

**SEVENTH FRAMEWORK PROGRAMME**

**FP7-FCH-JU-2008-1-CP**

**SP1-JTI-FCH.3: Stationary Power Generation & CHP**

**Topics Called:** Degradation and lifetime fundamentals

Project acronym: **DEMMEA**

Project full title: **“Understanding the Degradation Mechanisms of Membrane-Electrode-Assembly for High Temperature PEMFCs and Optimization of the Individual Components”**

Grant agreement no.: **245156**

Partners:

<b>Beneficiary Number *</b>	<b>Beneficiary name</b>	<b>Beneficiary short name</b>	<b>Country</b>
1	Advanced Energy Technologies	ADVENT	Greece
2	Foundation for Research and Technology Hellas-Institute of Chemical Engineering & High Temperature Chemical Processes	FORTH	Greece
3	Paul Scherrer Institute	PSI	Switzerland
4	Centre National de la Recherche Scientifique	CNRS	France
5	FUMATECH GmbH	FUMATECH	Germany
6	Institute of Chemical Technology Prague	ICTP	Czech Republic
7	Next Energy - EWE-Forschungszentrum für Energietechnologie e.V.	NEXT	Germany
8	Technical University of Darmstadt	TUD	Germany

## Executive summary

DEMMEA grouped together the different types of organizations; research centres, universities, SMEs and industry. More specifically, the consortium comprised 1 industrial partner (FUMATECH), 2 SMEs (ADVENT and NEXT) and 5 research institutes and universities (FORTH, CNRS, TUD, ICTP and PSI). The strong complementarity among the expertise of the partners in the context of the main objective of the project played a significant role in the overall success of reaching the expected milestones. The DEMMEA partnership had advanced knowledge, techniques and expertise in the fields of polymer electrolyte synthesis and electrocatalyst development, high temperature PEMFC technology and complementary experimental methods combining in-situ electrochemical analysis with state-of-the-art spectroscopic techniques. Hence, significant scientific knowledge and novelty was generated at the interface of the WPs and from the integration of all these scientific and technical skills.

The full duration of the DEMMEA project was 3 years and was separated into 7 work packages, WPs. One work package, WP1, included the management activities of the project according to the European project management standards. An additional work package, WP7, was dedicated to the dissemination of results to the scientific community and industry. The strategy for achieving the project goals included the employment of a large number of advanced characterization and analysis techniques for understanding the underlying degradation phenomena in the polymer electrolyte and the catalytic layer which influence and define the performance of the MEA and the integrated system. For the achievements of the project's goals ex-situ and in-situ testing methodologies were applied by the coordinated action of five technical work packages (WP2-WP6).

Because different tasks were integrated and many competencies were involved in each task, the project needed to be efficiently coordinated. Management was coordinated by Dr. S. Neophytides (chairman of the Steering Committee), while leaders among partners were appointed to manage one or several work packages. The project coordinator consolidated the project planning, progress reports, cost statements, budgetary overviews etc, using the inputs from the other partners. The communication between partners was also established and overseen. No conflicts between partners arose during the whole duration of the project.

The DEMMEA project created a common database ([demmea.iceht.forth.gr](http://demmea.iceht.forth.gr)) for all the project documentation (deliverables, publications, research experimental data, regular reports and minutes, etc.) as a common tool for communication. The content of the database was regularly updated and restricted by secure access control to consortium members and EC representatives.

One meeting every 6 months was organized for the decision making and/or when special issues arose. These half-yearly meetings played an important role in the communication strategy between the partners, the coherency between the work packages, the progress monitoring and the refinement of the objectives and the proper evolution of the work. All information (progress reports, minutes of meetings, relevant publications etc.) were transmitted to the project coordinator who adequately forwarded the content to the other partners.

A Mid-Term Assessment report on the progress of the research and the partners' plans was submitted before the end of the 20th month from the date of commencement. The project coordinator and the FCH-JTI organized a Mid-Term assessment meeting with WP leaders and the Commission's representative. The purpose of this meeting was to report on the progress and to redefine the Project Program for the remaining part of the contract. The comments of the reviewers on the management activities of the project were very positive; therefore no correction actions were necessary. Moreover, some very interesting comments on the technical part of the project were provided. The Consortium tried to implement these advices and improve the scientific work for the last 18 months of the project.

## Summary description of the project context and the main objectives

The state of the art high temperature PEM fuel cell technology is based on H<sub>3</sub>PO<sub>4</sub> imbibed polymer electrolytes. The most challenging areas towards the optimization of this technology are:

- (i) the development of stable long lasting polymer structures with high ionic conductivity
- (ii) the design and development of catalytic layers with novel structures and architectures aiming to more active and stable electrochemical interfaces with minimal Pt corrosion.

In this respect, the objective of the DEMMEA project was to understand the functional operation and degradation mechanisms of a high temperature H<sub>3</sub>PO<sub>4</sub> imbibed PEM and its electrochemical interface. The milestone of the project was the combined use of advanced experimental techniques that can lead to the development of prediction tools for the MEA's performance and stability. If we can really understand the fundamentals of the failure mechanisms, then we can use that information to guide the development of new materials or we can develop system approaches to mitigate these failures. Finally, it can enable the tailor-made optimization of the MEA into a commercially reliable product for stack manufacturers.

The activities of the DEMMEA project focused on:

- MEAs preparation and combined in situ electrochemical and spectroscopic investigation techniques and ex-situ post mortem characterization were used in order to study thoroughly the electrodes, electrolyte and the electrochemical interface aiming to the understanding of their stability and degradation mechanisms. Innovative characterization methods were developed and employed.
- Operational and degradation phenomena are not always easily accessible experimentally. Therefore, a mathematical model was developed, intended as a predicting tool for the MEA's long term and transient performance mainly focusing on the Pt corrosion, dissolution and ripening.
- MEA components' improvement can be achieved by introducing novel design and synthesis of more reliable components related to: (i) high temperature polymer electrolytes based both on aromatic polyethers with pyridine units and chemical structures based on PBI and AB-PBI derivatives, which exhibit high ionic conductivities, thermal, chemical and mechanical integrity at temperatures even up to 200°C and (ii) the synthesis of highly efficient catalytic layers with up to 5-fold decrease of Pt content using new modified carbon supports. The objective was to achieve a stable electrocatalytic layer with full metal electrocatalyst utilization at the electrode/electrolyte interface in order to lower Pt loadings and increase durability.

Below, the objectives and methodology broken down into the WPs are described in detail.

### WP1 Management of the Consortium

This work package covered all the management tasks for the overall coordination of the project and work package coordination. The objective was to ensure that:

- i) all budgetary actions were performed correctly, ii) the received funds were correctly distributed and accounted for, including independent auditing, iii) the work and tasks were completed in time, within budget, and satisfy high-quality requirements, and iv) reporting was done.

