Baglio, R.S. Amin, K.M. El-Khatib, S. Siracusano, C. D'Urso, and A.S. Aricò, *Phys. Chem. Chem. Phys., 2014, 16, 10414-10418, DOI: 10.1039/C4CP00466C*
10. **Metal oxide promoters for methanol electro-oxidation,** R.S. Amin, K.M. El-Khatib, S. Siracusano, V. Baglio, A. Stassi, A.S. Aricò**,** *International Journal of Hydrogen Energy Volume 39, Issue 18, 15 June 2014, Pages 9782–9790, doi:10.1016/j.ijhydene.2014.04.100*
11. **Synthesis of Pd3Co1@Pt/C core-shell catalysts for methanol tolerant cathodes of direct methanol fuel cells,** A. S. Aricò, A. Stassi, C. D'Urso, D. Sebastián and V. Baglio, *Chemistry: A European Journal . 2014 Aug 18; 20(34):10679-84. DOI: 10.1002/chem.201402062.*
12. **Activity of Co-N multi walled carbon nanotubes electrocatalysts for oxygen reduction reaction in acid conditions,** Luigi Osmieri, Alessandro H. A. Monteverde Videla, Stefania Specchia *A Journal of Power Sources, Volume 278, 15 March 2015, Pages 296-307; doi:10.1016/j.jpowsour.2014.12.080*
13. **Facile synthesis of Zr and Ta-based catalysts for the oxygen reduction reaction,** David Sebastián, Vincenzo Baglio, Shuhui Sun, Ana C. Tavares, Antonino S. Aricò, *Chinese Journal of Catalysis 36 (2015); DOI: 10.1016/S1872-2067(14)60253-9.*
14. **Graphene-supported substoichiometric sodium tantalate as methanol tolerant non-noble metal catalyst for the electro-reduction of oxygen,** David Sebastián, Vincenzo Baglio, Shuhui Sun, Ana C. Tavares, Antonino S. Aricò, *Accepted for publication in ChemCatChem; DOI: 10.1002/cctc.201403026R1*

DURAMET WORKSHOP

A DURAMET workshop was organized on 19th June 2014 during the CIMTEC 2014 - 6th Forum on new materials (Materials Solutions for Sustainable Energy) within the symposium on "Fuel Cells: Materials and Technology Challenges (website link)" - June 15-20 2014 Montecatini (Tuscany).

During the "**FA-4 DURAMET Workshop on Direct Alcohol Fuel Cells (DAFCs)**" 85 participants were registered and 20 presentations were given.

EDUCATION ACTIONS & OUTREACH ACTIVITIES

Over the the project duration, six education actions and outreach activities towards non-specialist scientists (university students) have been undertaken by the consortium, they are listed on the next page:

