PROJECT

PEMICAN

PEM with Innovative low cost Core for Automotive application

Funding: European (7th RTD Framework Programme)
Duration: Apr 2011 - Mar 2014
Status: Complete with results
Total project cost: €3,955,219
EU contribution: €1,861,352

CORDIS RCN : 97999

Objectives:

Up to now, much work has been performed on the catalyst but much on the active layers’ structure and on the two other major components (carbon and electrolyte) whereas they do have a major impact on the MEA’s performance and on Pt utilization.

Based on this analysis, PEMICAN proposes to reduce the Pt loading for automotive application down to 0.15 gram of Pt per kW, by a twofold approach:

1. to increase Pt utilization and power density by improving effective transport properties of ALs by tuning some properties of the electrolyte and by adding special carbon blacks in order to improve catalyst, electrolyte distribution and water management;
2. to reduce Pt loading by controlling its distribution: very thin layer on the anode side and gradients of Pt on the cathode side. These structured layers will be defined in order to optimise the utilization of the Pt.

The combination of these two approaches will allow reducing the total mass of Pt for a given power density.

Whereas the main objective of PEMICAN is to develop and manufacture MEAs with reduced quantity of Pt, it is supported by numerical modelling to help defining the best Pt distribution. Special structural and electrochemical characterizations will be done to improve the existing models and to analyse the performance of our MEAs as a function of manufacturing processes and properties of components. Performance and durability tests under automotive conditions will be performed and analysed.

PEMICAN will demonstrate gains in terms of Pt cost (g Pt/kW) obtained by improving the design and properties of the ALs. Its results will be useful also in the future when non pure Pt is available.

The Consortium is built-up on the expertises of 6 European organisations with complementary skills: 2 Research Institutes (CEA and INASMET), 1 University (IMPERIAL COLLEGE), 2 industrial suppliers (SOLEXIS, TIMCAL) and 1 automotive OEM (OPEL). Among these partners, 4 of them are active members of the FCH JTI.

Parent Programmes:
FP7-JTI - Specific Programme "Cooperation": Joint Technology Initiatives

Institute type: Public institution
Institute name: European Commission
Funding type: Public (EU)

Lead Organisation:

Commissariat A L Energie Atomique Et Aux Energies Alternatives
Address:
<table>
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| **RUE LEBLANC 25**  
75015 PARIS 15  
France  
**Organisation Website:**  
http://www.cea.fr  
**EU Contribution:** €737,028 | | |
| **Partner Organisations:** | | |
| **Imperial College Of Science Technology And Medicine**  
**Address:**  
Exhibition Road, South Kensington  
LONDON  
SW7 2AZ  
United Kingdom  
**Organisation Website:**  
http://www.imperial.ac.uk  
**EU Contribution:** €277,703 | | |
| **Imerys Graphite & Carbon Switzerland Sa**  
**Address:**  
STRADA INDUSTRIALE  
6743 BODIO  
Switzerland  
**Organisation Website:**  
http://www.timcal.com  
**EU Contribution:** €229,696 | | |
| **Fundacion Tecnalia Research & Innovation**  
**Address:**  
Parque Tecnologico De Bizkaia - Calle Geldo - Edificio 700  
48160 Derio  
Spain  
**Organisation Website:**  
http://www.tecnalia.com  
**EU Contribution:** €0 | | |
| **Solvay Specialty Polymers Italy Spa**  
**Address:**  
Viale Lombardia 20  
20021 Bollate (Mi)  
Italy  
**Organisation Website:**  
http://www.solvayspecialtypolymers.com  
**EU Contribution:** €277,515 | | |
| **Fundacion Inasmet**  
**Address:**  
Paseo Mikeletegi , Parque Tecnologico Miramon 2 | | |
Technologies:
Fuel cells and hydrogen fuel
Development of new Fuel Cells and Hydrogen (FCH) technologies
Development phase: Research/Invention

Key Results:
Final Report Summary - PEMICAN (PEM with Innovative low cost Core for Automotive application)

Executive Summary:
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A Polymer Electrolyte Membrane Fuel Cell (PEMFC) is a device for generating electric current from hydrogen and oxygen via electrochemical reactions. It is made up of an anode, a cathode, and a polymer electrolyte membrane that separates these two electrodes. Anode and cathode consist of a gas channel supplying the reactant gases, a gas diffusion layer whose purpose is to transport the gases from the channels to the reactants sites, and an active layer (AL) where the electrochemical reactions take place. The combination of membrane and ALs is referred to as Membrane Electrode Assembly (MEA).

On the anode side, hydrogen molecules are split into protons and electrons. While the protons move through the membrane to the cathode the electrons cannot pass the PEM and must move to the cathode via an external current circuit, for instance feeding an electrical engine to power a car. On the cathode side protons and electrons react with the oxygen to form water. Under typical operating conditions this water appears in vapour form but also liquid water may occur, especially under heavy load. For automotive applications oxygen is typically taken from the surrounding air while hydrogen is supplied from an on-board storage system. Such a system allows producing electricity with no other exhaust gases than water (no pollution).

The active layers consist of carbon black, a polymer electrolyte also referred to as ionomer, Platinum (Pt) acting as catalyst metal, and some open pore space. Since Pt is extremely expensive it is desirable to reduce Pt loading, especially for automotive application for which cost is a major issue to allow its commercial development.

Up to now, a lot of work has been performed on the catalyst of the active layers of PEMFC but much less on the structure of the AL and on the two other major components (carbon and electrolyte) whereas they do have a major impact on the performance of PEMFC and on Pt utilization.

Based on this analysis, PEMICAN has proposed to reduce the Pt cost for automotive application by developing: a) MEA based on AquivionR ionomer with a total Pt loading decreased step by step from 1 down to 0.1 mg/cm²; b) specific tuned raw materials (AquivionR ionomer and Carbon Blacks) to improve performance and durability; c) low loaded MEA with alternative manufacturing processes (Physical Vapor Deposition, Direct Electro Deposition, Pt gradients) to check their performance.