### WP2 Polymer Electrolytes

The performance and lifetime of a proton conducting high temperature H<sub>3</sub>PO<sub>4</sub> imbibed polymer electrolyte is characterized by the following factors:

- Its chemical and oxidative stability. During fuel cell operation the polymer matrix is exposed under two very aggressive factors. These are the elevated temperature and the high oxidative environment.
- The influence of the chemical structure of the polymer matrix on the proton conductivity of the acid doped polymer system.
- The leaching or evaporation of the H<sub>3</sub>PO<sub>4</sub> and the role of the polymer matrix.

The acid doping ability, conductivity and chemical and oxidative stability are directly related to the specific chemical structure of the polymeric material. It is vital to understand the way

the polymeric materials behave. This can be accomplished by the preparation and full characterization of polymer electrolytes with several chemical structures and different properties, as well as by the use of several experimental techniques which allow for a deeper insight of the degradation issues on an accelerated basis.

#### WP3 Catalysts and Catalytic layers

The state-of-the-art electrocatalyst, Pt supported on carbon, undergoes a gradual surface loss with time. The stability of the electrocatalysts and the efficiency of the catalyst utilization are issues which deserve special consideration. This section focused on taking it to the next level by preparing new structures that depict lower corrosion, as well as increased electrochemical surface area and higher utilization of the catalyst. More specifically, the approach included properly modified carbon allotropes (chemically modified or vertically aligned carbon nanotubes) with respect to the creation of an effective interface. The aim of these research activities was to lead to a more stable performance and a substantial decrease of the amount of Pt on the electrodes.

#### WP4 In situ spectroscopic study of MEAs

Fundamental understanding of high temperature PEM fuel cell degradation processes requires surface characterization of the metal-polymer electrolyte interface. X-ray absorption spectroscopy,  $\Delta\mu$  XANES and photoelectron spectroscopy are powerful tools for this research. For the realization of such measurements, the development of the experimental setups able to operate at the requested conditions giving reliable results was first priority from the beginning of the project. Thereafter, the objective was the use of in situ spectroscopic techniques for the study of the catalytic layer under fuel cell operation aiming to the thorough understanding of Pt corrosion, oxidation and agglomeration.

#### WP5 MEAs testing and degradation

In situ measurements give very important information on the degradation of the MEAs. As a base, standard state-of-the-art MEAs prepared from PBI derivatives (Fumatech) and pyridine based electrolytes (Advent) were studied by subjecting the MEAs to a series of in situ tests altering parameters like the partial pressure of the feed gases, water vapor, temperature and pressure. The durability of the system under normal operation, as well as under aggressive conditions was explored. The study of the materials after their use was also a revealing stage for the study of the degradation mechanisms. Furthermore, diagnostic tools for the determination of the electrochemically active surface area (EASA) under the conditions of high-temperature PEMFCs were explored.

#### WP6 Mathematical modeling of the catalyst degradation

The phenomena connected with catalyst degradation, especially those taking place under transient conditions, are not easily accessible experimentally. A suitable mathematical model can, therefore, be a powerful tool to illustrate local changes in key variables. The main aim of the project was the realization of a mathematical model of catalyst degradation in single cell of high temperature acid doped PEM type fuel cell (HT PEM FC) enabling (a) to elucidate the core of the catalyst degradation process, to understand the individual mechanisms and connections between them, (b) to predict long term stability of the catalyst in dependence on the operational conditions. The objectives were the proposal and implementation of a kinetic 2-D mathematical model and the evaluation of the required kinetic parameters related with Pt corrosion reactions. Validation of the model with experimental data of a single cell HT PEMFC consists the final and decisive step.

#### WP7 Dissemination and public awareness

- Disseminate appropriate information to the scientific community to raise awareness about the status of the technology. This can be realized through publications to international peer reviewed journals and participation to conferences, exhibitions and other relevant events.
- Create a common database for all the project documentation (deliverables, publications, management procedures, strategies, research experimental data, regular reports and minutes, etc.) as a common tool for communication.

## Description of the main S & T results/foregrounds

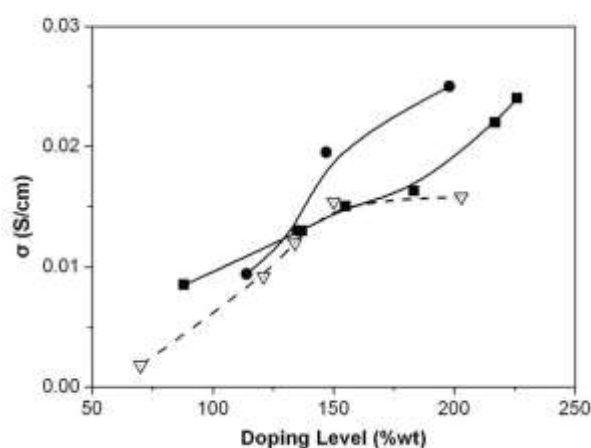
The objective of the DEMMEA project was to understand the functional operation and degradation mechanisms of high temperature  $\text{H}_3\text{PO}_4$  imbibed PEM and its electrochemical interface. The ultimate milestone of the project was the combined use of advanced experimental techniques that will lead in the design and development of an accelerated test and prediction tool for the MEA's performance. This can lead the tailormade optimization of the MEA into a commercially reliable product for stack manufacturers.

The activities of the DEMMEA project have been focused:

- on the synthesis of new polymer electrolytes based either on aromatic polyethers with pyridine units or chemical structures based on PBI and AB-PBI derivatives as a control group. Their stability was studied both ex situ and under MEA operating conditions.
- On the characterization and development of diagnostics for the study of the electrodes and the electrochemical interface aiming to the understanding of the stability and degradation of both the electrocatalyst and the electrodes, which led to the development of novel electrocatalysts based on functionalized carbon nanotubes and vertically oriented carbon fibers.

