PremiumAct

New Energy World JTI
fuel cells & hydrogen for sustainability

FCH JU Grant Agreement no.:	**256776**
Project acronym:	**Premium Act**
Project title:	**Predictive Modelling for Innovative Unit Management and Accelerated Testing Procedures of PEFC**
Funding scheme:	**Collaborative Project**
Area:	**SP1-JTI-FCH.3 Stationary Power Generation & CHP**
Start date of project:	**01.03.2011**
Duration:	**36 months**
Project Coordinator:	**CEA – Sylvie Escribano** **Tel: +33 4 38 78 94 06 - Fax: +33 4 38 78 94 63** **E-mail: Sylvie.escribano@cea.fr**

FINAL REPORT
(Word file to be attached to automatically edited final report)

Document properties		**FINAL REPORT (attached file)**	
Authors (Partner - Role)	S. Escribano (CEA)	WP partner	**WP7**
Other Authors (Partner - Role)	All partners J. Bonde (IRD) J. Roure (Soprano) C. Tregambe (ICI) P. Gazdzicky (DLR) A Casalegno (Polimi) T. Jahnke (DLR) M. Zago (Polimi) P. Schott (CEA)	WP leader	**CEA**
		Released by Author:	**25/04/2014**
		Released by WP leader:	
		Released by coordinator:	
Approved by (Partner - Role) **Date:**	**2014/04/25 Cood. CEA**	Date of first issue:	10/04/2014
Date of the latest version of Annex I against which the assessment will be made			2010/11/26
Dissemination level			
Distribution:	FCH-JU		

Revisions			
Version:	**Date:**	**Changed by:**	**Comments:**
V1	2014/04/10	S. Escribano	1st Draft
V2	2014/04/25	S. Escribano	Final with all contributions integrated

FINAL REPORT
(Word file to be attached to automatically edited final report)

TABLE OF CONTENT

Introduction: this document has been produced to be attached to the Final Report up-loaded directly on SESAM portal in order to give additional information, mainly illustrations of results and some more data about dissemination actions.

1 4.1 Final publishable summary report

1.1 Executive Summary

A general objective is to contribute to the improvement of stationary fuel cell systems durability, keeping in mind that the target required is 40000h. In this sense, the success of the project should help to overcome one of the main bottlenecks for European providers of stationary fuel cell systems and will contribute to cross cutting issues relevant for European R&D and fuel cell industry development. Thus, reliable systems corresponding to the technical specifications of the energy global market could be widespread, which will change the end-user habits towards the stationary energy management and will help to reduce greenhouse gas emission.

Premium Act specific objectives are to propose a reliable method to predict lifetime, based on validated accelerated degradation tests, to benchmark components and to improve operating strategies of real systems. The project addresses two types of technology: Direct Methanol (DMFC) and Proton Exchange Membrane Fuel Cells (PEMFC) operating with reformate hydrogen.

As far as the degradation understanding is concern, focus of Premium Act is on the core of the fuel cells: the Membrane Electrode Assemblies (MEA). The structure of the project is based on the following scheme: (i) initial information is requested from the real systems developed by the industry partners in order to (ii) define the reference conditions to which (iii) the MEA have to be submitted in controlled devices, namely short stacks and single cells, to (iv) check the nominal loss of the fuel cell performance and the degradation of components. Thereby, detailed in-situ and ex-situ analyses are conducted to characterize the degradation. In-situ tests are providing information about reversible or permanent performance loss as well as modifications, in electrochemical behaviour and properties, during ageing. Ex-situ methods are used to assess chemical, physical, and structural properties of the components with lateral and vertical resolution allowing a correlation of local degradation with heterogeneous conditions and operation in the stacks and cells. Segmented cell devices are also developed and used to directly relate local operating conditions to local performance. In order to enhance interpretation of non-homogeneous operation and understanding of local degradation phenomena, modelling is used mainly to enable better description and prediction of coupling phenomena. Models are developed from electrochemical local level for mainly degradation mechanisms description to more macroscopic cell level with mainly fluid transport and current distribution simulation.

The core idea of the project is to use the information coming from these degradation investigations to reach the final results of the project. Main differences compared to state of the art at the beginning of the project are related to the fuels used (methanol and polluted hydrogen) and to the anode catalyst containing both platinum and ruthenium, much less studied than pure hydrogen and pure platinum cases. New phenomena and mechanisms have been identified and deeply analysed for better understanding of the degradations inherent to these parameters, with regard to the fuel cell systems considered. As final outcomes, specific degradation mechanisms related to catalyst degradation with

particularly new evidences concerning ruthenium dissolution and re-deposition, or to local conditions, for both technologies; to polymers losses and transport properties particularly for methanol, have been identified but also qualitatively and quantitatively related to operating parameters (temperature, fuel composition) or methods (stops, air break, load cycles).
Thanks to this better understanding, accelerating features but also stabilizing conditions have been proposed to enable developing and validating on one hand, operating strategies for improving voltage stability and hence lifetime and, on the other hand, relevant specific accelerated stress tests to qualify more rapidly MEAs versus degradation for DMFC or PEMFC operating with reformate fuel cell systems.

1.2 SUMMARY DESCRIPTION OF PROJECT CONTEXT AND OBJECTIVES

A general objective is to contribute to the improvement of stationary fuel cell systems durability, keeping in mind that the target required is 40000h. In this sense, the success of the project should help to overcome one of the main bottlenecks for European providers of stationary fuel cell systems and will contribute to cross cutting issues relevant for European R&D and fuel cell industry development. Thus, reliable systems corresponding to the technical specifications of the energy global market could be widespread, which will change the end-user habits towards the stationary energy management and will help to reduce greenhouse gas emission.
Premium Act particular objectives are to propose a reliable method to predict lifetime, based on validated accelerated degradation tests, to benchmark components and to improve operating strategies of real systems. The project addresses two types of technology: Direct Methanol and Proton Exchange Membrane Fuel Cells operating with reformate hydrogen.
As far as the degradation understanding is concern, focus of Premium Act is on the core of the fuel cells: the Membrane Electrode Assemblies (MEA). The structure of the project is based on the following scheme: initial information is requested from the real systems developed by the industry partners in order to define the reference conditions to which the MEA have to be submitted in controlled devices, namely short stacks and single cells, to check the nominal degradation of both the fuel cell performance and the components. Deep *in-situ* and *ex-situ* analyses are conducted to characterize the two latter types of degradation. In-situ tests are giving information about reversible or permanent performance degradation as well as electrochemical behaviour and properties modifications during ageing. Ex-situ methods are used to assess chemical, physical, structural properties of the components with a local resolution allowing to better relate degradation to heterogeneous conditions and operation in the stacks and cells. Segmented cell devices are also developed and used to directly relate local operating conditions to local performance. In order to enhance interpretation of non homogeneous operation and understanding of local degradation phenomena, modelling is used mainly to enable better description and prediction of coupling phenomena. Models are developed from electrochemical local level for mainly degradation mechanisms description to more macroscopic cell level with mainly fluid transport and current distribution simulation. The core idea of the project is to use the information coming from these degradation investigations to propose accelerate tests for the prediction methodology, and, operating strategies expected as the final results of the project.

The project was organized through 7 workpackages, WP1 to WP4 dealing with research and technical work, the dissemination activities were in WP6 and mangement in WP7.

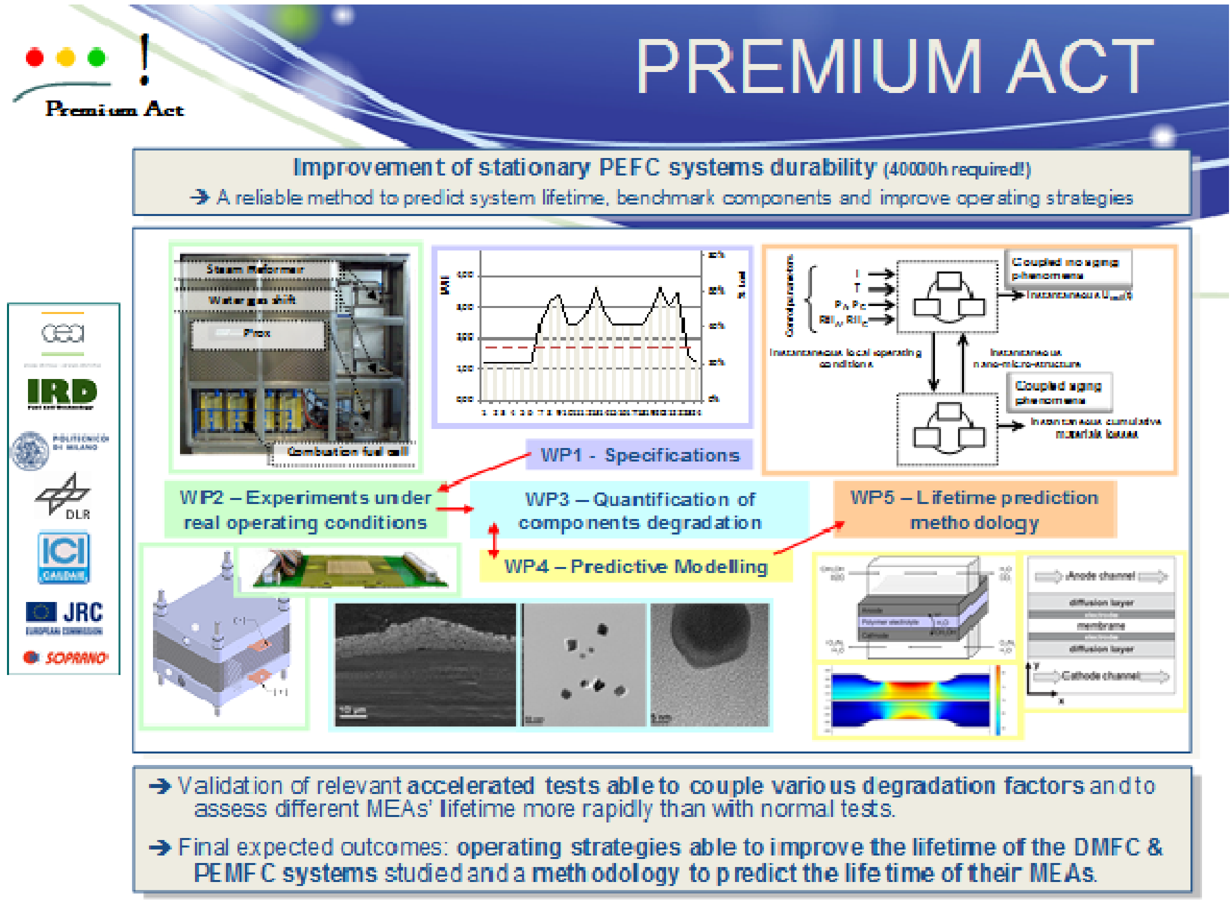


Figure 1: general organisation of the project with WPs, illustrations and main objectives

Since the work has been organised and conducted in two periods, the individual objectives of the WPs are reported below for the two periods.

All technical objectives listed below are of course related to the two technologies considered in the project, for the same type of micro-CHP application: Proton Exchange Membrane and Direct Methanol Fuel Cells.

For the first period, general objective was to start with all technical activities planned in order to get enough information about parameters influencing fuel cell degradation at the beginning of the second period which will be dedicated to the final goals of the project, namely the development of operating strategies and of accelerated degradation tests as a basis of a lifetime prediction methodology.

- For WP1 (Specifications): to define all components and protocols to be used at least for the first period: MEAs, cells and stacks, ageing conditions and current profiles, methods for in-situ and ex-situ analyses.
- For WP2 (Experiments under real operating conditions): to get information from field tests data and systems specifications to enable defining particular ageing conditions for smaller scale tests (single cells and stacks), to manufacture and provide reference MEA, to perform ageing tests following selected protocols in nominal representative

conditions, or critical conditions to acquire experimental knowledge about the impact of components or operating parameters on performance or on materials degradation. The development and use of specific methods or tools, particularly of segmented cell for local in-situ measurements for better understanding was also part of the first period goals.

- For WP3 (Quantification of components degradation): selection, if necessary development or adaption, and application of characterization techniques to analyse first the non aged reference components, to evaluate when relevant the interest of the method, and then to start with the analysis of the aged samples in order to identify composition or microstructure modifications. One important issue was also to perform these analyses with a vertical and a horizontal resolution in order to relate degradation to local conditions to get more accurate information for better understanding of mechanisms and relevant support to degradation models development.
- For WP4 (Predictive Modelling), to improve existing models describing cells and MEA operation, implementing specific conditions as defined by the systems considered, to develop models for a local description of the performance, to develop degradation models describing specific mechanisms for the technologies considered, to start integrating degradation phenomena in the performance models, in order to perform first evaluation of the selected mechanisms impact on local performance evolution.
- For WP5 (Lifetime prediction methodology), to start sensitivity studies for the evaluation of operating parameters impact, when coupled, towards degradation, with the aim to get information about particularly acceleration of performance degradation for enabling first proposal of composite accelerated tests. This WP includes also modelling validation with specific tests but, as for accelerated tests, main work was planned for the second period.
- For WP6 (Dissemination), to communicate about project aims and advancement as general aspect but, as major purpose, to organise a workshop on the characterisation of fuel cells MEA degradation.
- For WP7 (Management), to conduct coordination actions related to contractual, financial, administrative and scientific management, including all exchanges with the FCH-JU, ending the period by the preparation of the mid-term review *(incl. financial report, this first periodic report and the meeting with reviewers)*.

Th two major technical goals of the second period were:

- o The development of operating strategies to improve the lifetime
- o The development of accelerated degradation tests as a basis of a lifetime prediction methodology

The general aim was to use the main outcomes of period one, particularly all information about parameters influencing fuel cell degradation, to develop the ageing protocols enabling to stabilize the performance or on the contrary to accelerate the performance losses as requested to achieve the final goals of the project.

All technical objectives listed below are of course related to the two technologies considered in the project, for the same type of micro-CHP application: Proton Exchange Membrane and Direct Methanol Fuel Cells.