These technological objectives are supported by a scientific approach: a) characterize properties of raw materials to link to performance and durability; b) develop innovative tools to measure major properties
of active layers (proton conductivity, fundamental electrochemistry, gas diffusion…) to supply reliable inputs to modelling; c) develop Pore Network Model of the cathode to account for more realistic structure; d) improve performance models with better inputs and comparison to experiments; e) analyse limitation of performance as a function of Pt loading by combining fundamental characterization and modelling.

Even if the final target (0.15g/kW) has not been reached, PEMICAN has demonstrated the interest of Aquivion® ionomer, the capability to influence performance and durability by tuning properties of raw materials, demonstrated the gain in terms of Pt cost from 1 to 0.3 g/kW, analysed the main limitations of performance as a function of Pt loading. These results can be useful also in the future when non pure Pt is available.

Dissemination has been done by presentation to conferences, publications, patents and intermediate results have been presented to an Industrial Boarding. A public website www.pemican.eu will remain live until spring 2017.

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Project Context and Objectives:

A Polymer Electrolyte Membrane Fuel Cell (PEMFC) is a device for generating electric current from hydrogen and oxygen via electrochemical reactions. It is made up of an anode (A), a cathode (C), and a polymer electrolyte membrane (PEM) that separates these two electrodes. Anode and cathode consist of a gas channel supplying the reactant gases, a gas diffusion layer (GDL) whose purpose is to transport the gases from the channels to the reactants sites, and an active layer (AL) where the electrochemical reactions take place. The combination of membrane and ALs is referred to as Membrane Electrode Assembly (MEA).

On the anode side, hydrogen molecules are split into protons and electrons. While the protons move through the PEM to the cathode the electrons cannot pass the PEM and must move to the cathode via an external current circuit, for instance feeding an electrical engine to power a car. On the cathode side protons and electrons react with the oxygen to form water. Under typical operating conditions this water appears in vapour form but also liquid water may occur, especially under heavy load. For automotive applications oxygen is typically taken from the surrounding air while hydrogen is supplied from an on-board storage system. Such a system allows producing electricity with no other exhaust gases except water (no pollution).

The active layers consist of carbon black, a polymer electrolyte also referred to as ionomer, Platinum (Pt) acting as catalyst metal, and some open pore space. Since Pt is extremely expensive it is desirable to get along with as little Pt as possible, especially for automotive application for which the cost of such an engine is a major issue to allow its commercial development.

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Based on this analysis, PEMICAN has proposed to reduce the Pt cost for automotive application by a twofold approach: i) increase Pt utilization and power density by improving effective transport properties of AL by tuning some properties of the electrolyte and by adding special carbon blacks in order to improve catalyst, electrolyte distribution and water management; ii) reduce Pt loading by controlling its distribution: very thin layer on the anode side and gradients of Pt on the cathode side. These structured layers will be defined to optimise the utilisation of the Pt. The combination of these two approaches will allow reducing the total mass of Pt for a given power density.

Whereas the main objective of PEMICAN is to develop and manufacture MEA with reduced Pt cost, it is supported by a scientific approach: i) numerical modelling to define the best Pt distribution; ii) special electrochemical and fluidic transport characterizations to improve the existing models and to analyse the performance of MEA as a function of properties of materials. Performance and durability tests under automotive conditions has been performed and analysed.

PEMICAN has demonstrated gains in terms of Pt cost (g Pt/kW) obtained by improving the design and properties of the AL. These results can be useful also in the future when non pure Pt is available.

The Consortium is built-up on the expertise of 6 European organisations with complementary skills: 2 Research Institutes (CEA/Joël Pauchet, coordinator; TECNALIA/Alberto Garcia), 1 University (IMPERIAL COLLEGE/Anthony Kucernak), 2 industrial suppliers (SOLVAY SPECIALTY POLYMERS/Elvira Pagano; IMERYS GRAPHITE & CARBON, formerly TIMCAL/Marlène Rodlert) and 1 automotive OEM (ADAM OPEL AG).
The objectives of PEMICAN can be divided into technological and scientific ones.

**Technological objectives**

The main technological objectives are to produce:

- **MEA Level 0** by replacing the classical Nafion® by Aquivion® ionomer, \( \sim 540 \text{ mA/cm}^2 \) @ \( 0.675 \text{ V} \), \( \sim 360 \text{ mW/cm}^2 \), total loading \( \sim 300 \mu\text{g/cm}^2 \), Pt cost \( \sim 0.82 \text{ gPt/kW} \)

- **MEA Level 1** by decreasing the Pt loading (total loading \( \sim 200\mu\text{g/cm} \)) and keeping the same performance, Pt cost \( \sim 0.57 \text{ gPt/kW} \)

- **MEA Level 2** by increasing power density and checking durability
  - \( \sim 740 \text{ mA/cm}^2 \) @ \( 0.675 \text{ V} \), \( \sim 500 \text{ mW/cm}^2 \), total loading \( \sim 200\mu\text{g/cm}^2 \), Pt cost \( \sim 0.40 \text{ gPt/kW} \)
  - Performance loss \( \sim 5-10\% \) of initial performance over 1,000 h

- **MEA Level 3** by reducing even more Pt loading and/or to increasing even more power density with two options and always Pt cost \( \sim 0.15 \text{ gPt/kW} \)
  - **Level 3a** with higher power density and Pt loading: \( \sim 890 \text{ mA/cm}^2 \) @ \( 0.675 \text{ V} \), \( \sim 600 \text{ mW/cm}^2 \), total loading \( \sim 100\mu\text{g/cm}^2 \)
  - **Level 3b** with lower power density and Pt loading: \( \sim 520 \text{ mA/cm}^2 \) @ \( 0.675 \text{ V} \), \( \sim 350 \text{ mW/cm}^2 \), total loading \( \sim 100\mu\text{g/cm}^2 \)

  - Performance loss \( \sim 5-10\% \) of initial performance over 2,500 h

In order to do so, specific technological objectives are defined:

- Develop raw materials to improve performance
  - Aquivion® ionomers (Solvay) with different properties as water handling, proton conductivity and gas diffusion, to be used in the ink formulation; electrolytes development was based on modification of equivalent weight and to increase durability on the blending of ionomers with not-functionalized polymers. Furthermore chemical stabilized products were produced
  - Carbon blacks (Imerys) with different physical properties (electrical conductivity, size, porosity, surface properties...) to be used in the ink formulation or to produce MPL by DED and PVD, specific aim also to develop carbons with improved corrosion resistance.