### Polymer electrolytes operating at 180°C

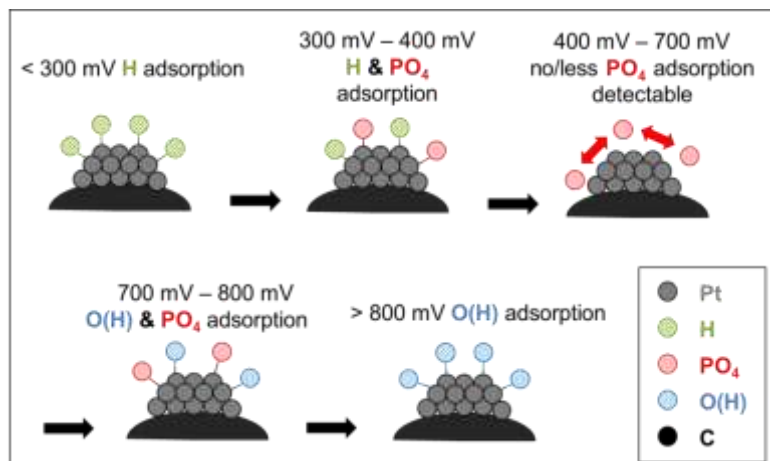
The performance and lifetime of a high temperature electrolyte is characterized by its acid doping ability, proton conductivity and oxidative stability, which are directly related to the specific chemical structure of the polymeric material. The versatility of the polymerization conditions and the large number of possible comonomers allowed the creation of numerous polyelectrolytes based on aromatic polyethers bearing different functional groups. These were synthesized from the pyridine diol and bisfluorophenyl sulfone along with monomers bearing either methyl side groups or sulfonic acid groups or carboxyl side group. All materials depicted excellent film forming properties, high molecular weights, good mechanical properties and high thermal stability. The phosphoric acid uptake differed with the structure but in all cases high doping levels were achieved while the membranes retained their mechanical integrity. Depending on the introduced functional groups, different modes of oxidative stability were obtained. Copolymers bearing pyridine moieties and methyl or carboxyl substituents showed exceptional oxidative stability under ex situ Fenton test conditions. The corresponding sulfonated copolymer analogs showed poorer oxidative stability due to the presence of sulfonate groups. In any case their stability was much higher than the reported values for sulfonated aromatic copolymers of the literature. Moreover for all copolymers, it was proven that acid uptake and proton conductivity are highly affected from the chemical structure of the copolymer, figure 1.



**Figure 1.** Acid doping level dependence of proton conductivity for copolymers with differentiations on the chemical structure (i.e. bearing different functional groups: methyl (-▽-), p-tolyl (-■-) and carboxyl (-●-) side groups) at room temperature.

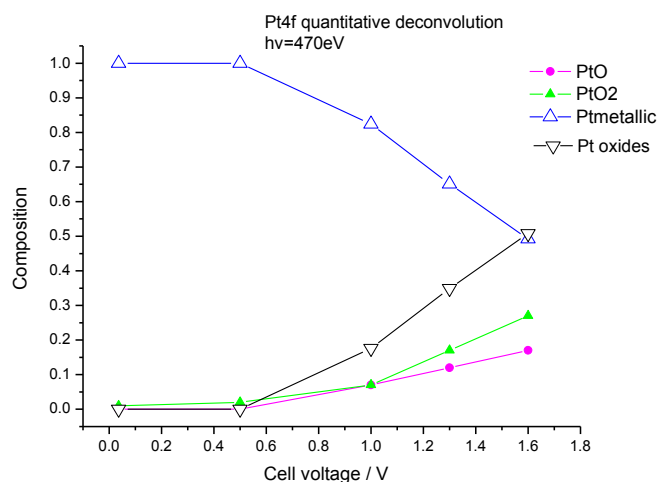
Novel spectroscopic techniques

$\Delta\mu$  XANES method has been developed and applied for the first time for HT PEMFCs.  $H_3PO_4$  and OH species were quantitatively identified on the catalyst as a function of the cell potential, while the CO coverage and humidification effect on the anodic catalyst under reformates was also investigated. An example is depicted in figure 2, where the adsorption behavior of phosphoric acid on Pt nanoparticles at elevated temperatures is depicted. At low cell voltages only hydrogen is present on the surface, while with an increase in the voltage phosphoric acid shows up and suppresses other adsorbates. At intermediate cell voltages, only phosphoric acid anions cover the Pt surface. Applying higher cell voltages, O(H) comes down on the cathode catalyst surface and forces adsorbed  $PO_4$  into registry again. At cell potentials higher than 800 mV only O(H) is left on the surface.



**Figure 2.** Cartoon illustrating the situation of adsorbates on the Pt surface at different cell voltages.

Moreover, ambient pressure photoelectron spectroscopy (APPEs) and scanning photoelectron microscopy (SPEM) were applied. APPEs at mbar water pressures allows to reproduce conditions relevant to the HTPEM operation and offers a unique possibility to in situ monitor the influence of the polarization on the electrode/electrolyte interface. It was possible to observe changes both on the metal side of the interface (Pt oxidation) and on the electrolyte side (electrode flooding with phosphoric acid). Figure 3 shows the results of the *in situ* observation of the Pt oxide formation, where the Pt oxides become noticeable at  $V_{WE-CE} = 1$  V, and suggest simultaneous growth of at least two types of oxide: Pt(II) and Pt(IV) which previously could only be observed using *ex situ* PES of emersed Pt electrodes.



**Figure 3.** Evolution of the atomic contributions of Pt(0), Pt(II) and Pt(IV) as resulted from the deconvolution of the Pt4f spectra obtained by means of APPEs.

SPEM allowed observing the morphology of the working interface. However, it requires low base pressures of the order of 10<sup>-5</sup> mbar where membrane drying results in an inhomogeneous potential distribution at the interface. Nevertheless, utilization of SPEM led us to an important conclusion of formation of reduced phosphorous species (most likely P) in the presence of hydrogen.

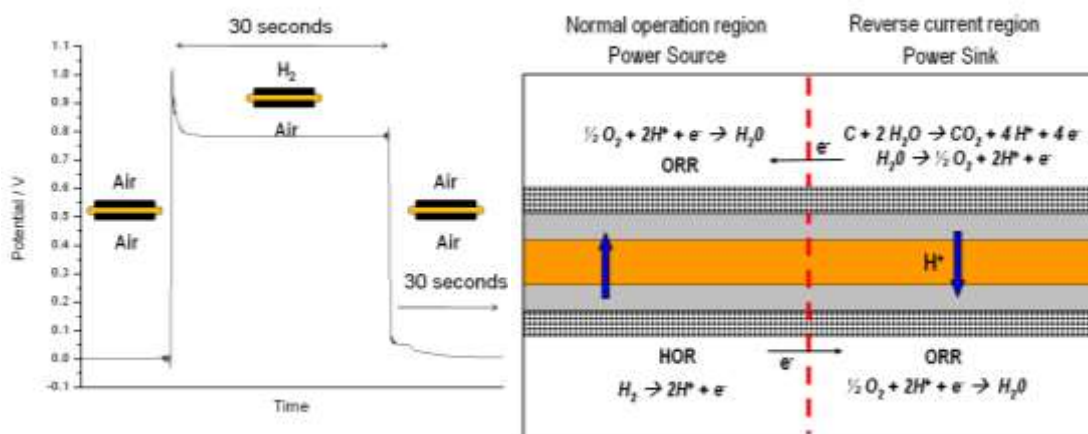
In situ electrochemical characterization