- For WP1 (Specifications): no specific activities but some up-date to be considered for the definition of benchmark components used in the second part of the project (reported in WP2).
- For WP2 (Experiments under real operating conditions): to continue with systems data collection or development for further applicability of strategies; to manufacture and provide additional reference MEA or stack, but also benchmark MEA (mainly defined as presenting different behaviour from the reference); to perform ageing tests following selected protocols in representative conditions as during period one to get in-situ data and give samples for ex-situ analyses on reference samples, but also on the benchmark components, to enable their comparison; to propose and start validating operating strategies
- For WP3 (Quantification of components degradation): mainly application of the characterization techniques decided previously as the most relevant; to continue with local analyses to relate degradation to local operation conditions for samples aged following different protocols including accelerated tests; to further identify or confirm particular mechanisms mainly responsible for performance degradation and needed to be enhanced by accelerated test.
- For WP4 (Predictive Modelling), to develop additional description of mechanisms or of operational functions and to implement those in performance cell models to enable simulating performance evolution; to enable the interpretation of electrodes or cell behaviour in correlation with the mechanisms supposed; to help developing accelerated tests and interpreting the acceleration.
- For WP5 (Lifetime prediction methodology): to continue with sensitivity studies; to use all other WPs data and sensitivity results about parameters able to increase the components degradation and to accelerate cell voltage losses to propose accelerated protocols; to develop and validate thanks to in-situ measurements and specific experiments, degradation rates modelling predictions, to confirm degradation mechanisms in accelerated tests evaluating ex-situ analyses results; to propose a general methodology for lifetime prediction including these accelerated tests.
- For WP6 (Dissemination), to communicate about project results in the events organized by FCH-JU, to exchange with other projects dedicated to similar topic as suggested by reviewers, to enhance scientific dissemination of the results and to consider further exploitation as recommended by the mid-term reviewers.

- For WP7 (Management), to continue the general coordination actions, with two main issues being the finalization of actions decided at the mid-term review, and the ending of the project with last meeting, and last reports.

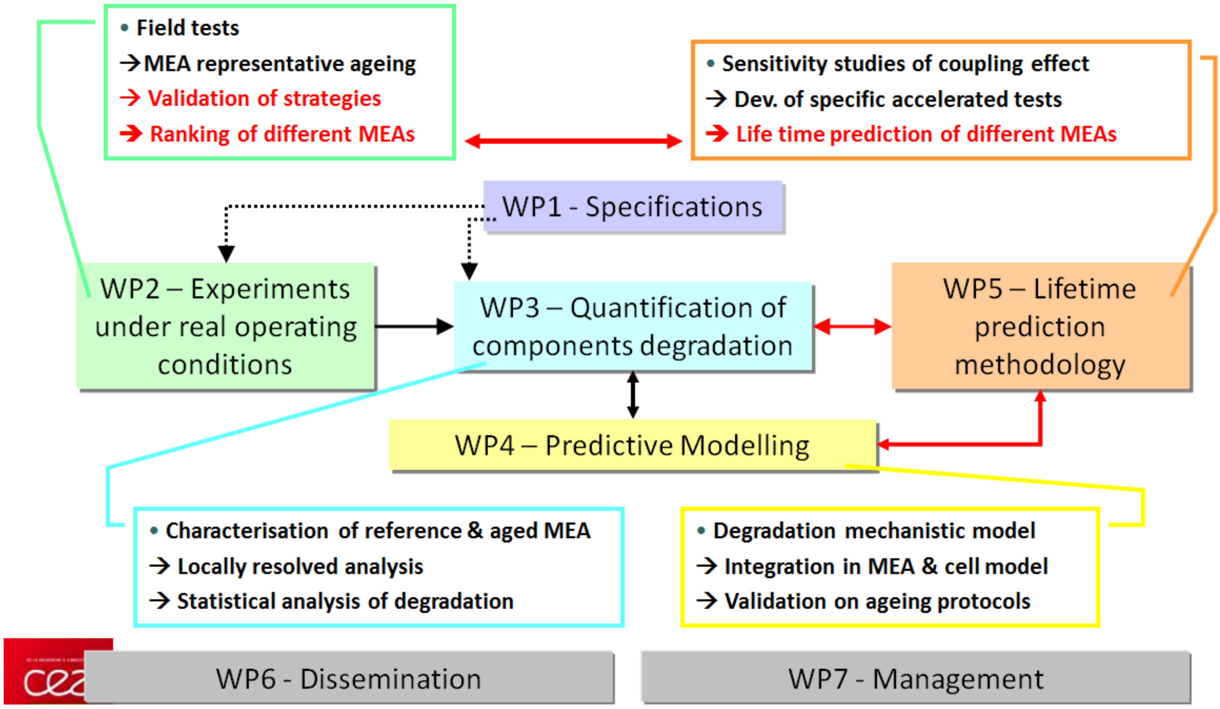


Figure 2: general organisation of the project with main tasks and links between WPs

1.3 Description of main S & T results/foregrounds

1.3.1 Introduction

For this final report, it has been decided to give a synthesis of Premium Act main outcomes by type of activities, more than by WPs as it is already done in the periodic reports.

The aim is hence to give here a better overview of the project outcomes during the first and second period considering particularly the points outlined below:

- New or original aspects of each activities and results
- Specific outcomes regarding degradation mechanisms with regard to existing knowledge

Final outcomes related to the two main goals: operating strategies and accelerated degradation for life time prediction methodology

Selected illustrations of results are also presented.

1.3.2 General context at the beginning of the project:

• Few data are available on the 2 technologies considered in the project: DMFC and reformate H_2 PEMFC

Comment: most of the mechanisms and ageing results described in the literature concern pure H_2 and automotive application.

• R&D work conducted in Premium Act is largely based on the consortium knowledge

Comment: partners involved have all specific background at state of the art level, directly applicable to complete the technical and scientific objectives of the project.

As a consequence, technical activities conducted and scientific results obtained on the two types of technologies considered present new and original aspects compared to existing data and knowledge.

1.3.3 Synthesis of new and original aspects of the activities and results

1.3.3.1 Outcomes related to systems

Possibility to exploit for durability and degradation understanding data of very long term tests available for the project with state of the art IRD DMFC components and systems:

- Availability of aged samples from real systems after degradation due to different critical conditions
- Availability of data for a systems operated more than 20000 hours in stationary conditions, one system operated more than 3500 hours with a degradation of10 – 15µV/h).
- In addition, for the DMFC systems the use of very specific electrode structures for MEAs allowed original information from analyses of both new and aged samples.

Design adaptation of the SOPRANO PEMFC CHP system balance of plant: flexible tool particularly suitable to validate innovative protocols in real operative conditions

- Targeted complete system lifetime of 10.000 hours initially while being able to reach the targeted 40.000 hours in future evolutions
- Design implementations focusing on net efficiency, overall product size, and components cost
    - Design modification to enable air bleeding
    - Development of an accurate process control
    - Process control implementation to enable innovative control strategies

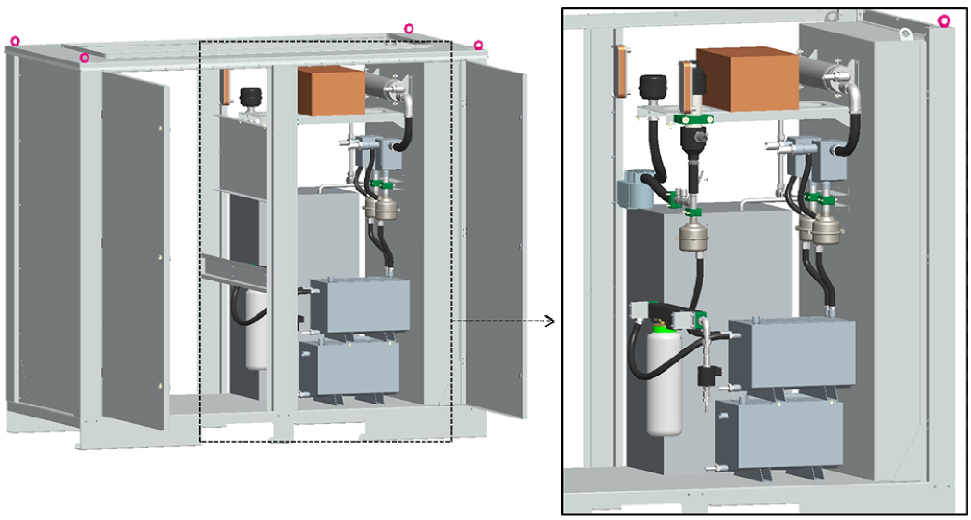


Figure 3: CAD view of the PEMFC-CHP module.

- Production of a compact Programmable Logic Controller for the process control of the PEMFC CHP system able to operate in harsh environment (EN61131-2 standard). It is composed of a base including a Digital Signal Processor and 4 modules which can be analog, digital inputs/outputs or special functions like relay modules, measurement system (See Figure 5).

Figure 4: Process controller with 2 modules.

EANA	16 input channels	Conversion from analog to digital signal	
ETOR	16 input channels	Acquisition of digital inputs	ETOR, STOR and SRELAIS modules can be used to provide on/off control of actuators, contactors, relays, or valves.
STOR	16 output channels	Sending of digital outputs to external devices	
SRELAIS	16 channels	Relay output module for control of electromechanical devices and for status or fault indications	
SANA VOLTAGE	16 output channels	Conversion from digital to analog voltage signal usable for an external device Several output levels: ±10V, 0-10V, 1-5V or others	
SANA CURRENT	16 output channels	Conversion from digital to analog current signal (e.g. 4-20mA) usable for external devices	
MCELL	36 cells inputs	Acquisition and conversion of cells voltages, from analog to digital signal usable for the controller. For fuel cells voltages or battery voltages mounted in series	
PT100	16 inputs (16 sensors)	Data acquisition from 3-wire-PT100 temperature sensors	

Figure 5: Modules already developed

Detailed information on the operation of the ICI PEMFC CHP system vs. fuel reformer management based on 1000 hours of operation: effect of fuel composition at system level useable for further studies at cell level

During the tests and normal utilization, data was collected and analyzed in order to better understand stacks behavior, which is influenced mainly by a set of variables like air and syngas thermodynamic properties, hydrogen and oxygen stoichiometry, cooling DI water characteristics.

From data analysis, CO concentration in the syngas seems to have an important role in the stack performance, identifying the fuel processor as the most critical component in system operations. Results show lower performance of the stack when fed with high concentration CO syngas.

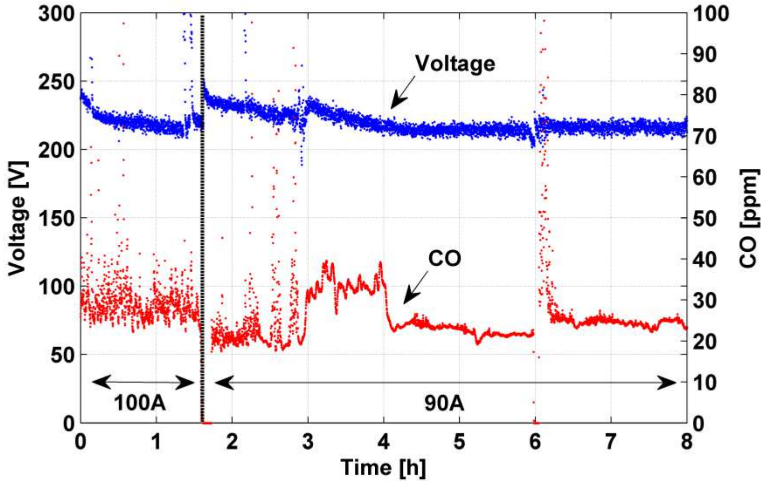


Figure 1 – Stack's performance with CO > 20 ppm

The introduction of some devices improved the system stability and therefore syngas quality; in particular the implementation of an air bleed system seems to enhance stack performance.
Benefit of air bleeding: the performance rises from under 250V to 265V with CO concentration over 20 ppm, and up to 293V with about 5 ppm. Furthermore, if a system component failure occurs (i.e. water circuit pump), and the CO concentration rises abruptly up over 20ppm, there's a loss in performance (10V/h ca.) which results completely recoverable when the CO concentration decreases.

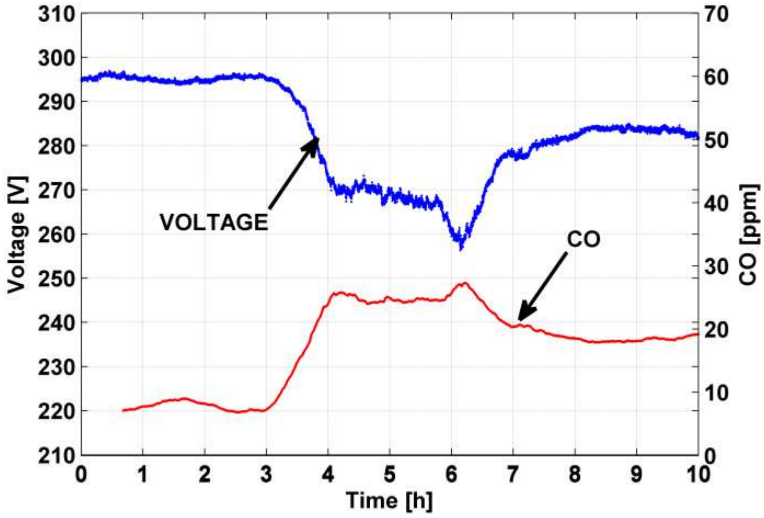


Figure 2 – Air bleeding and CO > 5ppm

Another recoverable loss in performance is connected to cathode oxygen concentration. When it is about 10.5% in cathode exhaust, doesn't result any problem, but if it rises the loss occurs because the membranes are not correctly hydrated and the recovering process requires many hours. So right now an improvement in cathode air control is in progress.

Best operation condition achieved are for: low CO concentration (under 5 ppm), regular and stable stack voltage over 300 V. A small performance loss during operation occurs.