- Manufacture active layers with reduced Pt quantity

- Adapt (CEA) manufacturing processes to produce active layers using Aquivion® as ionomer and then including also additional Carbon Black defined in the project

- For the anode, test innovative alternative techniques to produce very thin layers and low loadings
  - Produce (Tecnalia) and test first electrodes by Physical Vapour Deposition on GDL with commercial MPL and with MPL with specific Carbon Blacks
  - Produce (CEA) and test first electrodes by Direct Electro Deposition on GDL with commercial MPL and with MPL with specific Carbon Blacks

- For the cathode, improve techniques to better control the Pt location
  - Improve (CEA) manufacturing processes to produce robust, performing and durable low loaded active layers based on Aquivion® and specific Carbon Blacks
  - Validate (CEA) the feasibility to produce cathodes with gradients and compare to homogeneous electrodes

- Test the influence of different ionomer and Carbon blacks on performance (CEA)

- Perform durability tests on cycling protocol (CEA, Solvay)

**Scientific objectives**

The first set of scientific objectives is to better characterize the active layers:
• characterize (Solvay, Imerys) properties of the raw materials developed (ionomer and Carbon blacks)

• analyse structure of the active layers (CEA, tecnalia, Imperial) and develop innovative tools to measure their transport properties (Imperial, CEA); structure, porosity, proton resistance, electronic conductivity, water handling, fluidic transport (to compare to gas diffusion models)

• develop (Imperial) fundamental electrochemistry equations to compare to classical Butler-Volmer relationships

• supply models with more realistic inputs (CEA, Imperial)

The second set of scientific objectives is to better model performance of PEMFC:

• develop (CEA) and use Pore Network Model (PNM) of the cathode

  o develop a PNM at agglomerate’s scale to simulate the performance of a cathode, coupling fluidic two-phase transport, charge transport (proton and electrons), and electrochemistry

  o validate the fluidic PNM on dedicated experiments

  o supply performance models with more realistic inputs

• improve (Opel) and use performance modelling of PEMFC

  o collect material characterizations as input data for the model and continuously update this database according to project results

  o propose recommendations for Level 0-3 using the most recent set of input data

• analyse (CEA) performance limitations for low Pt loading

Project Results:

All the figures discussed below are given in the complete attached version.

Main achievements of technological approach

Main targets (CEA)

MEA Level 0 has been reached (and even exceeded) using classical manufacturing processes. Ink formulation and assembly conditions have been adapted to Aquivion ionomer to solve some unexpected performance issues. At the end, performance has been found to be even higher than the one with classical Nafion ionomer at low gas hydration level, which is a potential interest for automotive application.

MEA Level 1 has also been reached (and even exceeded) by lowering Pt loading down to ~ 50 (anode) + 150 (cathode) µg/cm². Preliminary durability tests have nevertheless shown a too high degradation rate (~300µV/h). After comparison to some others, the cycling protocol used, derived from former EU DECODE project, can be considered as an aggressive one, especially for the first 300 h of operation. Care shall then be taken when comparing degradation rates.

MEA Level 2 targets have been modified (following Mid-Term Review) to increase durability of MEA Level 1 rather than decreasing Pt loading. This modified target has been reached (~30µV/h) after intensive tests and developments by adding a subgasket, modifying the Aquivion grade and tuning assembly properties of MEA.

Even if MEA Level 3 targets did appear no more realistic, low loaded electrodes (100µg/cm² in total) has been produced and tested.

The main results are summarized in a figure that confirms that power density and durability decreases as Pt loading decreases. Durability has been improved with specific raw materials but power density seems clearly to be the main issue for the future, especially to fit the requirement of 1W/cm² as defined by AUTOSTACK project for automotive application. Pt loading has been reduced from 1 to 0.57 and could be realistically reduced down to 0.3 gPt/cm² (preliminary in-house results).

Development of new Aquivion ionomers (Solvay)

The original approach was based on the idea to produce electrolytes characterized by different properties and test them in electrode application in order to create a base knowledge of the link between ionomer characteristics and final MEAs performances. Till now many efforts were focused on ionomer as membranes and less information can be found on which ionomer aspects are important for electrodes applications.
Many different dispersions were produced though the fine tuning of copolymerization tetrafluoroethilene (TFE) and vinylethersulfonylfluoride (VESF) and the optimization of polymer post treatment. Comonomer content as a function of EW is reported in a figure.

These samples were characterized and used to prepare electrodes through different manufacturing processes. Furthermore testing of final MEAs were performed according to automotive conditions protocols.

It was showed that Aquivion ionomer performances can be better than Nafion.

It was selected one Aquivion ionomer to have a good compromise in term of performance and durability.

Dispersions prepared by blending ionomer with not functionalized fluorinated polymer were produced. Two extreme examples of electrolytes were selected in term of crystallinity. The product obtained from the blending of ionomer with a fluororubber FKM turned to be remarkable for the outstanding durability of MEAs prepared with it.

It was interesting to have within the consortium contacts and exchange information with who manufactures electrodes/MEAs and test them according to automotive conditions.

Main difficulties were linked to the development of dispersions considering the poor clarification of ionomer effects on MEAs characteristics and performances. Many different ionomers were proposed and tested but it was not easy to find out correlation between ionomer characterization and MEAs results. Probably a work focused on a reduced number of raw materials would be more fruitful. Furthermore it would be important to try to correlate ionomer properties with the analysis of active layers’ properties.

Deeper analysis will be performed on dispersion based the blend ionomer and FKM in order to clarify the poor testing performances.