Different types of MEAs were subjected to long term and accelerating testing. MEAs were studied and tested in single fuel cells with regards to their operating conditions' effect on performance, their long term stability and the determination of Pt electrocatalytic utilization and durability. The characterization and diagnostics of the MEAs' behavior were based on Electrochemical Impedance Spectroscopy in order to discriminate the behavior of the electrochemical interfaces and their contribution on the degradation. Electrochemically active surface area was determined based on CO adsorption and the formation of stable adsorbed species at the operating temperature of the MEA which could be oxidized electrochemically using potentiodynamic measurements. The aforementioned techniques were also used for the first time in a linearly segmented high temperature cell. Compression forces also have an impact on the physicochemical properties of the materials which in turn affect the fuel cell performance. The control of compression is an important requirement in order to be in a position to basically identify some of the degradation effects in HT-PEMFCs and to deconvolute their influence on the overall performance. Thus, developing and using the proper device, investigation of the MEAs under controlled conditions of temperature, pressure and compression took place.

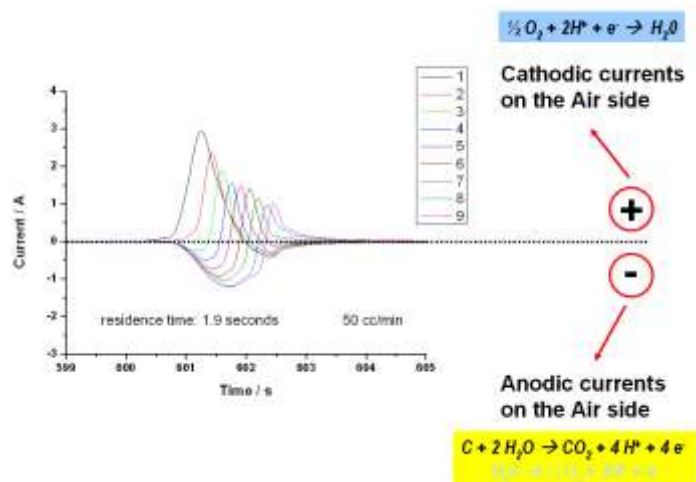
All the aforementioned study resulted in valuable information on the performance and stability of the individual MEA components, providing a comparative study between the different types of MEAs and shedding light into the effect of structure, morphology, architecture and preparational methodologies followed. This consisted the first step to the optimization and tailormade improvements of the HT MEA technology.

Degradation mechanisms - results

Start/stop cycles determine the operational lifetime of a fuel cell. Therefore, a start/stop protocol at 170 °C was applied to pristine MEAs in order to study its degradation. As shown in Figure 4, carbon corrosion on the oxidant side can be triggered when consecutive exchanges between H<sub>2</sub> and Air in the fuel compartment of the cell (anode) take place.



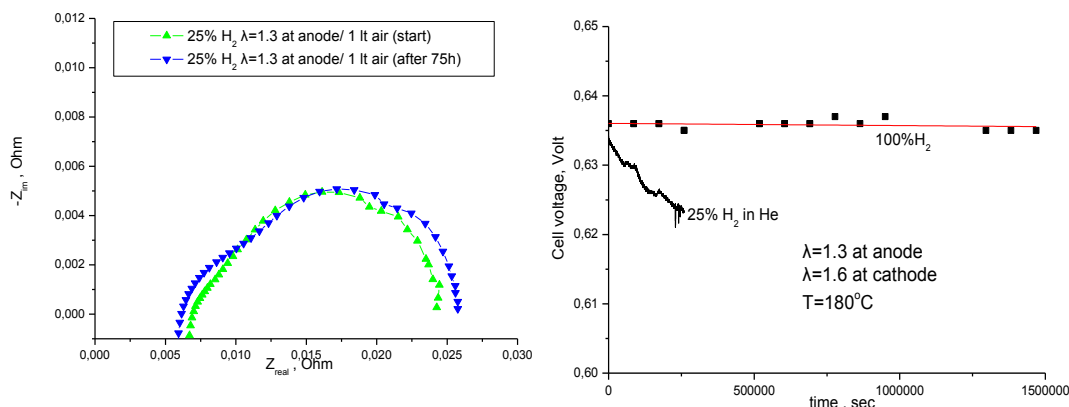
**Figure 4.** (left) The start/stop cycles can be seen here in respect to the cell potential and (right) the reactions that take place to maintain the balance of charge that has been triggered through the potential differences in the cell.



**Figure 5.** Transient internal currents flowing at the air electrode during a start cycle. Positive and negative charges are equal and the total sum is 0.

The segmented current collectors on the cathode of the cell recorded internal currents flowing during the passing of the H<sub>2</sub>/Air front through the anodic compartment of the cell, Figure 5. Positive currents are attributed to reduction processes and more specifically on the oxygen reduction reaction that takes place in the “power source” region of the cell. The negative currents are oxidative currents that depict the carbon corrosion and the oxygen evolution on the “power sink” region of the cell. Moreover, it was proven that the corrosion is smaller during start than during stop, while the corrosion shifts from the inlet to the outlet region when decreasing the residence time.

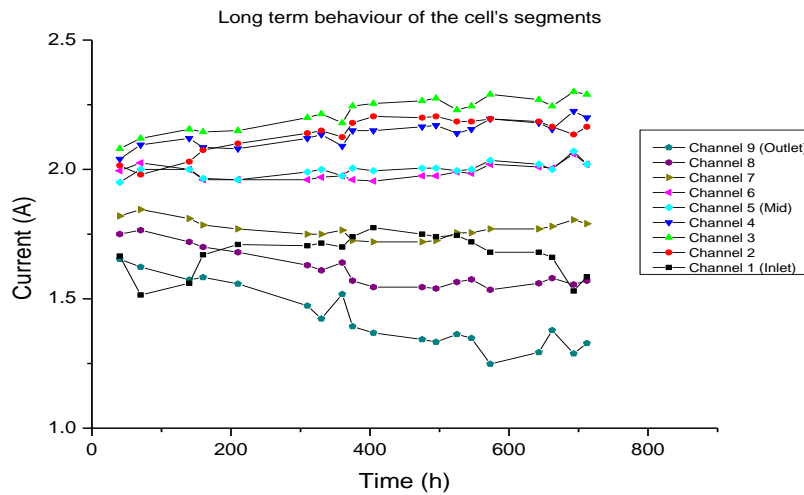
Furthermore, the stability of the operating performance of the single cell MEAs was focused on degradation issues related with H<sub>2</sub> crossover, catalyst degradation due to cell voltage and temperature cycling, as well as the anode behavior under reformate conditions. The operation of the anode under lean H<sub>2</sub> compositions results in a severe increase of the polarization resistance due to the limited kinetics of the H<sub>2</sub> oxidation and the depleted H<sub>2</sub> coverage on Pt particles, Figure 6a. Therefore, the MEA is subjected to severe performance degradation with time, Figure 6b.