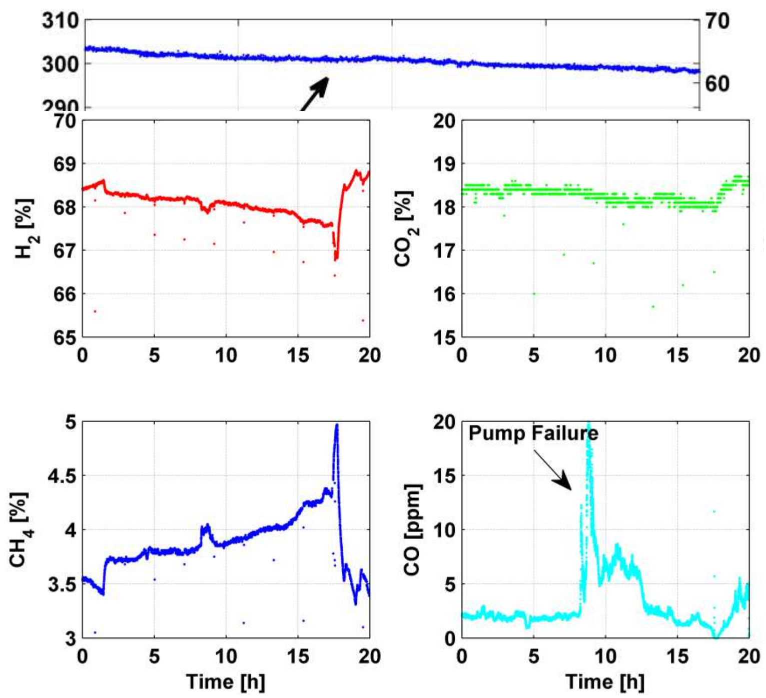


Figura 4 - Syngas composition during tests

Figure 5 – Summary of the main characteristics of the system/stacks during the course of the project

Another improvement on Sidera30 system is the development of a 110 single cell volt measurement. It makes possible find out failure on each stack's cell.

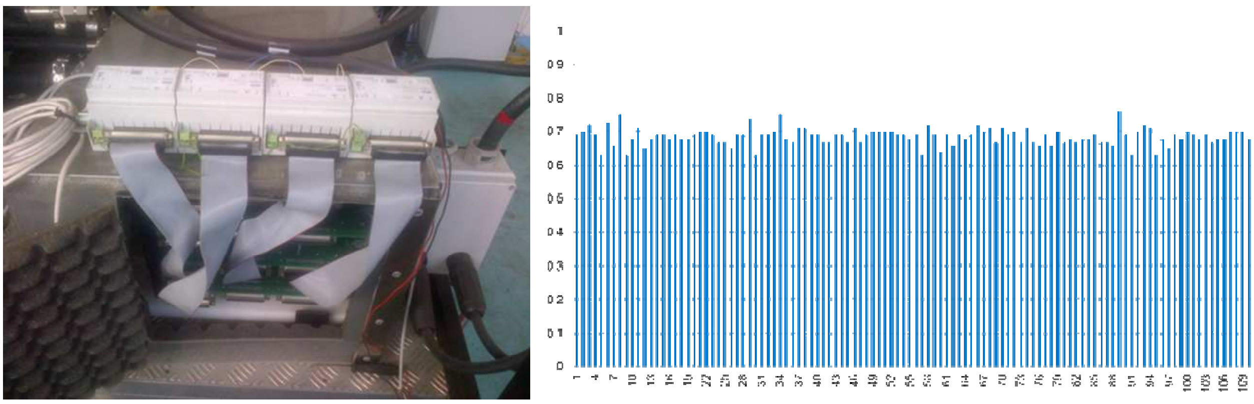


Figure 6: 110 single cell voltage measurement connected to one of the 4 stacks of the Sidera30 PEMFC ICI system & Voltage against the cell number in a certain moment

Definition of the the reference components

DMFC 5-layer Reference MEAs

Description	Product ID	Catalyst loading
Anode GDL	Sigracet 35DC	
Anode Catalyst	Cabot Dynalyst 62RKR4	1.8 mg PtRu/cm^2
Membrane	Nafion® N115CS	
Cathode Catalyst	Cabot Dynalyst 65KR2	1.2 mg Pt/cm^2
Cathode GDL	Sigracet 35DC	

LT PEM 5-layer Reference MEAs

Description	Product ID	Catalyst loading
Anode GDL	Sigracet 35DC	
Anode Catalyst	Hispec 10000	0.3 mg PtRu/cm^2
Membrane	Nafion® XL	
Cathode Catalyst	Hispec 9100	0.5 mg Pt/cm^2
Cathode GDL	Sigracet 35DC	

1.3.3.2 Outcomes related to DMFC in-situ testing

- Original insights on DMFC degradation test method in single cells:
    - parallel study of anode half cells and single cells used to identify anode/cathode contribution on both temporary/permanent degradation
    - real-time monitoring of cathode effluent composition, to evaluate methanol and water transport though the MEA
- Original insights on DMFC temporary degradation:
    - existence of anode temporary degradation: its origin is related to water and methanol concentration reduction at anode side, due to CO_2 accumulation in electrode and GDL, hindering reactants transport
    - temporary methanol crossover reduction is observed as a CO_2 content variation in cathode exhaust, coherently with the proposed interpretation of anode temporary degradation, while water content in cathode exhaust remain constant
    - cathode temporary degradation is most probably caused by a temporary reduction of ECSA, due to Pt or Ru oxides formation during operation at high potential (Ru presence at cathode is confirmed by ex-situ measurements)
    - proposal and validation of refresh cycles: dramatic reduction of temporary degradation; the proposed refresh cycles permit a recovery of temporary

degradation at both anode, permitting CO_2 removal from GDL/electrode, and cathode, determining the reduction of Pt/Ru oxides

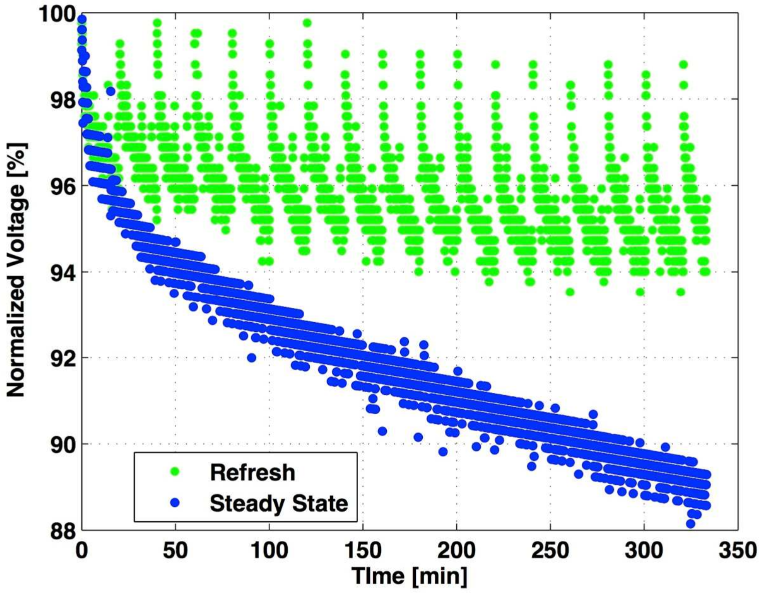


Figure 33. Comparison of cell voltage evolution during short term ageing test without or with applied refresh cycles.

- Original insights on DMFC permanent degradation (long term test >1000 h):
    - from EIS spectra, CV, polarisation curves: considerable reduction of cathode active area, mainly due to Pt dissolution/re-deposition, determining the major contribution to permanent degradation (about 70%)

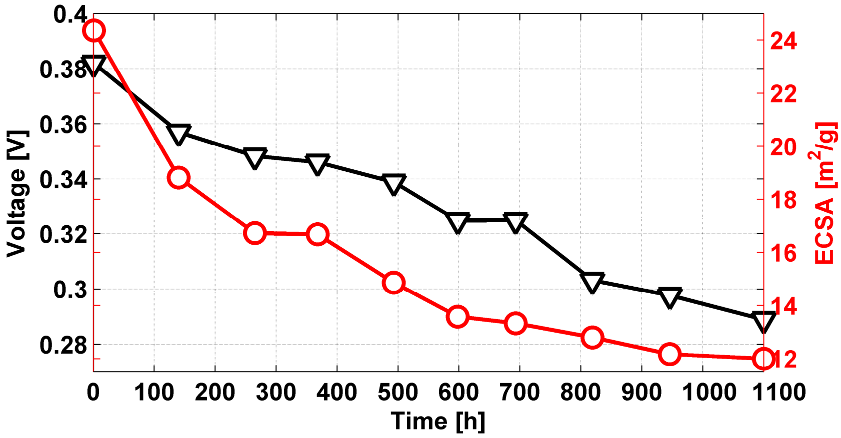


Figure 33. Comparison between cathode ECSA obtained through the CV and Voltage at nominal current density during the Polarization curves

- from EIS spectra, anode polarisation curves: reduction of anode catalyst effectiveness, mainly due to Ru dissolution/migration, determining the remaining contribution to permanent degradation (about 30%)
- membrane transport properties decrease is very limited
- comparing reference and benchmark MEAs: methanol crossover and water transport/flooding influences considerably the relation between cathode ECSA loss and performance decay

1.3.3.3 Outcomes related to PEMFC in-situ testing

- Original insights on the behaviour of PEMFC in single cells and short stacks: all ageing studies conducted in load cycling mode instead of stationary
    - Identification of reversible and permanent degradation for a single cell operated with load cycles and reformate fuel (1000 hours): carbon monoxide concentration has stronger impact on the reversible degradation,
    - Permanent degradation is much lower than reversible and related to catalyst layers activity decrease; no membrane degradation while using reinforced references (from EIS and cyclic voltammetry)
    - Evidence of an increase in reversible degradation when operating under reformate fuel compared to pure hydrogen, first direct and in-situ evidence that the anode tolerance can be the main issue.
    - Confirmation that too high CO content with non aged catalyst, or decrease of CO tolerance due to degradation, can lead to voltage oscillating behaviour related to a threshold allowing full coverage of the anode catalyst surface, causing fast increase of anode potential up to CO oxidation potential and total cleaning before starting again with pollutant adsorption.
    - Confirmation that load cycles lead to cathode catalyst ECSA losses and evidence by cyclic voltammetry and also by EIS (on high frequency anode activity resistance) of anode catalyst (PtRu) modifications of structure and properties.
    - Severe increase of performance degradation at high current density when operating with more dynamic load cycles or with reformate at higher CO concentration: high CO concentration and dynamic cycles identified as major parameters for further developments of accelerated tests

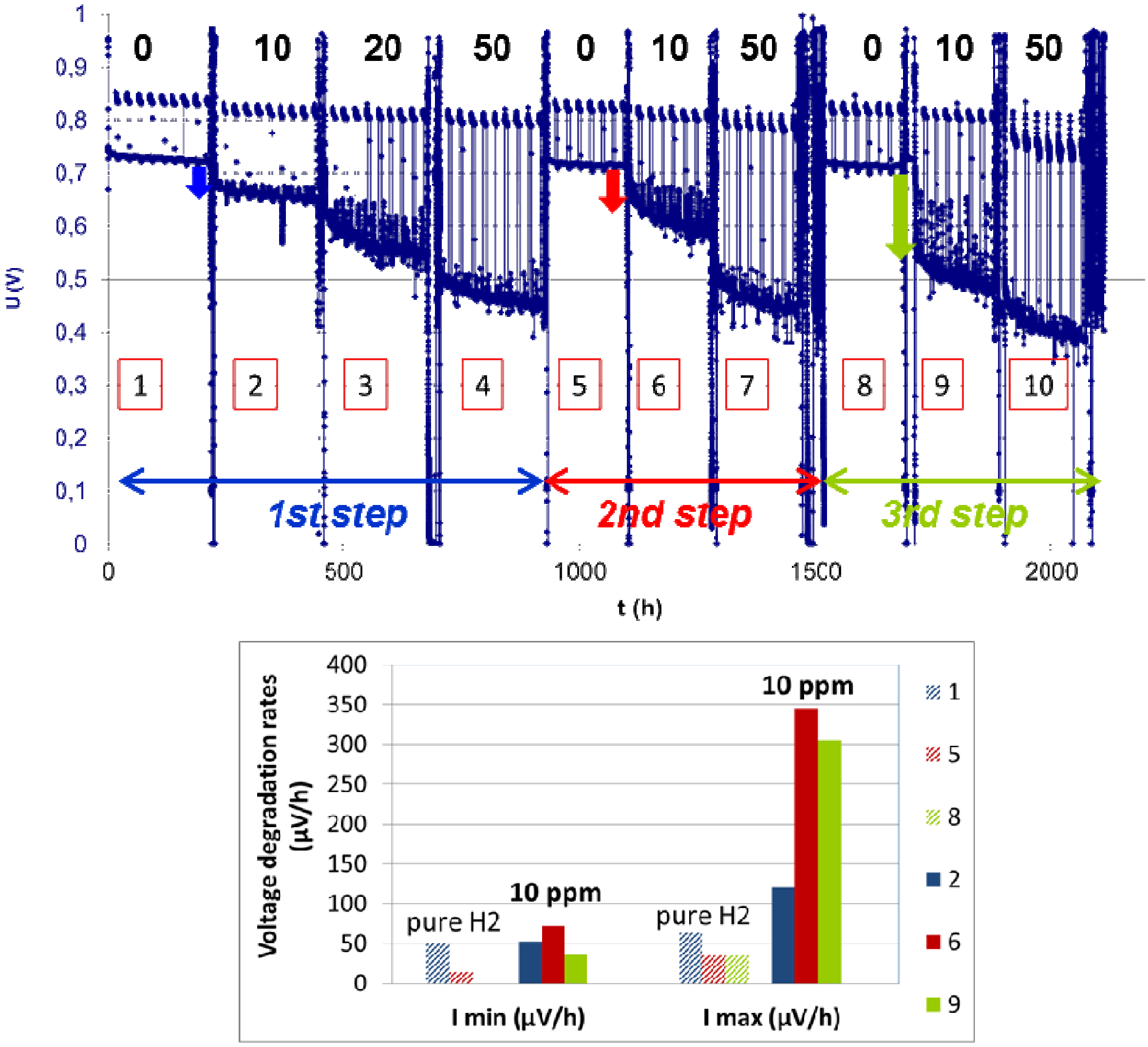


Figure 7: Cell voltage along the time for a reference IRD MEA tested under pure H2 and reformate H_2 with CO contents from 10 to 50 ppm (top) and voltage degradation rates during each stage of load cycles (down).