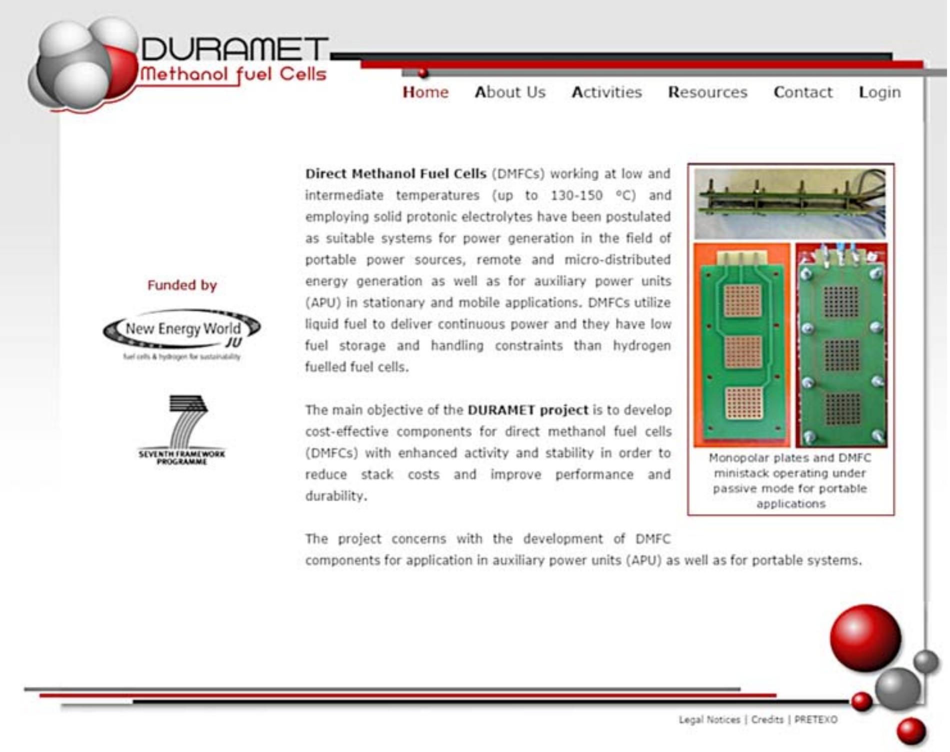
1. **November 5-10, 2012 - China Jiliang University in Hangzhou (P.R. China)** During a visit at the China Jiliang University in Hangzhou (P.R. China) on November 5-10, 2012, Stefania Specchia delivered a lecture for master students entitled “Advanced Research Activities @ POLITECNICO DI TORINO on Low-Temperature Fuel Cells” where the DURAMET project was presented.
2. **October 2012 - Politecnico di Torino, Torino, Italy** Once a year, usually in October, for the 3rd level course in POLITO, (open to all PhD students), the POLITO team shortly presented on-going EU projects on hydrogen and fuel cells: “Hydrogen technologies and fuel cells”. This course has 2 different teachers working in the DURAMET project: Stefania Specchia and Carlotta Francia, it represents a total of 25 hrs overall.
3. **September 2013 - University of Pavia, Italy:** Dr. Antonino S. Aricò from CNR-ITAE, a taught a course of the school "Energetica e Sensori" addressed to PhD students from 18th to 21st September 2013 at the University of Pavia, Department of Chemistry. The topic of these lectures was on Fuel Cells and more specifically on Direct Methanol Fuel Cells and DURAMET FCH-JU Project, also including a laboratory session.
4. **7 November 2013 - China Jiliang University**: Gre.En^2 Group activity on fuel cells and DURAMET project, lecture at the China Jiliang University (P.R. China), Stefania Specchia, POLITECNICO DI TORINO
5. **7 August 2014 - Westfälische Hochschule**: Gre.En^2 Group activity on fuel cells and DURAMET project, lecture at the Westfälische Hochschule (Germany), Stefania Specchia, POLITECNICO DI TORINO
6. **5 November 2014 - Tongji University Shanghai**: Gre.En^2 Group activity on fuel cells and DURAMET project, lecture at the Tongji University Shanghai (P.R. China), A.H.A. Monteverde Videla, POLITECNICO DI TORINO

DURAMET BROCHURE

To focus more on dissemination towards academic and industrial specialists, a leaflet presenting DURAMET objectives, consortium and output has been prepared prepared during the first 18 month period; it has been printed again and distributed during conferences, workshops … This brochure is also available for download from the DURAMET public web site: http://www.DURAMET.eu/brochure.html.

A.5. ADDRESS OF THE PROJECT PUBLIC WEBSITE

http://www.duramet.eu/



Direct Methanol Fuel Cells (DMFCs) working at low and intermediate temperatures (up to 130-150 °C) and employing solid protonic electrolytes have been postulated as suitable systems for power generation in the field of portable power sources, remote and micro-distributed energy generation as well as for auxiliary power units (APU) in stationary and mobile applications. DMFCs utilize liquid fuel to deliver continuous power and they have low fuel storage and handling constraints than hydrogen fuelled fuel cells.

The main objective of the **DURAMET project** is to develop cost-effective components for direct methanol fuel cells (DMFCs) with enhanced activity and stability in order to reduce stack costs and improve performance and durability.

Monopolar plates and DMFC ministack operating under passive mode for portable applications

The project concerns with the development of DMFC components for application in auxiliary power units (APU) as well as for portable systems.

COORDINATOR CONTACT DETAILS

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