Development of new Carbon Blacks (Timcal)

During the Pemican project Imerys Graphite & Carbon screened various carbon preparation routines. The aim was to prepare carbon supports with controlled size, optimized surface morphology and surface characteristics with respect to wettability for addition into the ink formulation at the cathode and catalyst support at the anode.

Six different carbon preparation routines were screened throughout the project and they are listed in Table 1. The first preparation (number 1 in the table) was the traditional manufacturing process. By adjusting the preparation parameters different carbons were obtained with a range of BET surface areas. The carbons prepared in this way were all relatively free from oxygen groups. The second preparation routine (number 2 in the table) screened was a carbon post treatment process with the aim to introduce and control the porosity. By adjusting the preparation parameters materials with very high porosity could be obtained and as a consequence they also had high BET surface areas. These materials had surface chemistry similar to the carbons without post treatment i.e. relatively clean and free from oxygen groups. It was concluded that with this post treatment the specific surface area could be controlled and a different porosity profile than the standard carbon blacks could be obtained. The third and fourth preparation routines selected were post treatment processes where oxygen groups were introduced. In this way the hydrophilicity should increase and the dispersability in aqueous dispersions could be improved. This could be particularly interesting when adding the carbon to the ink and in the preparation of the microporous layer for the gas diffusion layer. Depending on which of the two processes was selected the surface area obtained for the same amount of surface oxygen groups was different. One of the processes didn’t change the surface area while the other increased the surface area. It was concluded that with the right selection of process and its process parameters the hydrophilicity of the carbon black could be adjusted while maintaining a control of the porosity and specific surface area. The fifth and sixth preparation routines were selected in order to increase the crystallinity of the carbons and in this way increase the corrosion stability. It was observed that for both post treatment routes the materials had relatively low amount of micropores, compared with standard carbon black with the same surface areas and at the same time the degree of crystallinity had increased, as expected.

An overview of the impact of the different carbon preparation routes on the carbon properties is presented in a table.

At the start of the Pemican project Imerys Graphite & Carbon had limited understanding of carbon characterization and post treatment preparation procedures. The Pemican project made it possible for Imerys Graphite & Carbon to study existing post treatment equipment but also installation and study of new post treatment equipments. After thorough characterization (explained in Section 1.3.3) of all new carbons with a range of new and existing techniques, both at Imerys Graphite & Carbon and at external laboratories, knowledge of how to control the morphology, chemistry and graphiticity have been gained.
and Imerys Graphite & Carbon and a portfolio of carbon materials is now available that can be sampled to potential customers in application development and commercialization projects.

During the Pemican project new carbon materials developed in the project were selected from the six different preparation routes and sampled to collaboration partners in the project. The aim was to analyze the performance of the new carbons, identify the optimal properties of the carbon and finally prepare optimized carbons. Due to lack of time there was no possibility to screen such large amount of materials and only limited feedback could be obtained. However, the gained knowledge was translated into product specifications and process definitions that are required for decision about investment in technologies and industrialization of processes.

Different Carbons have been used to manufacture Micro-Porous Layers (MPL) on GDL for producing electrodes by Physical Vapor Deposition and Direct Electro-Deposition. Performance is similar to the one obtained with the more classical Vulcan Carbon, used in commercial MPL. This shows that these CB could be used as an alternative to Vulcan, hoping also improvements after optimisation of their properties.

Development of low loaded active layers by classical manufacturing processes (CEA)

Different manufacturing processes (ink jet, screen printing, knife coating...) have been used at CEA to produce electrodes with Aquivion ionomer and Pt loadings ranging from 200 (Anode) + 500 (Cathode) µgPt/cm² down 37 (A) + 74 (C) µgPt/cm². Unexpected low performances, typical of drying phenomena, and scattering have been observed and many tests have been done by combining carbon and new Aquivion grades to resolve this. At the end, these issues have been solved by adapting ink formulation and assembly conditions of MEA. The final performance is interesting as it is at least similar to the one with Nafion electrodes and even higher for low gas hydration level (RH 30%).

With this ink formulation, decrease of Pt loading has been made possible, on anode and cathode sides. Nevertheless tests have shown that power density (W/cm²) decreases and degradation rate (µV/h) increases as Pt loading decreases.

Even if the cycling protocol used in Pemican is more aggressive than others, it was decided to keep using it and try increasing durability as a priority. This has been achieved by introducing a sub-gasket, using one of the new grades of Aquivion ionomer developed in the project, and adapting again the assembly conditions of MEA. This demonstrates that Aquivion ionomer is a good candidate for MEA and that its properties have a major influence on durability.

Many attempts have also been done to increase performance (W/cm²) by tuning properties of ionomer and by introducing specific Carbon Blacks. Some results show that the “best” material does not always have the “best” performance, which could indicate a close inter-relationship between the different materials used, and the manufacturing process used. All the potential combinations (Aquivion ionomer grade, Carbon grade, manufacturing process, solvent, additives, concentration of materials...) have not been tested extensively but up-to-date no improvement has been found on performance. Perspectives could be to focus on the 1 or 2 Aquivion ionomers with the best compromise performance/durability and trying and improving ink formulation.

Development of low loaded active layers by Physical Vapor Deposition (PVD, Tecnalia)

PEMICAN has allowed TECNALIA to set up and optimise the fabrication of low loading anodes by the Physical Vapour Deposition technique. The project objective was to prepare under 0.2 mgPt/cm² MEA reaching automotive performance conditions. This implied the manufacture of anodes with platinum loadings lower than 0.5 mgPt/cm².