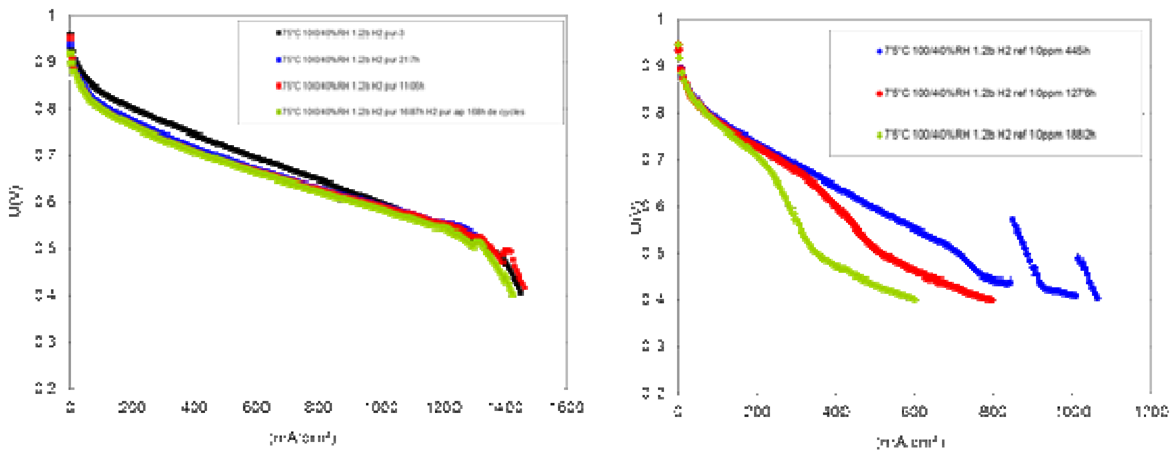


Figure 8: polarisation curves obtained under pure (left) or reformate H2 including 10 ppm of CO (right) of PEMFC single cell reference MEA during the CO Accelerated Test

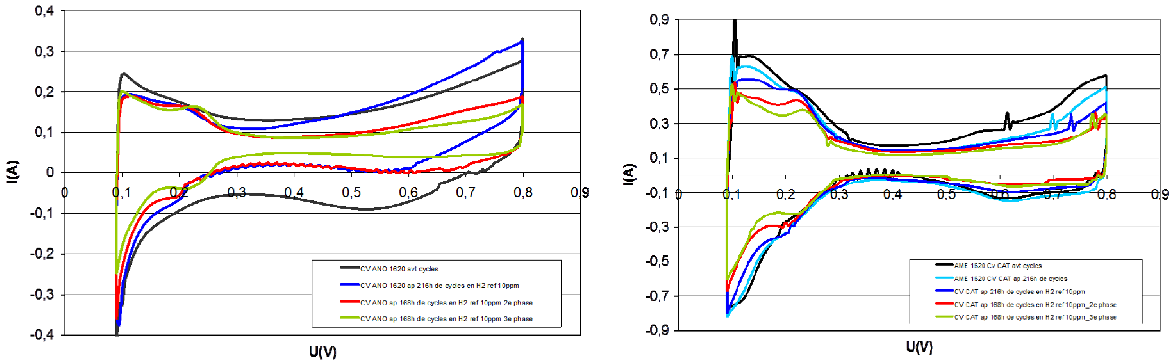


Figure 9: cyclic voltammetry obtained on anode (left) and cathode (right) of PEMFC single cell reference MEA during the CO Accelerated Test

- With segmented cell measurements applied in a 25cm² single cells it has been found that small amounts of CO in the fuel lead to a homogeneous degradation of the current density. In contrast, humidity gradients unambiguously lead to accelerated performance loss in areas with low local humidity, when considering more cathode degradation.

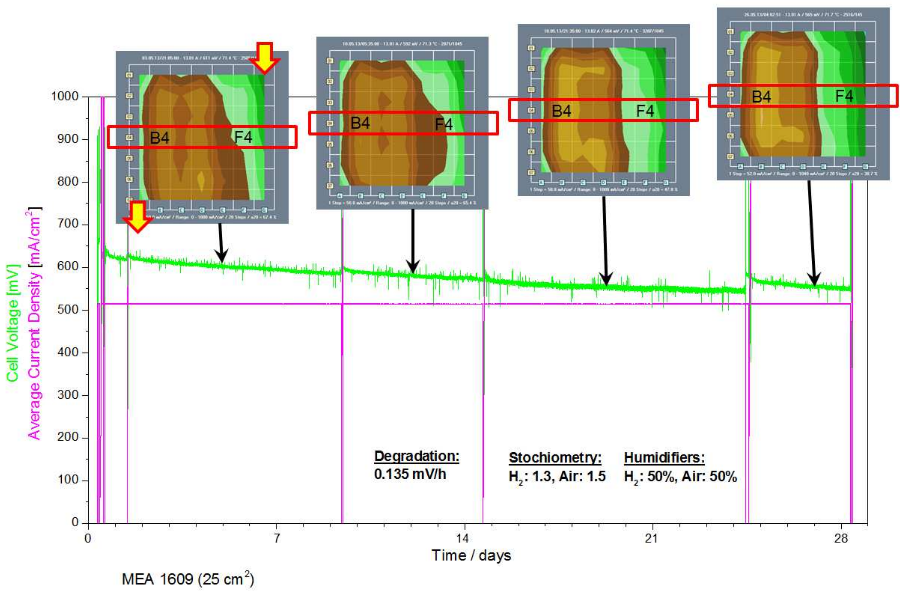


Figure 10: Operation of a PEMFC at humidity gradients along with current density distirbutions. The green areas (low values) and brown areas (high values) of the current density distribution correspond to flow filed regions with a low and a high local humidity, respectively. An increased degradation of regions with low local humidity can be observed.

- Availability and first operation of PEMFC stack with same components and same load cycles as in a single cell: systematic study of fuel composition enabling to get additional information compared to single cell for more accurate interpretation of degradation. Use of electrochemical methods for each cell analysis in a stack allowing further knowledge about local conditions impact at stack level (possibility to exploit for degradation understanding the possible heterogeneities among cells).
- Evidence of conditions enabling better voltage stability such as air bleeding, and temperature increase for fuel tolerance, and stops and restart for temporary degradation limitation; but with always a controlled use of the parameter to avoid additional degradation phenomena particularly related to membrane.

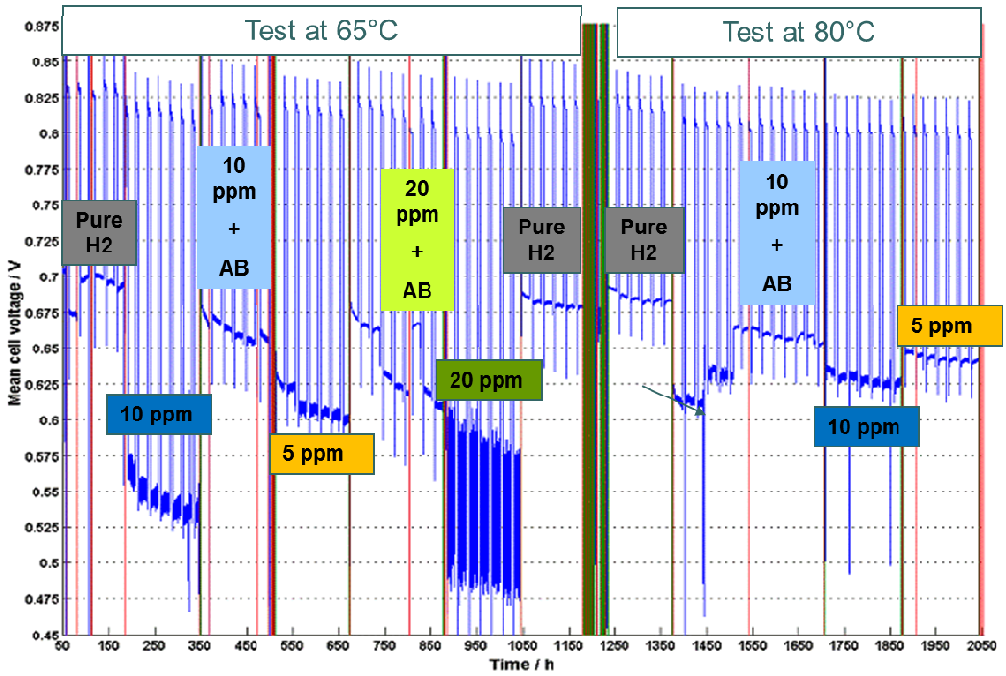
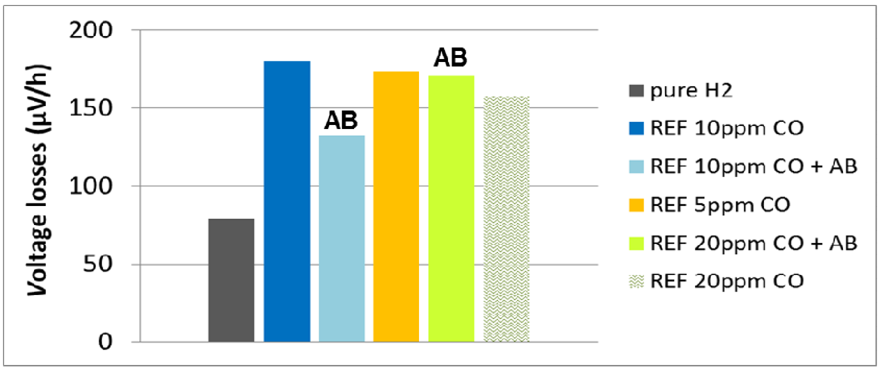


Figure 11: average voltage versus time (total test) of the IRD 10 cells stack with reference MEAs used to identify accelerating and decelerating features for operation under reformate.



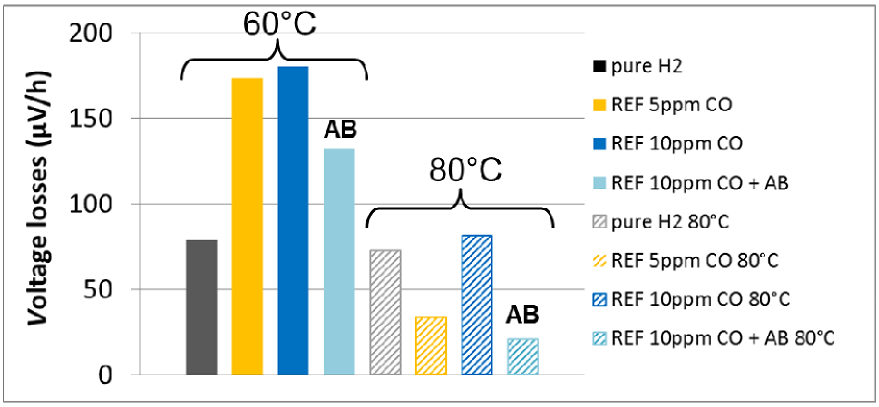


Figure 12: average voltage versus time during selected period of cycles for some conditions and voltage degradation rates calculated at higher current on the basis of 4 periods. IRD 10 cells stack with reference MEAs for operation under pure H2 or under reformate with various compositions and two temperatures.

- Validation on different MEAs in single cell and also at stack level of the accelerated ageing protocols proposed with more dynamic and higher load cycles, with increased CO centration stages during nominal load cycles, or combined protocols including both features. Identification of the accelerating effect of an increase water content (or partial flooding) for the degradation of anode catalyst.

1.3.3.4 Outcomes related to ex-situ analyses

New information retired from *ex-situ* analyses techniques:

- Vibrational spectroscopy techniques: Large area FTIRAS mapping and FTIR-ATR microscopy established for screening of all MEA components allowing for spatially resolved degradation of polymers. Yet, due to high scatter of the data the data evaluation needs statistical analysis procedures to provide reliable information. In the case of PEFC the GDL seem to be stable under and the PTFE does not change during aging. For DMFC MEAs, on the other hand, the PTFE distribution changes upon aging indicating a change of the hydrophobicity in accordance with XPS measurements *(Figure 13)*.

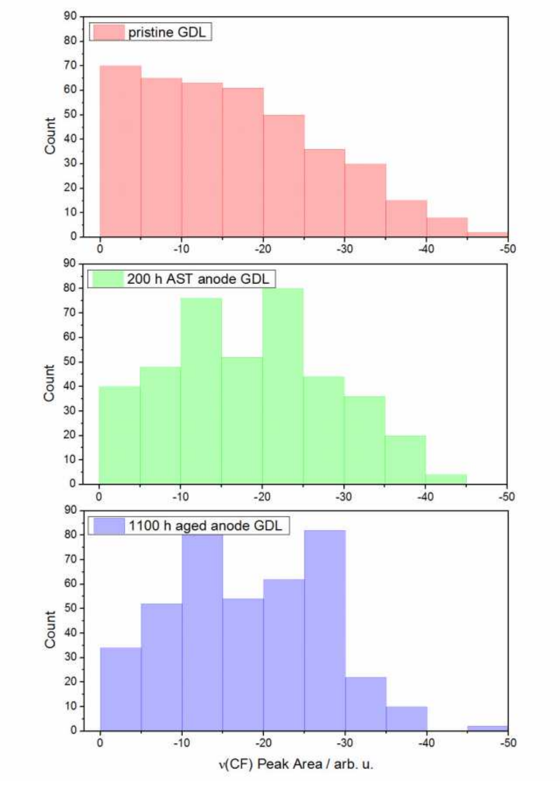


Figure 13: Histogram of C-F vibrational peak area distribution in the DMFC GDLs indicated in the figure. The data are taken from large area FTIR-ATR mappings. The changes of the distributions of the aged GDLs indicate a change of hydrophobicity upon fuel cell operation.

- Electron microscopy techniques:
- Application of standard and high resolution transmission electron microscopy (TEM) allowing to detect very small quantities of catalysts particles showing the very beginning of ageing (Ruthenium precipitates in the membrane of PEMFC)

- First use of last generation analytical TEM (FEI-Osiris) allowing accurate spatially resolved chemical analysis by X-EDS: identification of platinum core in Ru particles detected in the membranes. New approach for improved determination of mechanisms. In addition, use of high resolution TEM allowing to identify the atomic structure to ensure metallic phase of the particles detected.
- Identification of a new mechanism leading to Pt-core / metallic Ru petals involving the common Pt-band in the reduction of Ru species coming from anode Ru dissolution.