**Figure 6.** (a) Impedance spectra for ADVENT TPS<sup>®</sup> MEA at 180 °C and 0.2 A/cm<sup>2</sup> using dry H<sub>2</sub>/Air gases with stoichiometric ratio 1.3/11.0 and PH<sub>2</sub> 25%. (b) Long term stability test for ADVENT TPS<sup>®</sup> MEA at 180 °C and 0.2 A/cm<sup>2</sup> using dry H<sub>2</sub>/Air gases with stoichiometric ratio 1.3/1.6 and PH<sub>2</sub> 100% and 25%, respectively.

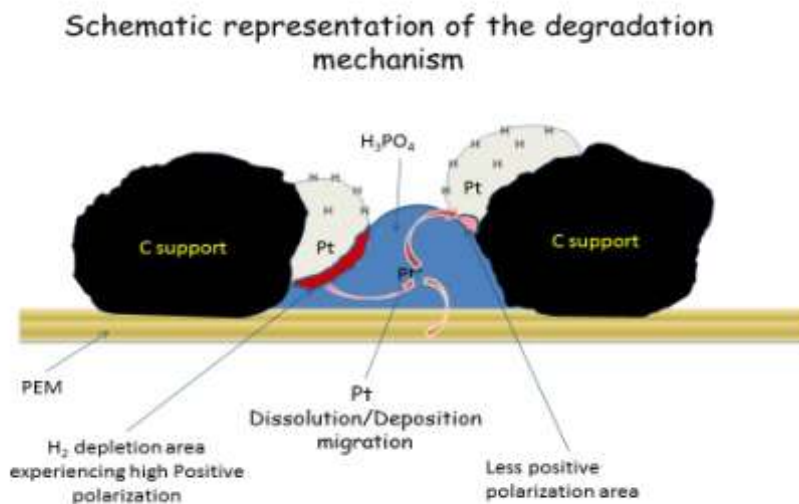
The segmented cell was further used to identify the most vulnerable parts of the MEA along the utilization pathway of H<sub>2</sub> and O<sub>2</sub>, as presented in Figure 7. It is worth noticing that an improvement of the cells’ performance is observed close to the inlet segments while severe degradation has been detected towards the outlet, where the partial pressure of the reactant gas is lower.





**Figure 7.** Long term behavior of the cell’s segments in counter flow mode.

According to the aforementioned arguments the degradation of the anode must be taken seriously into consideration especially when the anode operates under reformat gas. The main reason can be the severe depletion of hydrogen in various parts of the Pt particles in particular those covered by  $H_3PO_4$ . Figure 8 shows a schematic representation of the electrochemical interface and of the degradation mechanism under  $H_2$  lean conditions. The main peculiarity of the high temperature  $H_3PO_4$  imbedded MEAs is the impregnation of the catalytic layer with  $H_3PO_4$  so that a three dimensional ionic link can be established between the Pt nanoparticles and the  $H_3PO_4$  imbedded polymer electrolyte. Thus, during the course of the acid distribution and the formation of the electrochemical interface, part of the Pt can be covered by the  $H_3PO_4$  hindering the access and the adsorption of  $H_2$  on the Pt surface. This phenomenon is becoming severe when the partial pressure of  $H_2$  is low and consequently the diffusivity of  $H_2$  through the  $H_3PO_4$ . In this way, the  $H_{ad}$  depleted areas can experience more positive electrochemical voltage than the  $H_2$  covered areas, being suspect either for Pt dissolution and Ostwald ripening or carbon corrosion at the boundaries of the Pt nanoparticles and the carbon support resulting in the detachment of Pt from the carbon support.

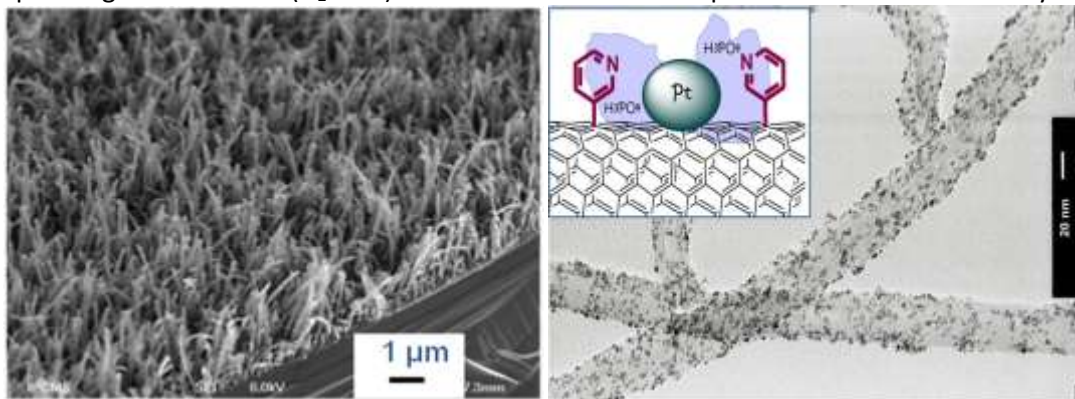


**Figure 8.** Schematic representation of the electrochemical interface and the degradation mechanism of the anode.

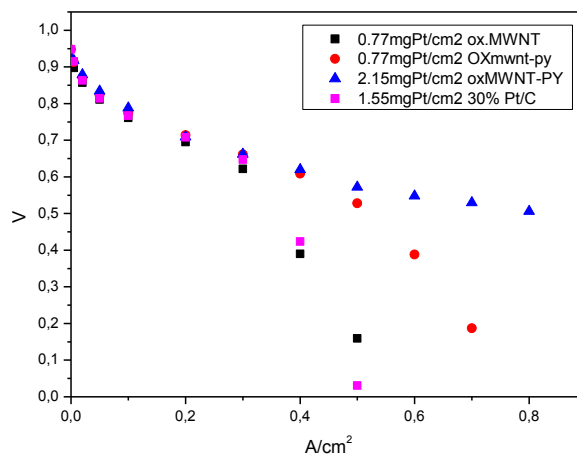
New high temperature electrocatalysts

Based on the above observations and conclusions the main factors that cause severe degradation on the anode is the low partial pressure of  $H_2$  in combination with the non-

uniform distribution of the  $H_3PO_4$  within the catalytic layer thus resulting in areas with depleted H coverage, so that Pt corrosion into  $Pt^+$  is enhanced. In this respect we proposed the development of catalysts based on chemically functionalized with pyridine groups carbon nanotubes (CNTs) (Fig. 9 right) and vertically aligned carbon fibers (VACNF) (Fig. 9 left) as a replacement for conventional random catalytic layers based on carbon powder supports. More specifically, the new supports were prepared aiming to the formation of an effective electrochemical interface and ultimately to enhance catalyst utilization. Pt nanostructured electrocatalysts were prepared and characterized. Physicochemical and liquid-electrochemical characterization gave very promising results. Very importantly, the in-situ electrochemical characterization performed suggests that the new layers based on Pt deposited on pyridine functionalized CNTs augment the efficiency and the stability of the anodic catalytic layers operating under limited ( $H_2$  lean) reformate conditions compared to conventional catalysts.