Magnetron sputtering, a PVD plasma coating process whereby sputtering material is ejected due to bombardment of ions to the target surface was the technique employed for the anode manufacturing. TECNALIA started with a DC power source (DC magnetron sputtering). The deposition process variables were studied, in order to assure the homogeneity and reproducibility of the electrodes. With this aim, the coating homogeneous area and platinum deposition rate were determined. Electrodes were prepared on commercial MPL and then substituted with MPL developed by the project partners. The Pt particles geometry and size observed by HR-SEM appear very similar and independent of the MPL. Anodes with platinum loadings ranging from 0.02 to 0.1 mgPt/cm² were manufactured and tested in single cell using cathodes level 0 (0.2 mgPt/cm²). The better performance and stability was obtained with the 0.062 mg Pt/ cm² anode. Taking this into account, it was compared the different MPLs when 0.062 mg Pt/cm² are deposited. No significant influences of the carbon substrate were noticed. A slightly better performance at high current densities of the commercial 24BC MPL is observed, but not as important to reject the CB60 and CB800 carbons developed by Imerys Graphite & Carbon.

A subsequent update of the PVD installing an AC power source, allowed the deposition of lower platinum loadings than with the DC source. Anodes with platinum loadings ranging from 0.002 to 0.03 mgPt/cm² were manufactured. To improve the triple phase boundary, the addition of ionomer to the MPL...
previously to the coating and/or to the catalytic layer after the coating was studied. The D79-20BS
ionomer solution supplied by Solvay was employed for the experiments. The ionomer was applied by
spraying it on the GDL (before coating) or GDE (after coating). The better performance was obtained
when 7 µg ionomer/cm² were applied to the MPL before the catalyst coating. No improvement was
obtained spraying the ionomer after the PVD process.

The anodes were tested in single cell employing anodes level 0 (0.2 mgPt/cm²) and level 1 (0.14
mgPt/cm²). It was established a relationship between anode and cathode loading (0.016-0.2 mgPt/cm²
(anode/cathode) for the level 0 and 0.03-0.14 mgPt/cm² for the level 1.

The study of Pt catalysts deposition by PVD led to the preparation of an optimum anode composed by
0.03 mg Pt/cm² and 0.007 mg ionomer/cm² (sprayed before the Pt coating) that was delivered to CEA
as Tecnalia’s anode level 2.

To increase the carbon specific surface before the PVD coating processes an oxygen etching process
before coating was planned. Unsatisfactory results were obtained, mainly attributed to two causes,
firstly by the fact that no ionomer could be applied before the PVD coating, so the triple phase contact
is hindered. Secondly the 3D structure modification after the etching could affect the electrode
performance.

The deposition of platinum oxides was studied due to the characteristic acicular structure of the PtO²
that could increase the catalyst surface. Process parameters were adjusted. The typically acicular
structure of the platinum oxide was obtained. After the deposition, the reduction under H₂ atmosphere
at different temperatures was achieved. Finally the addition of ionomer before and after the PVD
processes was taking into account. The MEA performance decreased compared with the Pt anodes
prepared by PVD. Although the results were not as satisfactory as the Pt anodes, the platinum oxides
prepared by PVD opened future research lines to improve the electrocatalyst performance.

The PEMICAN project allowed TECNALIA to better understand the parameters that influence the
platinum deposition by PVD. The manufacturing process of PEM anodes with very low Pt loading (<
0.010 mg Pt/cm²) using the PVD technique have been optimised and the required performance for MEA
Level 2 has been achieved.

Further research is needed to increase the electrochemical activity of the electrode and therefore to
reach performance and durability properties similar to actual electrodes with a clear reduction in the
catalyst loading. Issues like ionomer distribution and MEA manufacturing process need to be
investigated more in detail.

Detailed information of the anodes preparation by PVD is given in the deliverables D.3.1.2, D.3.2.2,
D.3.3.2 and D.3.5

Development of active layers by Direct Electro Deposition (DED, CEA)

Electrodeposited Pt electrodes were successfully prepared at CEA on micro-porous layers with different
Carbon Blacks. Carbon support micro structure seems to be the major impact that affects the Pt
distribution. Low micro pores amount carbon supports have shown to better disperse the Pt
nanoparticle may be due to a better impregnation of the carbon.

Fuel cell tests of the as-prepared electrode do not show satisfactory results, even though as anode the
performance was quite interesting (380mA@675mV), this performance is still far below the targets. On
the cathode side the situation is even more severe since only 140mA where obtained at 675 mV.

These results show even the Pt structure seems in agreement with state of the art of catalyst in term of
particle size, efforts are still required to optimize the active layer structure to well balance ionomer
content, amount of impurities and to improve performance.

Development of structured active layers (CEA)

Cathodes with gradients of Pt in the thickness and between inlet/outlet have been produced. Results
show that Pt is more efficient close to the membrane and close to the outlet but the performance is
lower than with homogeneous active layers for the same Pt loading. Nevertheless, as a reduced number
of configurations have been tested, more tests could maybe allow defining a more interesting
structured MEA. Gradients between rib/channel can be produced and would also need to be tested.

Main achievements of scientific approach

Characterization of the properties of the ionomer (Solvay)

Material characterizations were performed both with in-situ and ex-situ test.

Water based dispersions characterization was performed in terms of viscosity at 25°C (Rheometric RFS
III with Couette geometry in steady rate sweep test mode). Dispersions D70-D98 refer to samples characterized by different equivalent weights (from 700 to 980 g/eq) while dispersion A is the blend ionomer/modified PTFE, dispersion B is the blend ionomer/FKM.

From each dispersion sample cast membranes were obtained in order to measure in-plane proton conductivities as a function of RH at 80°C, in a BekkTech cell; in-situ oxygen and hydrogen permeability were analysed from cast membranes; water uptakes in boiling water were measured to evaluate ionomer water affinity; thermal properties of precursor polymers were obtained: TGA, MFI, Tg and Heat of fusion.

The dispersion D98-20BS turned to be the best solution because of a compromise between performances results and durability achievement. As it can be observed from results above, the characterization of this material highlighted the lowest conductivity among the samples prepared within the project, poor water uptake and reduced oxygen and hydrogen permeability. The polymer was stabilized in order to eliminate those groups which could react with peroxide-derived radicals produced during fuel cell operations. Finally this material was characterized by high crystallinity.

Characterization of the properties of the Carbon Blacks (Imerys)

A carbon black consists of spherical elementary particles (primary particles) that are fused together in three dimensional aggregates. The size of the primary particles, but also the porosity present on the carbon surface determine the surface area (BET) of the carbon. In addition, the chemical groups on the surface of the carbon will define the interactions with other materials.