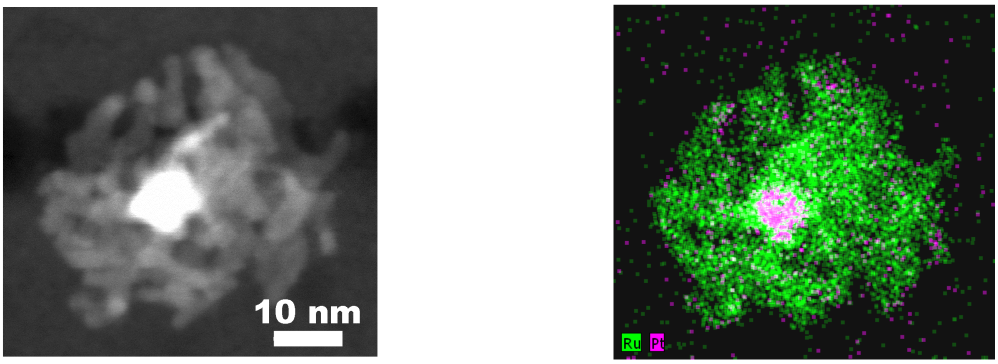


Figure 14: Precipitate located in the membrane of MEA IRD1616, on the cathode side of the air inlet. It is about 40 nm in size and has a flower morphology. (Left) STEM/HAADF image. (Right) Pt and Ru elemental map, acquired via X-EDS imaging. The particle contains 10 at% Pt – 90 at% Ru. It exhibits a Pt-rich core with a Ru-rich petals..

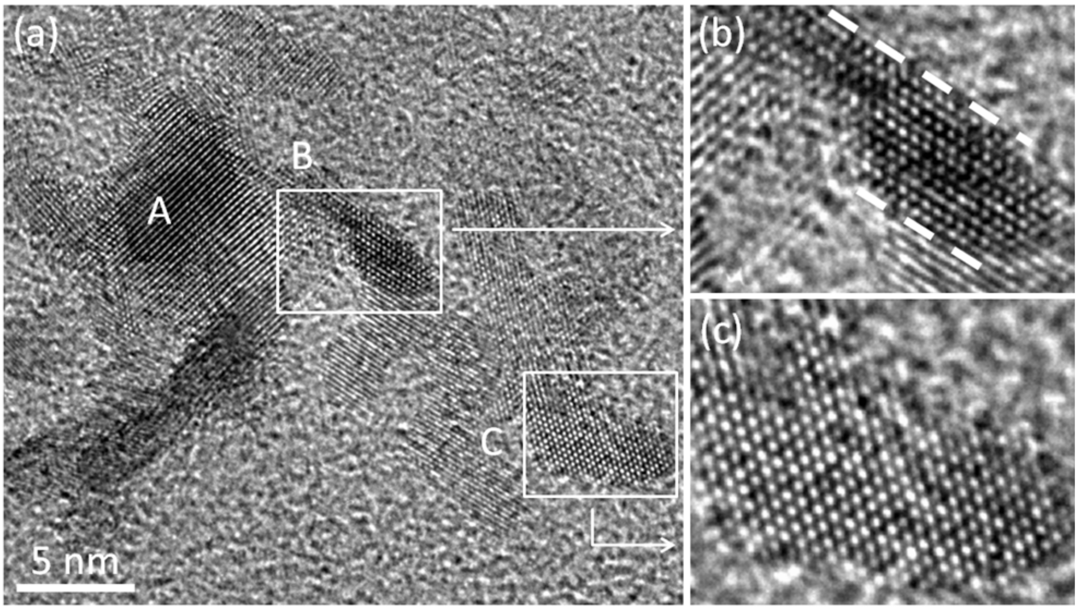


Figure 15: a) HRTEM images of a precipitate located in the precipitation band at the air inlet. b) and c) higher magnification of respectively zone B and C of image a) showing the hcp structure of the petals.

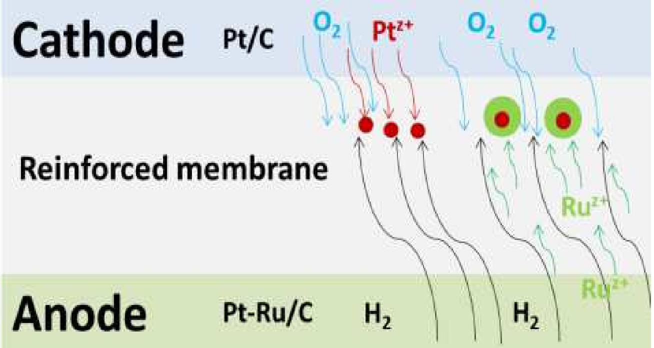


Figure 16: Diagram depicting the mechanism leading to the formation of the precipitates located in the precipitation band.

- Enhanced knowledge of Ru dissolution mechanisms: evidence of occurrence whatever the operating conditions, even in cases with low anode potentials and identification of parameters influencing qualitatively and quantitatively the dissolution and further re-deposition of the ruthenium (in the membrane or anode microporous layer particularly).

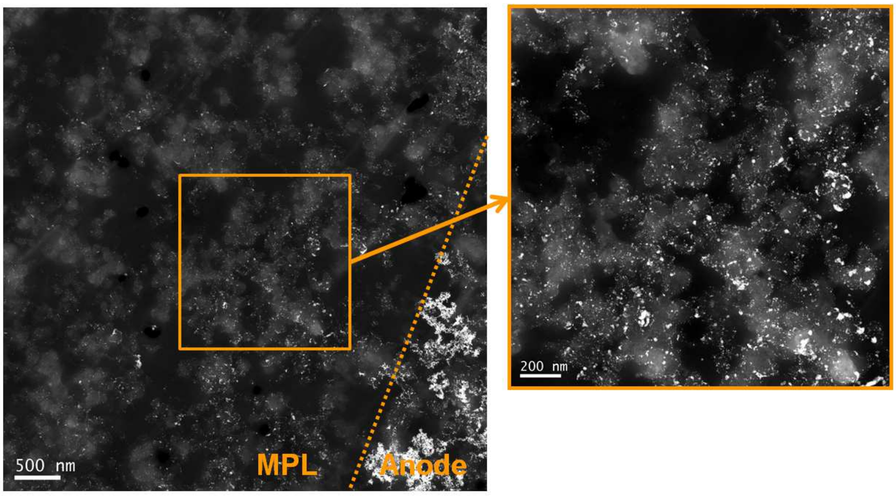


Figure 17: TEM images of the anode MPL of a PEMFC MEA aged in high CO content AccST protocol. A large quantity of Ru precipitated inside the MPL.(right) larger magnification of the MPL Probably is the main origin of the anode Ru depletion..

- Of particular interest for the project, all mechanisms related to catalysts degradation (cathode or anode) have been confirmed to be enhance quantitatively when applying selected accelerated ageing and also, no additional mechanism is provoked by these AccST.

- Electron microscopy/spectroscopy techniques:
- A new depth profiling method in combination with XPS has been established to analyse porous media, such as MPL and CL. Thereby, the upper surface layers are

successively removed by delamination with adhesive tape with subsequent XPS analysis, see . The analysed depth reaches from around 0.5 µm to a few tens of micrometers (i.e. macrostructure). Moreover, this approach is chemically non-destructive providing chemically non-falsified depth profiles, in opposite to ion etching (decomposition of polymers). In the Premium Act project it has been successfully used to analyse catalyst degradation; especially, with this technique the Ru cross-over in DMFC was analysed in very detail showing a uniform redistribution of anodic Ru in the cathode CL. Moreover the data show that in DMFC Ru cross-over occurs mainly at the beginning of operation and proceeds only very slowly upon further operation, see Figure 19.

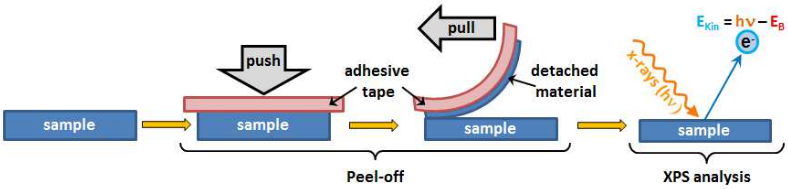


Figure 18: Scheme of the peel-off depth profiling technique.

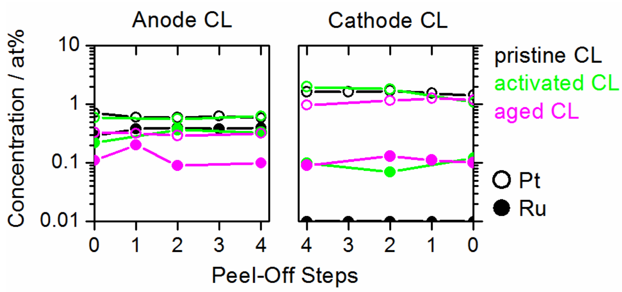


Figure 19: Peel-off depth profiles of the anode and cathode CL of the pristine, activated (30 h operation) and aged MEA (1100 h operation).

- Standard XPS has been used to study all components of MEAs. For instance, in the case of GDL it clearly shows the decomposition of PTFE within the gas diffusion layer *(Figure 20)*. Specifically, in the C1s spectra of the anode GDL the increased signal in the range between 285 and 290 eV clearly indicates a chemical decomposition of the PTFE. In contrast, the PTFE in the GDL on the cathode is not chemically decomposed.
- The loss of polymers, especially at the CL , can be cleary observed.

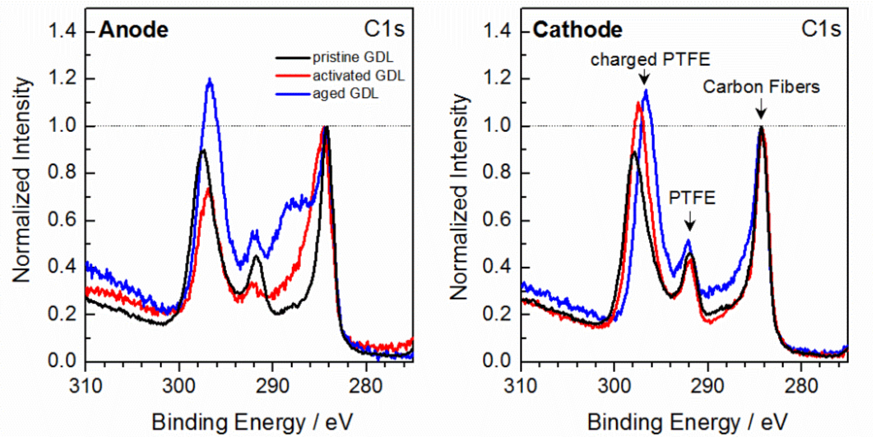


Figure 20: XPS spectra of the C1s regions of the pristine, activated and 1100 h aged DMFC GDLs. The spectra are normalized with respect to the intensity of the 284 eV peak. In the spectrum of the aged GDL the peak in the range between 285 and 290 eV is typical for carbon in a CF-C compound, i.e. it is taken as an evidence for chemically decomposed PTFE (fluorine depletion).

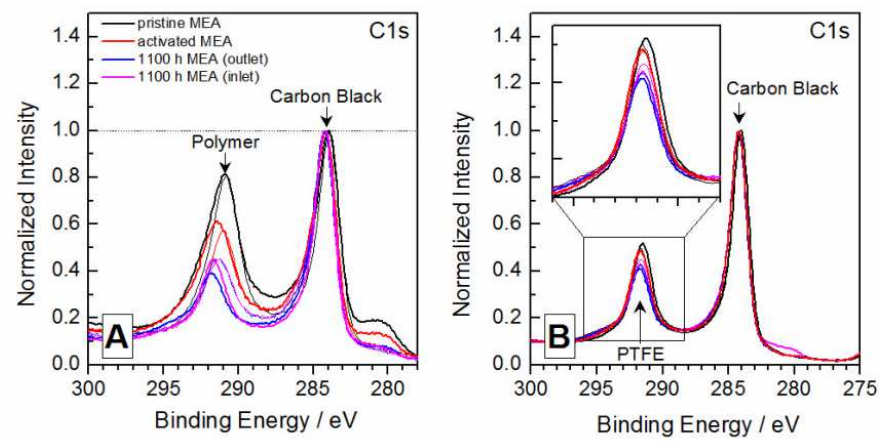


Figure 21: Loss of polymers in MPL and CL of DMFC MEA. The images how XPS spectra of the C1s regions of the pristine, activated and 1100 h aged catalyst layers (A) and micro porous layers (B). The thick and thin lines correspond to the anode and the cathode side, respectively. The spectra are normalized with respect to the intensity of the 284 eV peak.

A comparison of degradation effect found in an 1100h aged DMFC MEA and a DMFC MEA operated at 200h at an AST, as presented in the paragraph about DMFC in-situ testing, has been conducted showing good correspondance of conclusions obtained by XPS analyses.