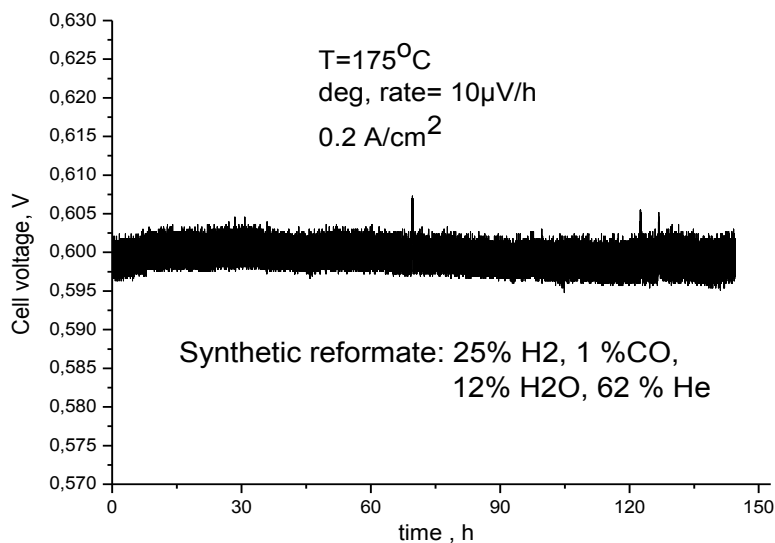
**Figure 9.** SEM image of VACNF grown by the catalytic chemical vapor deposition on  $TiO_x/Ti/Si(100)$  base (left). TEM micrograph of 20%  $Pt/(ox.MWCNT)-Py$  (right).



**Figure 10.** Polarization curves of different MEAs at  $180^\circ C$ . The amount of PA sprayed at the electrodes, was kept constant for all tested MEAs,  $2gPA/gPt$ . Wet synthetic reformate gas was fed at the anode ( $\lambda_{H_2}=1.2$ ): 50.7%  $H_2$ , 2%  $CO$  and 33.5%  $H_2O$  and 13.8%  $Ar$ . At the cathode pure  $O_2$  was used ( $\lambda_{O_2}=2$ ).

The 30%  $Pt/(ox.MWCNT)-Py$  electrocatalyst was integrated into the structure of ADVENT MEAs. A comparison of the different electrocatalysts using synthetic reformate gas is shown in Figure 10. The MEA employing the commercial catalyst at the anode, 30%  $Pt/C$ , suffers a significant voltage loss reaching limiting current at a value of  $0.5 A/cm^2$ . Similar behavior was observed for 30%  $Pt/(ox.MWCNT)$  but with half Pt loads compared to  $Pt/C$ . For the case of 30%  $Pt/(ox.MWCNT-Py)$  electrocatalyst a substantial improvement in the cell's performance was observed, again with low loading compared to the commercial  $Pt/C$  catalyst. This improvement is attributed to the higher ECSA and Pt utilization of the newly synthesized electrocatalyst, in combination with the stabilization of the ionic conductive pathway in the electrodes due to pyridine groups under high water partial pressures.

Moreover, in Figure 11 a long term experiment is depicted at 175°C and 0.2 A/cm<sup>2</sup> using reformat with 25% H<sub>2</sub>, 1% CO, 12% H<sub>2</sub>O, 62% He for about 150 hours. The MEA impressively showed very small degradation rate (10 μV/h) under these marginal conditions which is 10 times less than the degradation rate of the state of the art Pt/C based electrode.

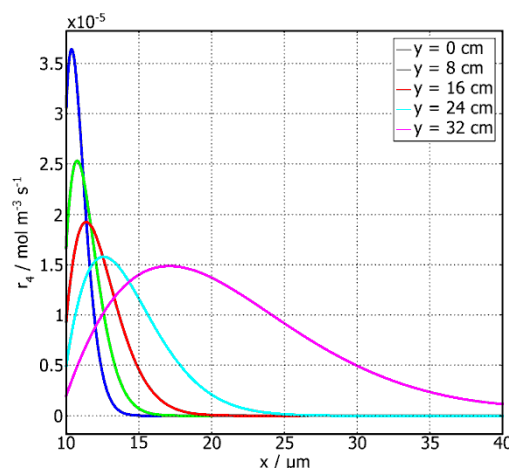


**Figure 11.** Long term stability test for a MEA employing the 30% Pt/(ox.MWCNT)-Py electrocatalyst at the anode at 175 °C and 0.2 A/cm<sup>2</sup> using reformat with 25% H<sub>2</sub>, 1% CO, 12% H<sub>2</sub>O, 62% He and Air with stoichiometric ratio 2.0.

Mathematical modeling

The phenomena connected with catalyst degradation are not easily accessible experimentally. A suitable mathematical model can, therefore, be a powerful tool. As a first step the mathematical model of LT PEM FC describing platinum catalyst dissolution, movement and redistribution at the cathode and inside the cell was developed and implemented into the COMSOL environment. Moreover, a two-dimensional model version was designed allowing assessment of the effect of reactants and products partial pressure variation along the gas flow channels on the fuel cell catalyst degradation. The final 2D model allowed observing effect of the reactant gases partial pressure variation both in the flow channels and in the catalyst layers. By means of this model one may reasonably describe the Pt deposition inside the membrane. On the base of the model calculations the data relevant for the modeling of the Pt dissolution and redistribution in the high temperature PBI/H<sub>3</sub>PO<sub>4</sub> fuel cell were identified.