Many characterisation techniques are needed to fully analyse the morphology and chemistry of the carbon materials and several were used in the Pemican project.

X-ray diffraction (XRD) was used to study the degree of crystallinity, particularly important for the materials that were post treated at high temperatures where an increase in crystallinity is usually observed. With transmission electron microscopy (TEM) the size of the elementary particles can be characterized; this technique also offers a way to visualize the structure and crystallinity of the carbon material. The Oil Absorption Number (OAN) and the Stoke Diameter was also analysed for most new carbons. These techniques offer important information about the aggregate structure and branching. The specific surface area (BET) and porosity are of high importance and were analyzed with nitrogen gas adsorption where models such as t-plot and BJH were used for evaluation of micro- and mesoporosity.

The surface of a carbon black is heterogeneous and consists of graphitic planes, edges of those and amorphous regions. Edges are more reactive and oxygen or other elements are predominantly located there. Oxygen in the surface can be bound in the form of various groups. The chemistry can be analyzed with a range of techniques and those selected in the Pemican project were pH, Interstitial Gas Analysis (IGA), Tof-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) and XPS (X-ray photo electron spectroscopy).

Some of the characterization data for selected carbon materials are summarized in a table.

The Pemican project also made it possible for Imerys Graphite & Carbon to develop a new test for measuring the specific volume electrical resistivity of dry carbon black powders. It is a 2-point method where the carbon material is pressed with a piston in a mould and the resistivity is measured as a function of pressure.

A corrosion test could also be set-up at Imerys Graphite & Carbon in order to give important ex-situ feedback of the corrosion stability of the new carbons. The method consists in preparing a slurry with the carbon material in an aqueous solution of Aquivion D79-20BS and a small amount of 1,2-propane diol. The dispersion is coated on carbon paper, dried and sintered. The paper is then immersed in 1M H2SO4 (80°C) and the corrosion current is measured at 1.2 V vs. NHE for 2 hours using a Red Rod (Ag/AgCl) reference electrode (See Deliverable 2.3.2 for further details). The mass loss of carbon can then be calculated. An example of the corrosion current vs. time is shown for three different carbon materials in a figure and the mass loss of carbon vs. the BET specific surface area is shown in a figure. It was also evaluated to use thermo gravimetric analysis (TGA) as a faster screening of the ease of oxidation of the carbon materials. The carbons were heated to 900 °C in air and the weight loss was monitored. A correlation between the corrosion mass loss from corrosion tests and the onset of mass loss in the TGA was found but the scattering was rather large in TGA and it would be difficult to use this technique to predict the oxidation of the carbons.

Characterisation of the structure of the active layers (CEA)

Pore size distribution of the active layer seems to have two peaks (see figure below); thickness of MEA Level 1 electrodes is small, around 6 µm for the cathode and 0.5 µm for the anode.
Fresh and aged MEA have been analysed by Scanning Electron Microscopy. No degradation of the (reinforced) Aquivion membrane has been seen but on the cathode side the Pt nanoparticle size increases from 3-4 nm for the fresh MEA to 5-6 nm for the aged MEA, which could let thinking to the electrochemical Ostwald rippenning mechanism. Analysis by Tafle slope indicates that ohmic resistance is higher for aged MEA, maybe in relationship with the degradation of the ionomer (to be confirmed).

Characterisation of the transport properties of active layers

Within this section we have made measurements of fundamental parameters of fuel cell catalyst layers. In order to do this we have used a mixture of already developed techniques and the development of new techniques to obtain the required parameters.

Water adsorption and management within the active layer (Imperial)

The water management properties of the CL where investigated using dynamic vapour sorption. As expected, we found that changing the relative humidity of the atmosphere resulted in an initial rapid uptake of water. However, we were surprised to see that this was then followed by a much slower uptake of water that took many hours to complete. Similar behaviour was observed with platinum supported on carbon without ionomer.

The adsorption isotherm for PEMICAN cathode CL with 6hrs/pt equilibration times is illustrated in a figure, while a typical time domain response for a 10% RH step is illustrated in a figure. When plotted versus the root of time, the mass of adsorbed water shows two clear linear regions; one at short times with a small time constant, and one at long times with a large time constant. This behaviour suggests that two different diffusion controlled process occur during water adsorption.

We observed significant hysteresis in the water adsorption isotherm of the CL with an equilibration time of 6 hours. The magnitude of this was slightly less in the absence of ionomer but was still prevalent throughout the full RH range. This behaviour confirms that the source of the kinetically slow process is adsorption by carbon, and that the ionomer film acts to further hinder the process.

Improve gas transport measurements of the active layer (Imperial)

Throughout the course of these investigations, significant deviations between experimental data and equations classically used to describe gas phase transport where observed. This discrepancy is commonly missed owing to the fact that most studies only use one permeating fluid. For example a figure plots the pressure drop through SGL-24BC using a variety of probe gases and illustrates the inaccuracy of Darcy’s law. Significantly more accurate and meaningful parameters can be determined using models that include Knudsen flow, such as the binary friction model. This treatment found that Knudsen diffusion plays a critical role in the pressure-driven transport of gasses through the gas diffusion layer and the catalyst layer, contributing >80% of the apparent viscous transport coefficient. Importantly, this approach also provides a convenient experimental method to measure the Knudsen diffusivity of the medium which a parameter typically estimated from porosimetry measurements.

The identification of the importance of Knudsen diffusion was also incorparated into the determination of diffusion parameters, in order to accurately determine the relative importance of Knudsen and binary diffusion. Correctly de-convoluting these two diffusion pathways is difficult owing to the fact that diffusive fluxes are typically superimposed on bulk fluid motion. Using our experimentally determined Knudsen diffusivities and adopting models that explicitly include the bulk fluid motion encountered during diffusion experiments (such as the Dusty Gas model), we found that Ficks’ law overestimates the magnitude of the binary diffusion coefficient. The magnitude of this discrepancy appears to be greater in the CL, and is in part due to the small pore size encountered in this layer.