MEA Component	1100 h aged MEA	200h AST aged MEA	Agreement
Anodic GDL	PTFE decomposition (and redistribution) carbon corrosion	Strong PTFE clustering carbon corrosion	NO
Cathodic GDL	No significant changes	Strong PTFE clustering	NO
Anodic MPL	Slight loss of polymer of relative to carbon content		YES
Cathodic MPL	(Adsorption of catalyst from anode side) Slight loss of polymer of relative to carbon content		YES
Anodic CL	Catalyst dissolution Loss of polymer		YES
Cathodic CL	Adsorption of Ru from anode side Loss of polymer		YES

- Ex-situ analyses of the GDLs transport properties

Preliminary Accelerated Stress test has been defined and applied for DMFC Gas Diffusion Layers: it has been shown that a variation of material properties could imply a modification in mass transport regime

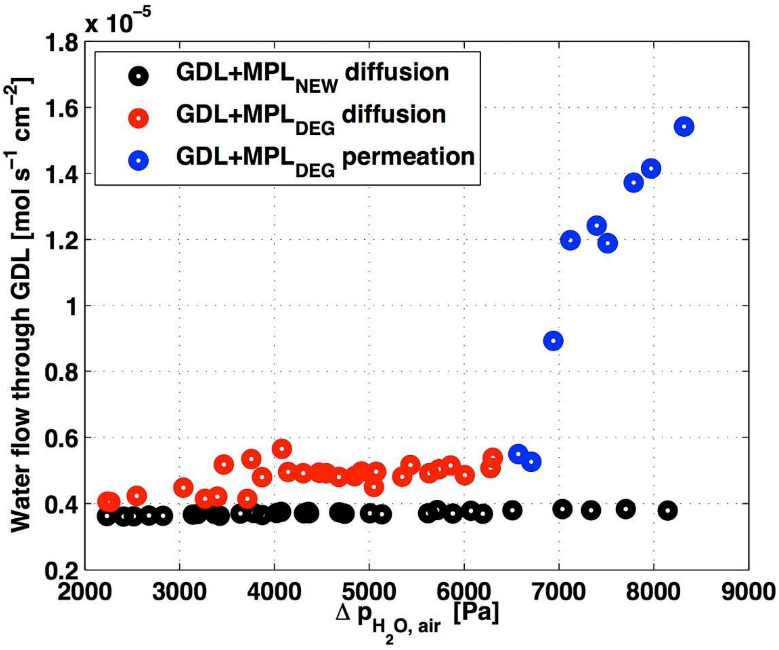


Figure 22. Comparison between Specific water flux through GDL with MPL at 60°C as a function of water/air pressure difference for pristine and degraded samples

1.3.3.5 Outcomes related to DMFC modelling

New insights on modelling in DMFC:

- Single cell model including a complete and accurate description of water management and flooding effects. The developed model is validated over a wide range of operating conditions, with respect to different typologies of measure and with different configurations of GDLs properties. ;
- Detailed two-phase mass transport phenomena through anode porous components revealed that the main methanol transport mechanism is gas diffusion. The modeling result also implies the possibility to design an optimized DL with balanced mass transport loss and reduced methanol crossover.

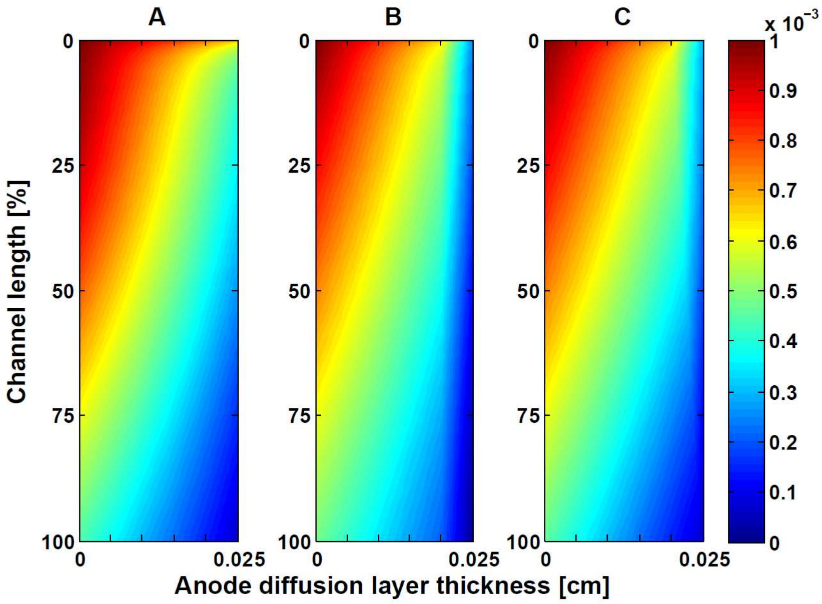


Figure 23 : Methanol liquid concentration across anode DL at i = 0.25 A cm-2 A) GDL of constant thickness, B) GDL+MPL of constant thickness, C) optimized GDL+MPL.

- New approaches and models developed for the simulation of anode impedance behaviour, permitting a better interpretation of DMFC anode operation (Methanol Oxidation Reaction) and temporary degradation.;
- New model of Ruthenium dissolution: mechanism included into the MEA model and effect studied spatially resolved within the anode catalyst layer (quicker dissolution near the membrane).
- New model of platinum particle growth based on Ostwald ripening and coalescence developed and included into MEA model. Validation of degradation model by aging tests.

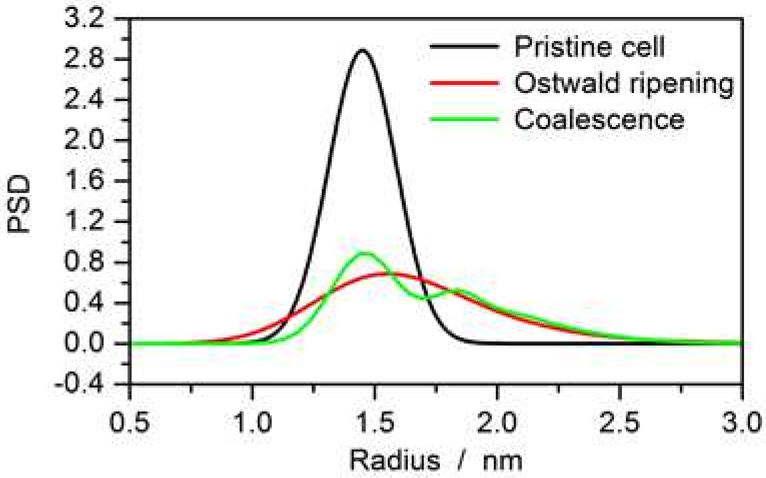


Figure 24 : Simulated change of particle size distribution (PSD) due to Ostwald ripening and coalescence after loss of 20% ECSA

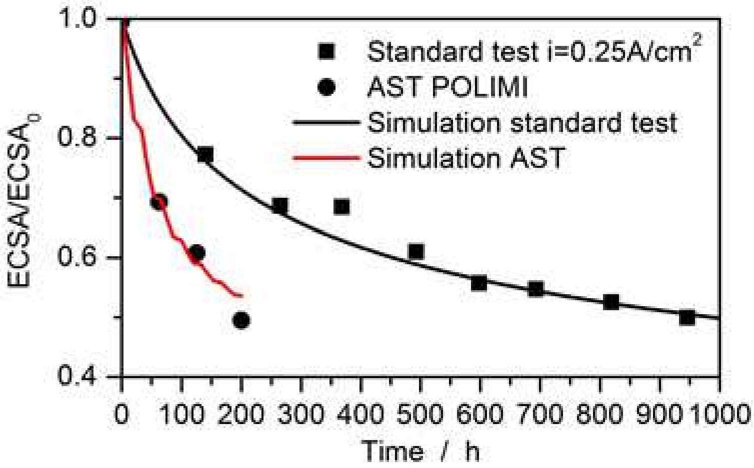


Figure 25 : Validation of the detailed degradation model: Comparison of simulated and measured loss of ECSA under standard conditions and for the AST.

- Empirical correlation based on detailed degradation model derived and included into single cell model for lifetime predictions, evidencing the possibility of severe local degradation at channel inlet during AST tests.
- Study on propagation of uncertainty indicates that knowing the initial particle size distribution is important for accurate lifetime predictions.

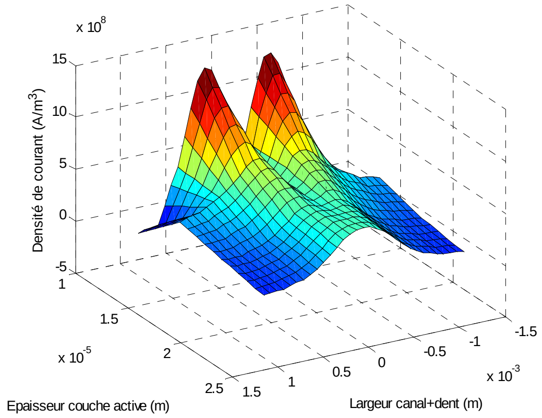
1.3.3.6 Outcomes related to PEFC modelling

<u>New insights on modelling in PEMFC:</u>

- New approach based on the interaction of a mechanistic model describing degradation mechanisms and a fluidic model computing the local conditions for the description of electrodes and performance degradation. The coupling has been completed and tested for platinum dissolution, but can be extended to other mechanisms;
- Implementation of local active area degradation in PEMFC fluidic model: evidence of an increase of the initial heterogeneities with horizontal and vertical resolution (from gas inlet to outlet, in the rib and channels and in the thickness of electrode from the membrane to the gas diffusion layer)

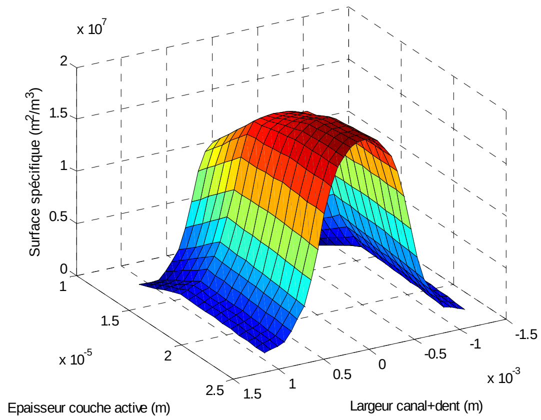
Qualitative experimental validation of the predicted degradation at the stack level. Comparison of experimental degradation rates with simulation prediction for various operating conditions.

Current density distribution at t=1000h



Current density distribution in the cathode CL after 1000h. The figure shows the current production (in A/m^3) as a function of the position in the catalyst layer.

Platinum surface at t=1000h



Platinum surface local degradation after 1000h in the cathode CL.

Figure 26 : MEA degradation at rib/channel level : the degradation is much higher under the channel than under the rib. This can be explained by different loval operating conditions.

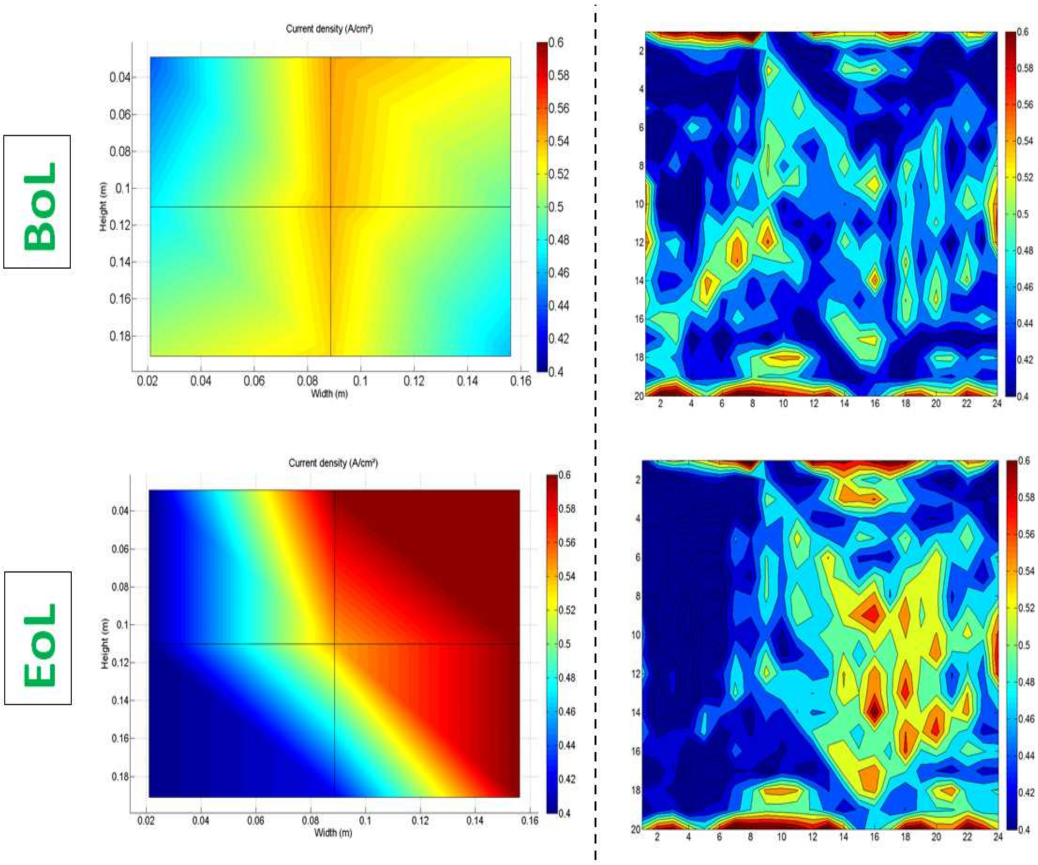


Figure 27 : Current density redistribution due to degradation at cell/stack level (simulation on the left, experimental on the right) : as the air inlet (on the left of the figures) of the cell is more degradated, the current density shifts toward the middle and the outlet of the cell

The simulation results show :

- that the degradation at the MEA level may be very heterogeneous between rib and channel, and also through the thickness of the calalyst layer (depending on the operating conditions);
- that the cell level model is able to predict, at least qualitatively, the inhomogeneous degradation from the inlet to the outlet, and the consequence on the current distribution.

1.3.4 Specific outcomes regarding degradation mechanisms with regard to existing knowledge

1.3.4.1 List of main mechanisms recognized to occur from literature and consortium knowledge

Irreversible degradation (SoA):

Catalyst layer

- Platinum dissolution + migration
- Growing of larger Pt particles by Electrochemical Ostwald ripening
- With PtRu catalysts used anode side: Ruthenium dissolution + migration
- With PtCo catalysts used cathode side: Cobalt dissolution + migration
- Carbon corrosion
- Site blocking (by non reversible contaminants)

Membrane

- Mechanical damage (related to local hydrothermal cycles, or to chemical degradation)
- Chemical degradation leading to chain scission (incl. mechanism due to Fe contamination)

Gas Diffusion Layers

- Reduction of hydrophobicity (PTFE dissolution)

Reversible degradation (SoA):

Catalyst layer

- Hydrocarbon based contaminations: can be removed by refresh cycle
- Site blocking (mainly CO)
- Catalyst oxidation

Membrane

- Drying out (locally at air inlet for PEMFC only when partially humidified air is used)

Gas Diffusion Layers

- Water accumulation

1.3.4.2 List of mechanisms identified by the project in aged MEAs of Premium Act systems

Non reversible (Premium Act outcomes):

- Electrochemical Ostwald ripening/coalescence (?): growing of Pt particles identified in PEMFC and in DMFC aged cathode samples after single cell test

Mechanism causing the first permanent performance losses visible on polarisation curves and electrochemical impedance spectra and the evolution of the cyclic voltammograms cathode side towards more define peaks.