Figure 12 shows the values of the rate of the Pt<sup>2+</sup> reduction by H<sub>2</sub> across the membrane and different positions along the flow stream. Of course, the thickness of this region strongly depends on the hydrogen partial pressure in the catalyst layer at the anode and consequently inside the membrane phase. For example, extremely low concentrations of hydrogen appear in the region close to the gas outlet. Here the Pt<sup>2+</sup> ions are reduced with lower rate and the reduction occurs almost across the entire membrane width. It is also clear, that in such a case a certain portion of the platinum ions penetrate also to the anode catalyst layer. This finding shows that the degradation of the MEA can be more severe towards the outlet of the reactor which can cause electronic conduction across the electrolyte.



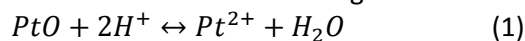
**Figure 12: (left)** Reaction rate of  $\text{Pt}^{2+}$  reduction by hydrogen across membrane ( $x$  direction) and at different positions  $y$  along the flow channel; potentiostatic mode  $U = 0.8$  V, initial particle radiuses:  $r_{\text{Pt1}} = 2$  nm,  $r_{\text{Pt2}} = 3$  nm,  $y_{\text{O}} = 0.21$ ,  $y_{\text{H}} = 1$ ,  $v_{\text{H}_2} = 0.25$  m  $\text{s}^{-1}$ ,  $v_{\text{O}_2} = 0.42$  m  $\text{s}^{-1}$ ,  $k_4 = 100$  m<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>; operational time - 15 min.

The objective of the subsequent work was modification of the model proposed to describe catalyst degradation in the HT PEM cell. Evaluation of kinetic parameters of the main processes responsible for degradation was necessary. A kinetic mathematical model was proposed and implemented in COMSOL Multiphysics™. The required kinetic parameters were evaluated from analysis of the experimental data using the proposed mathematical model. Finally, the results of the mathematical model were compared with the results of experimental measurements of a long-term stability of performance of single cell HT PEM FC.

## Conclusions

In conclusion, the results depicted herein clearly demonstrate the DEMMEA project progress and scientific and technological impact. From the scientific point of view, some failure mechanisms of the current technology MEAs have been identified using a series of ex-situ and in-situ experimental techniques including in-situ spectroscopy XANES adopted for the first time for this purpose. Specifically the main milestones of the project can be summarized as follows:

- By the use of in situ XANES spectroscopy the coverage of the  $\text{H}_2$ ,  $\text{PO}_4^-$  and  $\text{O}(\text{H})$  species on the cathode has been identified. According to the model reactions used to describe the dissolution of Pt it is expected that Pt corrosion can be significant at intermediate cell potentials where the coverage of oxide species  $\text{O}(\text{H})$  and  $\text{H}^+$  concentration are high so that they can result in the highest dissolution rate of Pt according to reaction:



- In addition according to the mathematical modeling the degradation of the polymer electrolyte in terms of Pt dissolution and dispersion within the membrane depends considerably on the crossover rate of  $\text{H}_2$  as well as on cell operating voltage and current density. In this respect according to the XANES spectroscopy the fuel cell must operate above ca 700mV so that  $\text{H}^+$  accumulation and high concentrations at the cathodic interface is avoided and thus the rate of the dissolution reaction (1) is minimized.
- The degradation of the anode is severe under certain reformate conditions (low  $\text{H}_2 < 50\%$  and high  $\text{H}_2\text{O} > 20\%$  content) either due to the slower kinetics of  $\text{H}_2$  oxidation under lean  $\text{H}_2$  reformates or due to the interaction of  $\text{CO}$  and  $\text{H}_2\text{O}$  towards the formation of stable formate species on the Pt surface. In addition the non uniform distribution and the flooding of  $\text{H}_3\text{PO}_4$  acid within the catalytic layer may cause non uniform distribution of H coverage on the Pt surface causing the development in the H depleted areas of more positive overpotentials thus inducing the dissolution of Pt and the oxidation of the support.
- In order to cope with the aforementioned problems novel supports and electrode structures have been developed based on pyridine modified carbon nanotubes. This new support prevented the sinterability of the anode and improved significantly the performance

and long term stability of the anode under reformate conditions and at least half of the Pt loading as compared to the conventional catalyst.

The industrial partners have already benefited by the optimization of their commercial products through the implementation of the project results.

Dissemination of the information to the scientific community has been done through the publication of selected information from the experiments and data analysis of the project in high level publications in international “peer-reviewed” journals, and relevant international conferences and exhibitions. Moreover, one session devoted to the DEMMEA project was organized and took place during the ELMEMPRO conference, August 2012, Czech Republic (<http://www.elmempro.com>). For public communication purposes, non sensitive information were shared on a public project web site: [demmea.iceht.forth.gr](http://demmea.iceht.forth.gr)

## Impact

Nowadays, we are faced with an increasing need for alternative and environmentally friendly energy sources and energy transforming systems. This need can be covered through the use of hydrogen as energy carrier, which can be produced from renewable energy sources e.g. solar or wind energy either through water electrolysis or to a lesser extent biofuels. The transformation of the stored H<sub>2</sub> energy into useful electrical energy can be accomplished by the massive use of fuel cells as efficient and environmentally friendly converters of chemical energy into electricity.

Fuel Cells play a primary role in the following application areas:

(A) *Stationary applications.* The main application will be residential cogeneration and district cogeneration in the 100kW range for the near and medium term. Units in the MW power range are envisaged for the longer term.

(B) *Transport applications.* The potential of fuel-cell technology for higher efficiency and zero emission has already been demonstrated worldwide by various vehicles using hydrogen as fuel, both from onboard storage and from hydrocarbon reforming. It underlines the perspective of this technology as a long-term solution towards sustainability of the rapidly growing transport market.

(C) *Portable applications.* They are defined by a maximum power of 5 kW and the property of portability of the device. The modular design makes it easy to adjust fuel cell power to the application as required.

The integration of this technology in the energy production system is of vital importance for the self sustained development of the human activities in harmonization with the natural environment. The every-day life can benefit by the use of Fuel Cells primarily due to the great reduction in air pollution emissions that FCs can achieve. Energy produced by a fuel cell will be characterized as high quality energy because of the high conversion efficiency from chemical to electrical energy (~50%) almost twice as high compared to internal combustion engines, and because of the zero emissions of pollutants and greenhouse gases (due to the recycling of CO<sub>2</sub> to produce renewable fuels) to the environment. The extensive use of fuel cells will cause a steep reduction of air pollutants in metropolitan areas. Such a scenario will certainly improve the living conditions and infrastructures in less favored regions through for example rural electrification and consequently through the economic development and the quality of life in these regions. In parallel fuel cell development will intensify the massive production of renewable fuels (like methanol by the CO<sub>2</sub> reduction with renewable H<sub>2</sub>, or bio ethanol) with positive effect on the economy of rural areas. The European economy will no longer depend on imported oil, which is a significant instability factor for industrialized economies. The reduction of dependence from oil markets will secure the European economies.