Correctly determining these diffusion parameters, we predict an interesting property of the CL that largely results from its diffusivity being described by transition region equations rather than continuum equation. Specifically, in such systems the effective diffusion coefficient is a function of the concentration gradient and the composition of the gas that is diffusing. That rather unique diffusion function can then be used to calculate the diffusivity of the electrode as the system approaches a limiting current scenario, and this is plotted in a figure.

Interestingly, we find that the diffusivity of both the GDL/MPL and of CL increases as the system approaches mass transport limitations. Further, the magnitude of this effect is larger in the case of the CL, reaching an enhancement factor greater than 50%. In the case of the GDL/MPL, which is close to a classical diffusion media as indicated by its small D12/DKn ratio, the magnitude of this effect is significantly less. From this treatment it is clear that Knudsen diffusivity plays a crucial role in the mass transport of PEMFC electrodes, particularly so at high current densities and within the catalyst layer. It further emphasizes the need for correct models and constants to accurately describe mass transport within operating fuel cells.

Development of improved electrokinetic equations for the ORR and HER (Imperial)
An ideal system to study the electrokinetics of the ORR and HOR would have the high mass transport achieved in fuel cells and the ability to accurately measure the electrode potential. To achieve such a system a novel electrode structure was developed, and this structure is illustrated in a figure. The electrocatalyst is supported on a hydrophobic porous membrane that acts as a gas diffusion layer. A thin layer of gold is used as the current collector. This electrode is placed on top of an aqueous electrolyte to establish an ionic conducting pathway, while the gas of introduced at the back of the electrode. These ultra-thin catalyst layers have superior mass transport relative to diffusion in aqueous electrolytes.

We have modeled the current-overpotential-temperature surfaces of the ORR and HOR using semi-analytical expressions that where derived at Imperial. We found that the Butler volmer model provided a poor basis for studying the electrokinetics of the ORR. A figure illustrates this fitted surface for the ORR, showing an improved fit throughout the overpotential-temperature range studied. The same figure shows the fitted surface for the HOR.

Using the derived equations, an optimization was performed to determine the limiting Pt loading needed to achieve 1 W cm–2 at 0.675 V and under the operating test conditions used in PEMICAN. We calculate that the optimum loading is 7.2 g cm–2 at the anode, and 63.3 g cm–2 at the cathode, for a total loading of 70.5 g cm–2.

Measurement of proton resistance of active layers (CEA)

In the frame of PEMICAN, we setup a method which allows determining the specific proton resistance of an active layer. It is based on techniques reported in the literature but improvements have been done in order to have a better control of the local water reparation and, then an increased accuracy and reliability. We conclude that the proton resistance of the active layer decreases as the water activity increases as expected considering the behavior of the ionomer. We have shown that the specific resistance of the active layer with a Pt loading of 0.3 mg/cm² and heat-treated bellow 180°C is higher with Aquivion than with Naftion. This is unexpected considering the lower equivalent weight of Aquivion. Nevertheless, it is qualitatively in agreement with the results of the fuel cell tests. This has been ascribed to a restriction proton conducting path in link with the ionomer repartition. We can assess that the proton conducting path in the active layer cannot be described as a thin layer with a conductivity one or several order of magnitude lower than the conductivity of the membrane. The value of conductivity of the ionomer in the active layer is not strongly different than the conductivity of the ionomer within the membrane.

Thanks to PEMICAN project an improved method for the measurement of the specific proton resistance of the active layer is available. This knowledge of this parameter is of prime interest for the understanding of the performance of a fuel cell and can be used as it is. Even if it is difficult to have a quantitative value, this method allows comparing active layers differing in composition and

In order to go deeply in the analysis, that is to say, to be able to extract from the measurement a quantitative value of ionomer conductivity, microstructural characterizations of the ionomer repartition is needed.

Improvements of the setup are still needed to be able to make measurements with a good reliability for a water activity higher than 0.8.

The effect on the active layer specific resistance of the type and of content of the ionomer content, as well as the active layer thickness must be studied. The measurements should be carried out as a function of temperature.

Improvement of performance modelling (Opel)

The most crucial requirement for reliable simulation results are reliable input data. At the beginning of PEMICAN 29 out of 37 material parameters representing the MEA had to be taken from estimates in open literature or engineering experience while only eight were known from reliable sources. During the project another 14 parameters could be sourced from laboratory measurements and/or pore network modelling for actual project materials. While the goal of complete parameterization with reliable values could not be reached completely this marks a big step forward. Once the performance model can be completely parameterized with authentic values it can be used as a reliable design tool for PEMFC.

Furthermore the model was extended to cover spatial inhomogeneities of Pt and/or ionomer content and post-processing was extended to give more information on local current generation.

Development of Pore Network Model (PNM) of the cathode catalyst layer (CEA)

Classical transport models used in performance models of PEMFC are based on the so-called average approach and do not account for real structure of the materials. To be more representative of a cathode catalyst layer an innovative 3D PNM model has been developed, based on experimental Pore Size
Distribution, and coupling the different transport processes between the agglomerates (secondary pores) of a cathode: fluid (gas, liquid water), charge (proton, electron), heat, electrochemistry.

This model has been validated on dedicated or existing experiments on two-fluid transports, gas diffusion and sorption isotherms. Results confirm that classical gas diffusion models most probably over-estimate gas diffusion inside the electrodes and under-estimate liquid flooding. First analysis has shown that non-uniform electrodes could be of interest to increase performance of PEMFC.

Analysis of the performance limitations (CEA)

Starting from MEA Level 1, experimental results have shown that when Pt loading (µgPt/cm²) decreases performance (W/cm²) decreases, but also electrode thickness decreases and Pt efficiency (A/µgPt) increases. This confirms that the thinner the electrode the more efficient the Pt and that the transport limitations are key issues to increase performance.