- Ru dissolution in PEMFC:

1-Evidence of Pt-core/Ru-petals flower shape particles detected in the membrane

2-Ru deposition occuring in the anode MicroPorous Layer in accelerated conditions

Ru dissolution in MEAs aged under load cycles is the mechanism causing the additional permanent performance losses visible on polarisation curves under reformate hydrogen and responsible for the evolution of the anode electrochemical properties as visible on one hand by cyclic voltammetry with reduced capacitive charge and in worse cases sharpening of hydrogen adsorption/desorption peaks reflecting more Pt behaviour and by impedance spectroscopy with an increased high frequency contribution due to poorer anode activity under reformate. *It can be reminded that this degradation does not negatively impact the operation under pure hydrogen for the duration considered: this appears consistent with the common knowledge claiming the reversibility of degradation due to reformate and carbon monoxide*.

- Ru dissolution in DMFC: detection of Ruthenium species at cathode side and membrane of an MEA aged in a DMFC system

Mechanism causing probably a part of the anode permanent losses; a probable influence on cathode temporary degradation is suspected

According to XPS analysis Ru cross-over occurs mainly at the beginning of the operation (during conditioning of the MEA), and proceeds only slowly upon further operation.

- PTFE decomposition in DMFC GDLs: Long-time operation leads to gradual chemical decomposition of PTFE in anodic GDL likely leading to a change of hydrophobicity. With XPS fluorine depleted components can be observed after long time operation (*Figure 20)*

- Loss of polymers in the CL and MPL on both, the anode and the cathode side: a slight loss of polymers is observed (no decomposition) that occurs predominantly at the beginning of operation *(Figure 21).*

Reversible (Premium Act outcomes):

- CO pollution in PEMFC: tests conducted in single cells and short stacks with reformate fuel containing various CO concentration

Mechanism causing, and measured by, cell voltage decrease at low and high current density. Reversibility confirmed with polarisation curves under pure Hydrogen.

CO identified and confirmed as causing non reversible degradation under reformate operation because the consequence is the loss of ruthenium: impact of CO on permanent degradation clarified as an accelerating feature when increasing its concentration because direct increase of anode potential and of dissolution

- Anode CO_2 accumulation in DMFC (electrode/GDL): identified by electrochemical impedance spectra and mass transport analysis

Mechanism causing anode temporary degradation. Reversibility confirmed with different refresh cycles.

- Pt/Ru oxides formation in DMFC cathode catalyst: identified by electrochemical impedance spectra and specific test with different operating strategies

Mechanism causing cathode temporary degradation. Reversibility confirmed with different refresh cycles.

1.3.5 Specific outcomes regarding operating strategies

Operating strategies are addressing the temporary (or reversible) degradation. The aim is find methods enabling to stabilize the performance, or to reduce the cell voltage losses during ageing tests.

1.3.5.1 Operating strategies related to DMFC systems

- Validation of operating strategies, based on refresh cycles (duration: few minutes), able to mitigate temporary degradation have been identified; refresh cycles can be optimize to minimize temporary degradation

- Validation of an operating strategy (duration: some hours) to fully recover performance has been developed

- Possible phenomenon: the minimization of temporary degradation determines a positive effect on permanent degradation both in single cell s and in systems

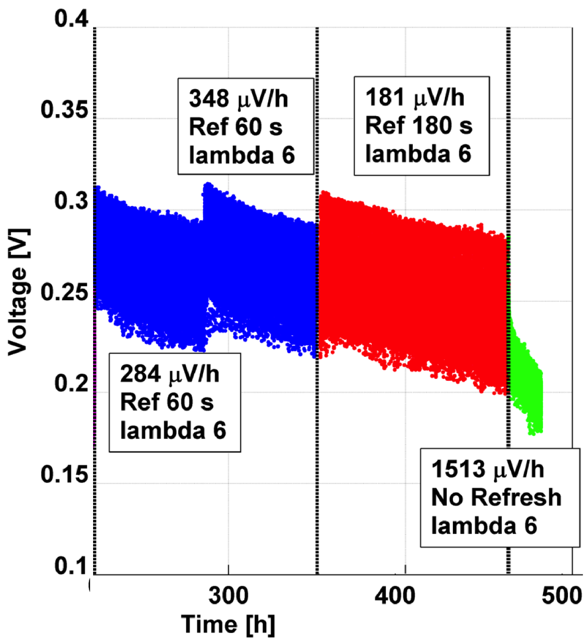


Figure 28: Sensitivity analysis on Refresh Duration for DMFC operation in reference conditions

1.3.5.2 Operating strategies related to PEMFC systems

Experimental results

- Confirmation of the positive impact of stops during load cycling. Local in-situ conditions are supposed to be modified towards less heterogeneity during stops of the load, thus allowing higher average power when restarting current production.

- Validation at stack level of the positive impact of continuous air bleeding (less than 1% for low CO concentration of 10 ppm in the reformate) to first increase the performance but most of all to decrease the voltage degradation rates (minus 25% at high current during day/night type load cycles at 65°C)

- Validation at stack level of the positive impact of increasing temperature from 65 to 80°C again to first increase the performance but mainly to decrease the voltage degradation rates (minus 60% at high current during day/night type load cycles without air bleeding).

Simulation results

Simulation results *(Figure 29)* show that some operating parameters impact strongly the degradation of the cells. The system operating strategy should be designed to remain as close as possible to optimal operating conditions in terms of lifetime. This is especially the case if we consider an hybrid system, where the battery gives more freedom for the power demand to the fuel cell during a cycle *(Figure 30).* The simulations show that an balance can be found between minimizing the hydrogen consumption and preserving the state of health of the stack *(Figure 31).*

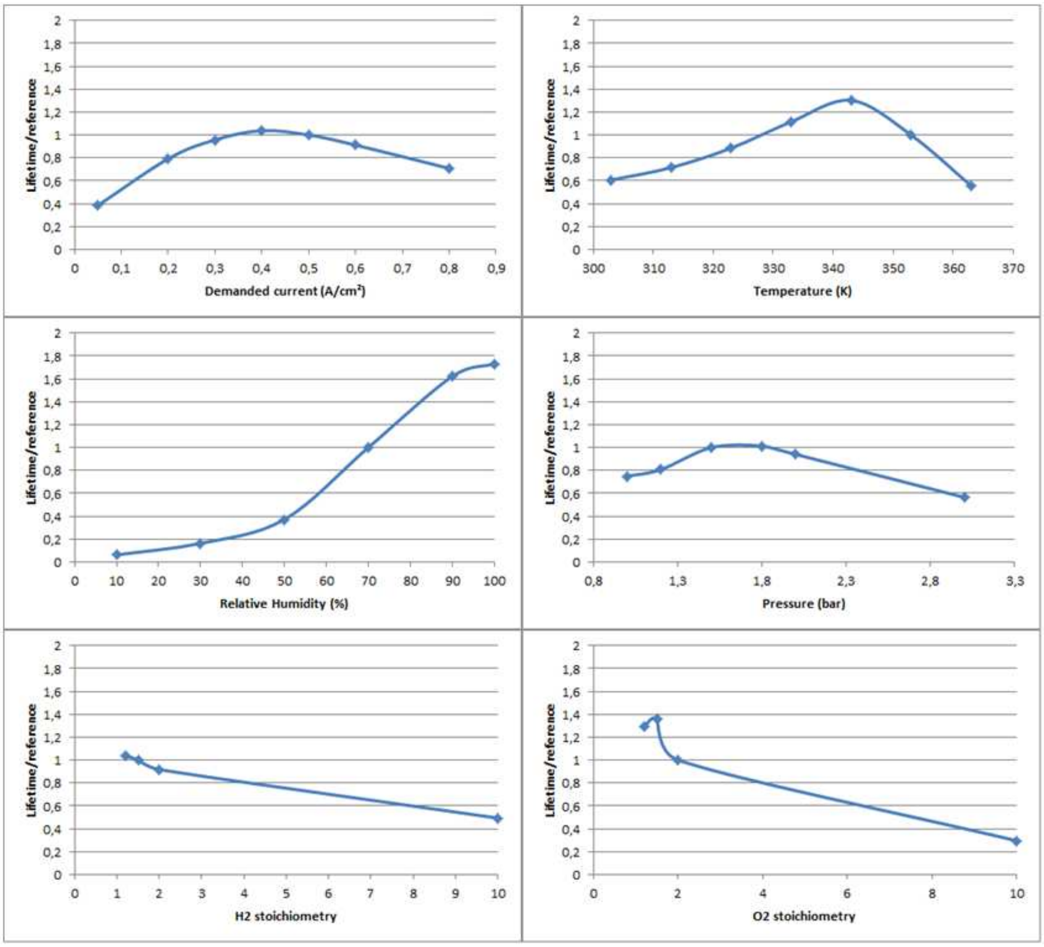


Figure 29 : Effect of operating parameters on cell predicted lifetime

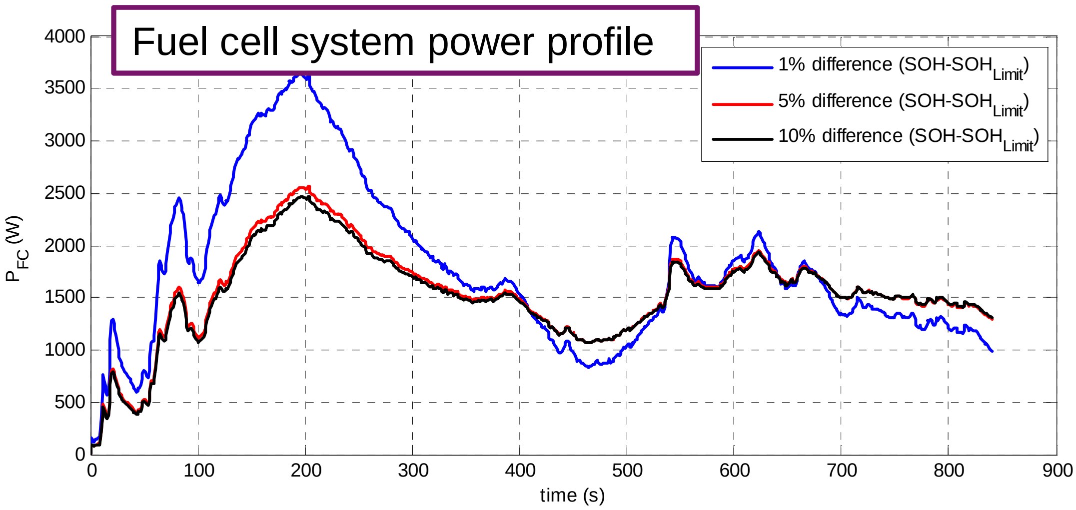


Figure 30 : Power profile for the fuel cell during a cycle, considering different tolerances in terms of degradation

ΔSoH (%) (initial condition)	100*(Surface losses/ 44cm²) (%)	Consumption (gH2/km)
10	0.0485	17.87
5	0.0480	18.20
1	0.0463	20.99

Figure 31 : Pt surface losses and fuel consumption for different degradation constraints. Mitigating the degradation down to 1% for the simulated cycle increases the hydrogen consumption by 17%.

1.3.6 Specific outcomes regarding lifetime prediction methodology and accelerated tests

1.3.6.1 Accelerated tests related to DMFC systems

- Qualification of several AST protocols have been tested and analysed both in single cells and in systems
- AST protocols based on load cycle are affected by a complex fuel cell behaviour: anode/cathode potentials are uncertain as well as temporary degradation effects
- Development and validation of a new AST, based on OCV and air break periods: it permits to accelerate cathode ECSA loss by a factor 5 approximately; performance decay acceleration factor, generally about 6-7, strongly depends on MEA properties

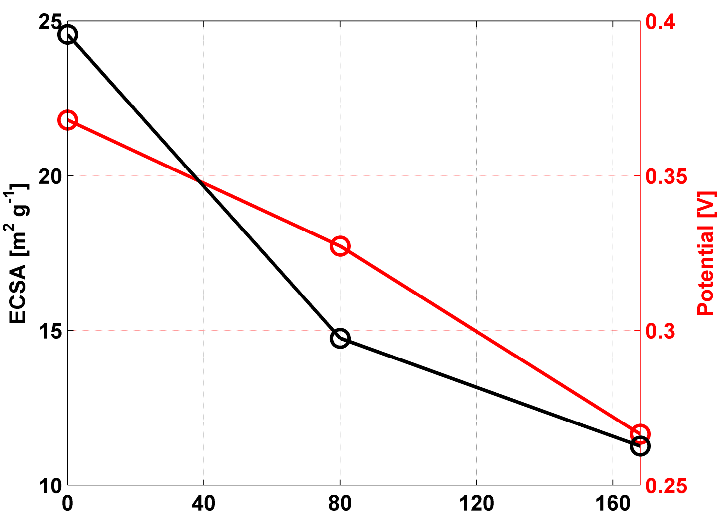


Figure 32: Comparison between cathode ECSA obtained through the CV and Voltage at nominal current density during the Polarization curves

- XPS analysis show that for DMFC MEAs the applied AST partially lead to similar degradation as standard aging. Specifically, regarding the degradation of CL and MPL the observed changes in AST and aged samples agree. The degradation observed in GDLs, however, is completely different for the AST and the 1100h aged DMFC MEA.

See Table summarizing the ex-situ results.

1.3.6.2 Accelerated tests related to PEFC systems

- First generation of AccSt protocols have been developed to check the negative impact of increasing CO content during lmoad cycles and to check the potential negative impact of more dynamic load cycles, including higher maximum current to increase the voltage amplitude during cycles.
- Based on performance (voltage) evolution during the cycles, calculated degradation rates, but also in-situ diagnostics of anode and cathode evolution, and in parallel ex-situ analyses of aged samples, proposed accelerating protocols have been validated: meaning that they do accelerate the degradation of the performance (higher rates in µV/h) but enhancing the original mechanisms, what is looked for, and not provoking new mechanisms or uncontrolled failure what would invalidate the protocol.
- Combined AccST including higher CO content and also more dynamic and higher load cycles have been thus developed as final proposal for PEMFC operating under reformate.
- AccST protocols have been tested and analysed both in single cells and stacks
- It has been shown that the MEA initial components, such as anode catalyst loading has a non negligible impact on the behaviour of the MEA versus acceleration of degradation. The conclusion is thus that the accelerating protocol can be tuned in order to be more efficient depending on the initial characterization of the components.
- Thanks to tests in stacks, water content in the anode has been also identified asa possible accelerating feature.