In addition the high temperature PEM fuel cell technology has approached a level of technological significance according to which the benefits and applications are highly estimated worldwide. The elevated operating temperature can facilitate faster electrokinetics for the electrocatalytic reactions. The fuel cell is producing high quality waste heat which can be used for other purposes, thus resulting in highly efficient exploitation of the produced energy in total. Moreover, voluminous heat exchangers can be avoided so that the integrated fuel processors with high temperature PEM fuel cells results into a threefold decrease of the system volume, in comparison to the corresponding systems comprising low temperature PEM fuel cell technology.

According to the 2008 Annual implementation plan (AIP) of FCH JU: Fuel cell stacks for stationary power applications require an operational lifetime up to 40,000 hours. Improved understanding of failure mechanisms is required to ensure reliable prediction of cell and stack failure.

In this respect, the goal of this project was the development of a highly efficient PEMFC through the optimization of the individual components of the core of the fuel cell, the Membrane Electrode Assembly, MEA. This was accomplished through the understanding of the physical origin of the operation and degradation phenomena that take place, which

permitted the tailor-made optimization of the MEA through the proposal of new materials (PEMs and catalysts) into a commercially reliable product for stack manufacturers.

### **The DEMMEA project**

The activities of this project were mainly focused on the stationary applications area. The PEMFC operated at elevated temperatures of 120 up to even 200°C has a great potential to simplify stationary systems and reduce costs. It could also prove successful for units larger than required for residential use. Stationary applications are important for the early market, since they are not dependent on a hydrogen infrastructure.

The results demonstrate the DEMMEA project scientific and technological impact. From the scientific point of view, some failure mechanisms of the current technology high temperature MEAs have been identified using a series of ex-situ and in-situ experimental techniques. Very importantly, new methodologies and experimental techniques for the study of such systems were developed opening the road to future research studies and achievements. Novel polymer electrolytes have been prepared aiming to stable structures at elevated temperature. The novel electrocatalytic systems with new architectures prepared seem to overcome certain limitations of the current state of the art formulations towards the improvement of performance and stability of the HT MEAs.

This project developed methodologies and diagnostics for the study and understanding of the degradation mechanisms of the high temperature fuel cells based on phosphoric acid imbibed polymer electrolytes, thus posing an ambitious technological and research challenge. The improvement of the MEA technology through the successful implementation of the DEMMEA project's activities can be viewed as an enabling technology, opening the road to a wide variety of new applications, which could increasingly come from renewable sources. The High-Temperature PEM Fuel Cell stack will allow significantly simpler balance of Plant thus resulting in an increase in the volume power density of the integrated system thus seining valuable space. In addition the optimization and development of new diagnostic tools will strengthen the Pre-normative inputs for testing and control methods as well as for safety procedures.

The main direct and indirect socio-economic benefits from the DEMMEA project include cost reduction of the MEA components and thus the overall fuel cell, achievement of reliable and efficient operation and therefore opening/broadening of the fuel cell market with the obvious economic (employment, rural regions) and environmental beneficial impact.

One of the most decisive operating parameters and of high significance regarding the economically efficient operation of membrane cells is their working temperature. The use of Nafion® membrane confines the operating temperature within the range of 80-90°C, due to the dehydration problems. The operation of the cell at temperatures at or higher than 180°C, results in a series of advantages. The DEMMEA project led to tailor-made optimization of the current PEM technology in terms of performance and stability, making them directly competitive and realistic and opening the way to the replacement of Nafion with less expensive materials.

Pt so far was proven to be the most active electrocatalytic material for both H<sub>2</sub> oxidation and O<sub>2</sub> reduction reactions. However, the price of Pt is extremely high and its resources can be considered rather limited. Another important aspect is the catalyst utilization. A large portion of precious metal is likely not utilized in conventional catalytic layers due to an inadequate design. Even more, Pt has been shown to corrode, witnessed as an apparent loss of platinum surface area over time associated with platinum crystal growth. Although the main focus lies on the degradation of the cathode side, the degradation of the anode must be taken seriously into consideration especially when the anode operates under reformate gas. This knowledge was gained through the successful course of the DEMMEA project, which enriched the understanding of the degradation mechanisms in the MEA level.

DEMMEA also reached to the next level by proposing new electrocatalysts (VACNF and pyridine modifies nanotubes) that show increased catalyst utilization. The presence of pyridine moieties was proven to provide a homogeneous distribution of phosphoric acid throughout

the catalytic layer, thus imposing the contact of Pt with the proton conducting media, increasing the extent of the three-phase boundary and ultimately the catalyst's utilization. In addition the performance and stability of these materials under harsh reformat conditions (i.e. lean H<sub>2</sub> (<50%) and water rich (30%) gas) was remarkable even at relatively low Pt loadings as compared to the conventional Pt/C based anodic electrodes.

Given the above, the DEMMEA project helped to result in lower cost, robust and highly efficient MEAs with validated high performance (power densities exceeding 0.17 W/cm<sup>2</sup> at a cell potential of 700 mV in a single cell level) as the key component for High Temperature PEM fuel cell applications. The industrial partners – participants ensure the fast commercialization of the results and already benefited through the optimization of their commercial products. This fact promoted the evolution of the industry, especially the SMEs involved, while affected favourably the market penetration for the PEM fuel cell technology.

This project contributed to the in depth understanding of the operational and degradation phenomena of a high temperature MEA, while new methodologies and experimental techniques for the study of such systems were developed by several academic partners. This will have significant impact on the future evolution of the research activities of these partners especially on the continuation of the study of diagnostic tools for the study of HTPEM technology.

The potential of the hydrogen and fuel cell economy is very high. The impact in European job market is also important. The DEMMEA project attracted young scientists while, in turn, their advanced knowledge benefited the project evolution. In addition, the project generated highly-skilled scientists and researchers in PEM fuel cell technology able to provide Europe with expertise in advanced technologies. The contact established between academia and high technology industry stimulated high level scientific career opportunities.

Thus, important technological and research knowledge is produced, which is to be shared with the scientific community, the relevant industry and the wider public through the proper dissemination mechanism allowing accessing the project results by all interested parties. Dissemination of the information to the scientific community has been done through the publication of selected information from the experiments and data analysis of the project in high level publications in international “peer-reviewed” journals (above 15 publications in peer-reviewed journals), and relevant international conferences (above 65 oral and poster presentations). Moreover, one session devoted to the DEMMEA project was organized and took place during the ELMEMPRO conference, August 2012, Czech Republic (<http://www.elmempro.com>). The information is also posted in the project website: <http://demmea.iceht.forth.gr/index.php>.