To better understand this, a performance model has been updated with inputs from characterization (electrochemical equations, proton resistance of membrane and active layer, gas diffusion), and of modeling (gas diffusion from PNM) and used to analyze performance limitations of a PEMFC with the target of 1W/cm² (Autostack target defined for automotive application @ 50%RH, 80°C, 1.5b, H2/air, 0.675V). A total Pt loading of 70 µgPt/cm² should be enough in the “ideal” case (no transport losses in the MEA) but does not seem realistic in the “real” case (with transport losses). First analysis shows that, in the case of very low loaded MEA, the most important limitation is proton resistance in the membrane then in the active layer then gas diffusion. In the case of higher loadings (around 200 µgPt/cm² in total) transport losses in the active layer could be of the same order of magnitude as the one in the membrane.

Potential Impact:

Opel

Opel could significantly improve parameterization and depth of detail of its Comprehensive PEM Fuel Cell Model (COPEM). The improved model already contributed to a deeper understanding of the physics and chemistry of the cathode AL during the project and it is now an even stronger tool for future fuel cell research. The improvement of parameterization also means considerable progress towards using COPEM as a design tool for fuel cell development which is highly desirable for automotive production cells.

Finally Opel highly appreciates the progress made in developing low Pt MEAs for automotive applications. The commercial availability of such MEAs would significantly contribute to decreasing the price difference between fuel cell and internal combustion engine vehicles.

Solvay

In Solvay polymerization techniques were optimized in order to produce a wide range of equivalent weights. Furthermore post treatment procedures were re-examined because of dispersions are based on polymer characterized by different crystallinity water affinity.

New methods were developed to produce dispersions from blending ionomer and perfluorinated polymers. The aim was to obtain dispersion stable in the time.

Solvay learned from the project that it is very important to have a flexible technology to produce ionomers in order to satisfy the different customers’ requirements and techniques to produce electrodes.

It was prepared a draft of paper which gather all information on Aquivion ionomers development and related material characterizations.

Imerys Graphite & Carbon

The participation in the Pemican project has enabled Imerys Graphite & Carbon to install new carbon post treatment equipment and screen those. The influence of the post treatments and changes in the treatment parameters on the carbon properties is now well understood. Imerys Graphite & Carbon was also able to study and evaluate an ex-situ test with potential to screen the stability of carbon materials. Knowledge of the carbon stability is important and will serve in all future fuel cell activities. As a result of the project a database with materials and properties of different carbons is available that now can be used for customer related projects and application development. Analytical know-how within Imerys Graphite & Carbon was significantly increased and improved and new methods for carbon surface characterization were evaluated within this project and finally installed. The gained knowledge in the new technologies and the technical and economic feasibility studies that were carried allowed for decisions for investments in industrial equipment and the industrialization of developed preparation routines. During the project one process was up-scaled in a two stage process from lab to semi-
industrial process. Imerys Graphite & Carbon could also participate with an oral presentation and conference paper at the EFCF Forum in July 2013. The participation to this conference helped Imerys Graphite & Carbon to make new contacts in the fuel cell field.

Tecnalia

For TECNALIA, the participation in the PEMICAN project has allowed to go deeper in the catalyst preparation by means of PVD. Thanks to the knowledge acquired, TECNALIA’s has been involved in new research projects, one European (Nano-Cat FCH-JU 2012) working in the catalyst deposition by PVD for PEM stacks and another national project regarding to PVD prepared catalysts for metal-air batteries.

TECNALIA has gained knowledge about catalyst morphology and electrochemical activity related to the deposition parameters; electrode morphology and influence of the ionomer and carbon support on the catalyst layer, and MEA testing. The project also has allowed TECNALIA the development of characterization methods for better understanding of the catalyst performance and its integration into PEMFC systems. This experience allows tecnalia position as a strategic partner for PEMFC development projects, thinking not only in R&D but also in product development.

TECNALIA contributed with a poster at the Carisma Conference in July 2012 in Copenhagen.

Imperial

Imperial will have presented results obtained with the help of the PEMICAN project at two international conferences by the summer of 2014. As work on several areas continues it is likely that further presentations will be made in the future.

Imperial has so far published one paper containing work carried out for PEMCAN with a further three (including a collaboration with Solvay) planned. As the experiments for these papers are incomplete they are likely to be published towards the end of 2014 and the beginning of 2015.

Imperial’s contributions have been mostly scientific and little opportunity has arisen for the generation of exploitable knowledge. Nevertheless during the project Imperial’s links with the other partners have improved substantially. This is a tangible benefit to both research related to PEMICAN and to future research.

Much of Imperial’s involvement with the PEMICAN project has involved building test benches to better characterise low loading MEAs. These will continue to be improved and used beyond the end of the project feeding into other areas of research and are of continuing benefit to other projects.

Cea

The coordination and participation to PEMICAN allowed CEA to actively develop low loaded active layers taking advantage of the numerous materials supplied by the partners. Deep insights in ink formulation, assembly procedures dedicated to AquivionR, as well as alternative manufacturing processes were performed. Low loaded MEA have been done and their performance limitations have been analysed thanks to modelling and fundamental experiments. Models can now be considered as more predictive as their inputs and physics have been improved thanks to innovative characterization of transport properties of active layers, considered up-to-date as bottlenecks for understanding and design. CEA has produced publications on Pore Network Modeling applied to active layers, submitted a patent and presented some oral presentations at conferences. Most of the outputs of PEMICAN will be used as most as possible in future projects to even more improve modelling, understanding, characterization, performance and durability of PEMFC.

List of Websites:

The address of the public website is www.pemican.eu. This website will remain live until the spring of 2017. Update to content can be requested though the webmaster@pemican.eu (advertised on the website). Graham Smith of Imperial graham@gtsmith.co.uk will continue to host and technically maintain the website.

Documents:

Final Report Summary - PEMICAN (PEM with Innovative low cost Core for Automotive application)

STRIA Roadmaps: Vehicle design and manufacturing
Transport mode: Multimodal transport
Transport sectors: Passenger transport, Freight transport
Transport policies: Other specified
Geo-spatial type: Other