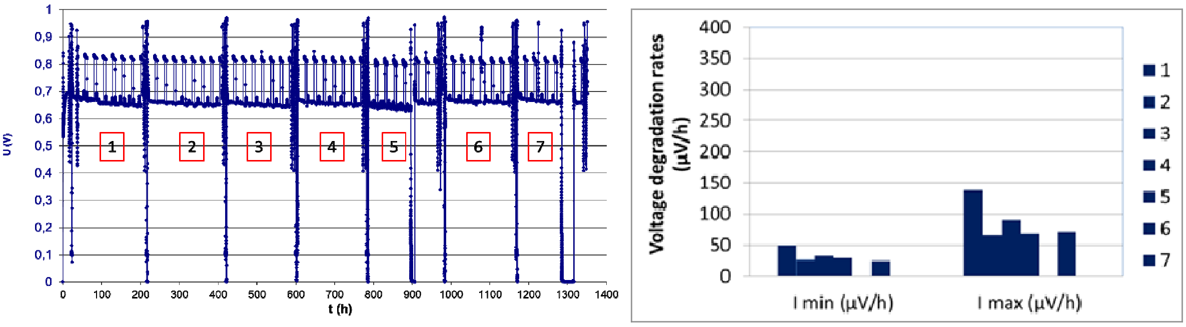


Figure 33: REFERENCE TEST (ONLY 10ppm CO) - Cell voltage along the time for a reference IRD MEA tested under reformate H_2 with CO content 10 ppm - Cell voltage degradation rates during each stage of load cycles (down).

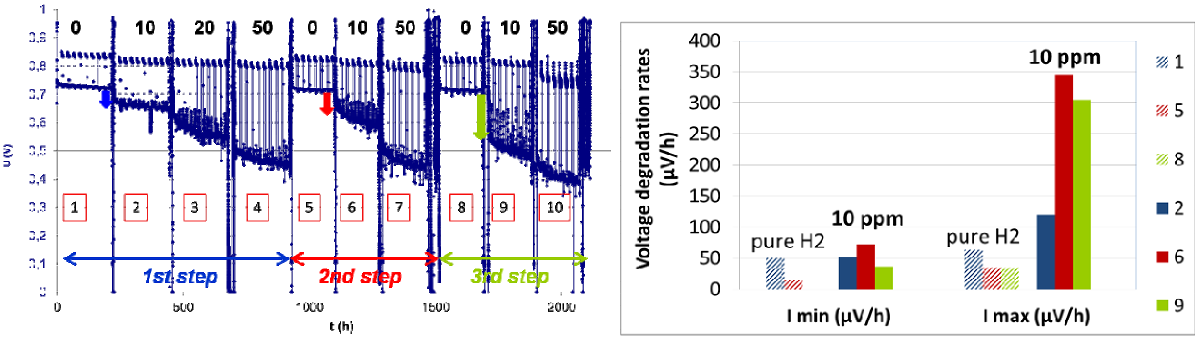


Figure 34: AccST TEST (0 – 10 – 50 ppm CO) - Cell voltage along the time for a reference IRD MEA tested under pure H2 and reformate H_2 with CO contents from 10 to 50 ppm (top) and voltage degradation rates during each stage of load cycles (down).

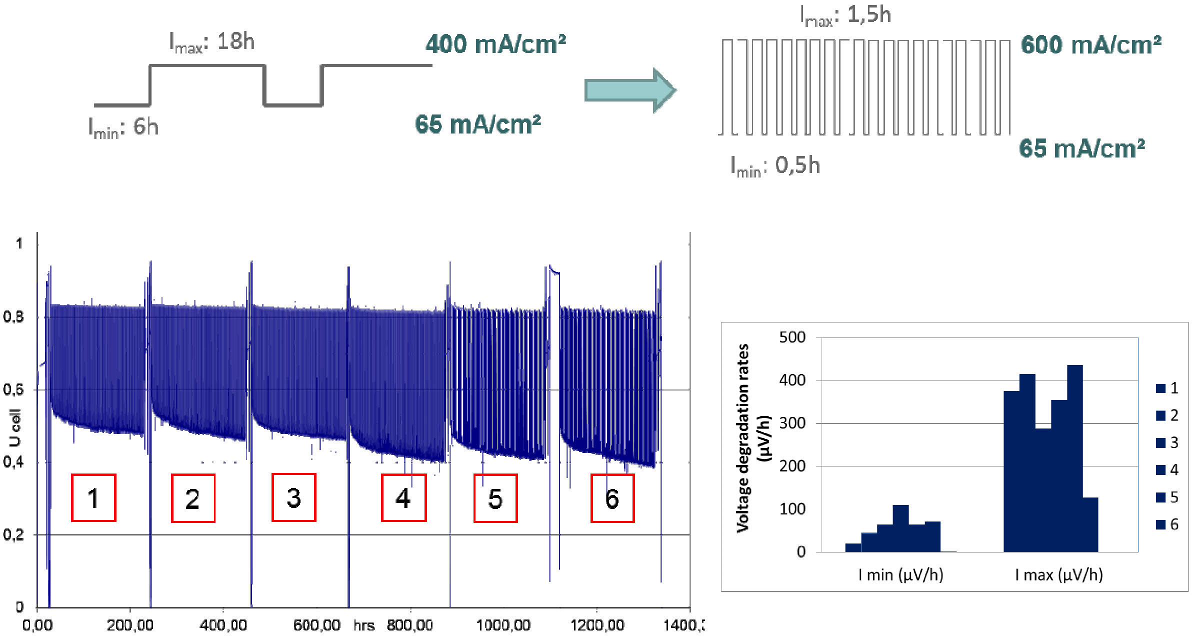


Figure 35: Cell voltage along the time for a reference IRD MEA tested under reformate H_2 with 10ppm CO (left) and voltage degradation rates during each stage of load cycles (right).

1.3.6.3 Conclusion about lifetime prediction methodology

A lifetime prediction methodology has been developed; it is composed of:

- a systematic experimental characterization of the MEA in different operating conditions
- testing of the MEA in reference condition for a short period, performing complete diagnostics at meaningful time periods
- AST is performed for a short period equivalent to a long term testing
- detailed models of degradation mechanisms are calibrated on both AST and reference condition testing results. Simple correlations are tuned to the simulations and integrated in MEA models
- MEA models are used to predict the decay of performance and MEA lifetime

The lifetime prediction methodology is validated positively on 2 DMFC MEAs

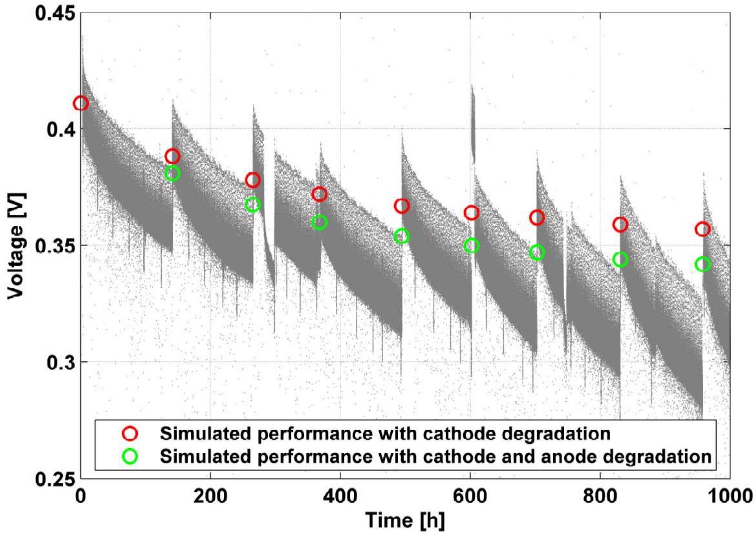


Figure 36 : Reference MEA

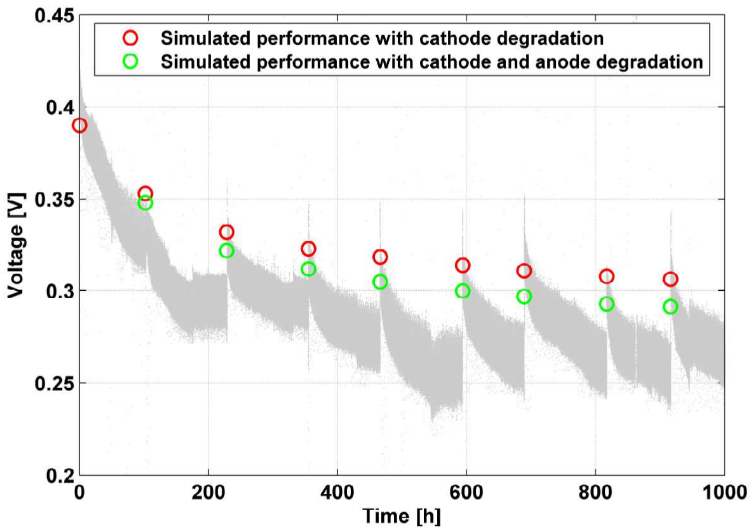


Figure 37 : Benchmark MEA

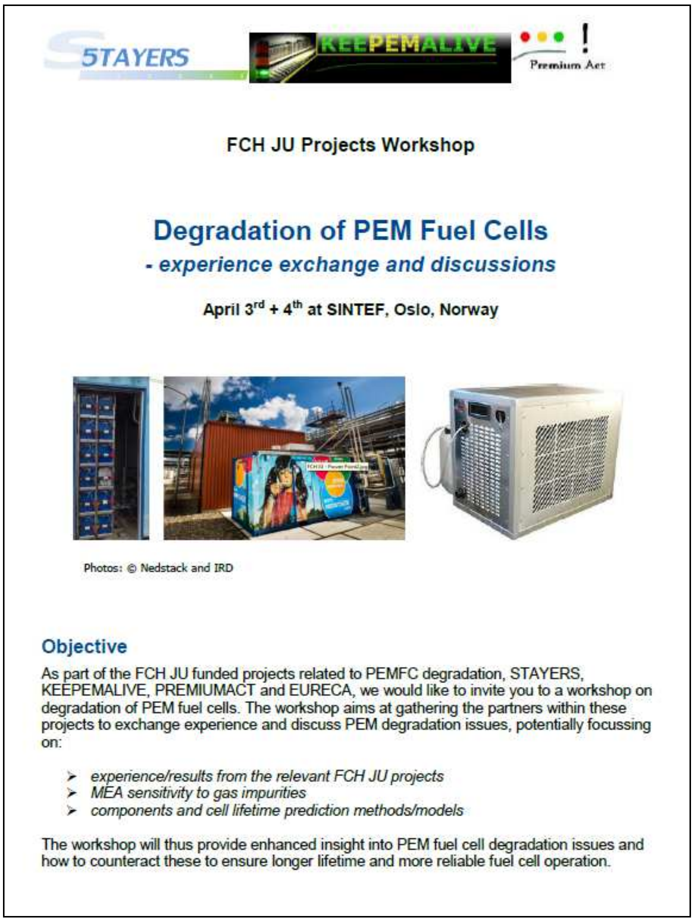
The same methodology could be applied to PEMFC, but to be effective it needs that the simulations take also into account the anode degradation.

1.4 Potential impact and main dissemination activities and exploitation results

Main dissemination actions have been:

- first classical, with the production of communications and publications in international conferences and scientific journals (see tables);
- to contribute to reporting and dissemination events organized or promoted by the FCH-JU;

- and as specific actions, to co-organize a common workshop with FCH-JU projects KEEPEMALIVE (lead. Sintef) and STAYERS (lead. Nedstack) dealing with stationnary application "Degradation of PEM Fuel Cells", held in Oslo in April 2013, where degradation studies conducted in the project have been presented on both PEMFC and DMFC;
- and particularly to organize a dedicated Premium Act workshop about "characterization and quantification degradation".


STAYERS KEEPEMALIVE Premium Act

FCH JU Projects Workshop

Degradation of PEM Fuel Cells

- experience exchange and discussions

April 3rd + 4th at SINTEF, Oslo, Norway

Photos: © Nedstack and IRD

Objective

As part of the FCH JU funded projects related to PEMFC degradation, STAYERS, KEEPEMALIVE, PREMIUMACT and EURECA, we would like to invite you to a workshop on degradation of PEM fuel cells. The workshop aims at gathering the partners within these projects to exchange experience and discuss PEM degradation issues, potentially focussing on:

- *experience/results from the relevant FCH JU projects*
- *MEA sensitivity to gas impurities*
- *components and cell lifetime prediction methods/models*

The workshop will thus provide enhanced insight into PEM fuel cell degradation issues and how to counteract these to ensure longer lifetime and more reliable fuel cell operation.

Figure 38: flyer of the common workshop about degradtion of Fuel Cells

The **international Workshop on *"characterization and quantification of MEA degradation processes"* was organised on September 26-27, 2012 in Grenoble at CEA – Minatec**. The purpose of this workshop was to show the contribution of different characterisation methods for better understanding and quantification of the degradation mechanisms of PEMFC components. Around 50 people attended the workshop, people coming either from industrial or academic institutions inside the Europe community. Five speakers, internationally recognized, have been invited to present their work:

- **Atsushi Ohma** from Nissan Research Center in Japan,
- **Karren More** from Oak Ridge National Laboratory in USA,
- **Hans Bettermann** from University of Düsseldorf in Germany,
- **Laetitia Dubau** from LEPMI-University of Grenoble in France
- **Arnaud Morin** from LITEN CEA-Grenoble in France.

Nineteen other presentations were given by the other participants of the workshop. They gave a good overview of the state of the art of research on this topic. Many presentations focused on the degradation mechanisms of both the active layers and the membrane whereas other presentations showed different techniques and strategies developed in order to localise, across the MEA surface area (in plane or through plane) or between the different MEA in a stack, the zone where the MEA degradation is the most severe. All these presentations gave rise to fruitful discussions and probably will emerge on new collaborations between the participants.

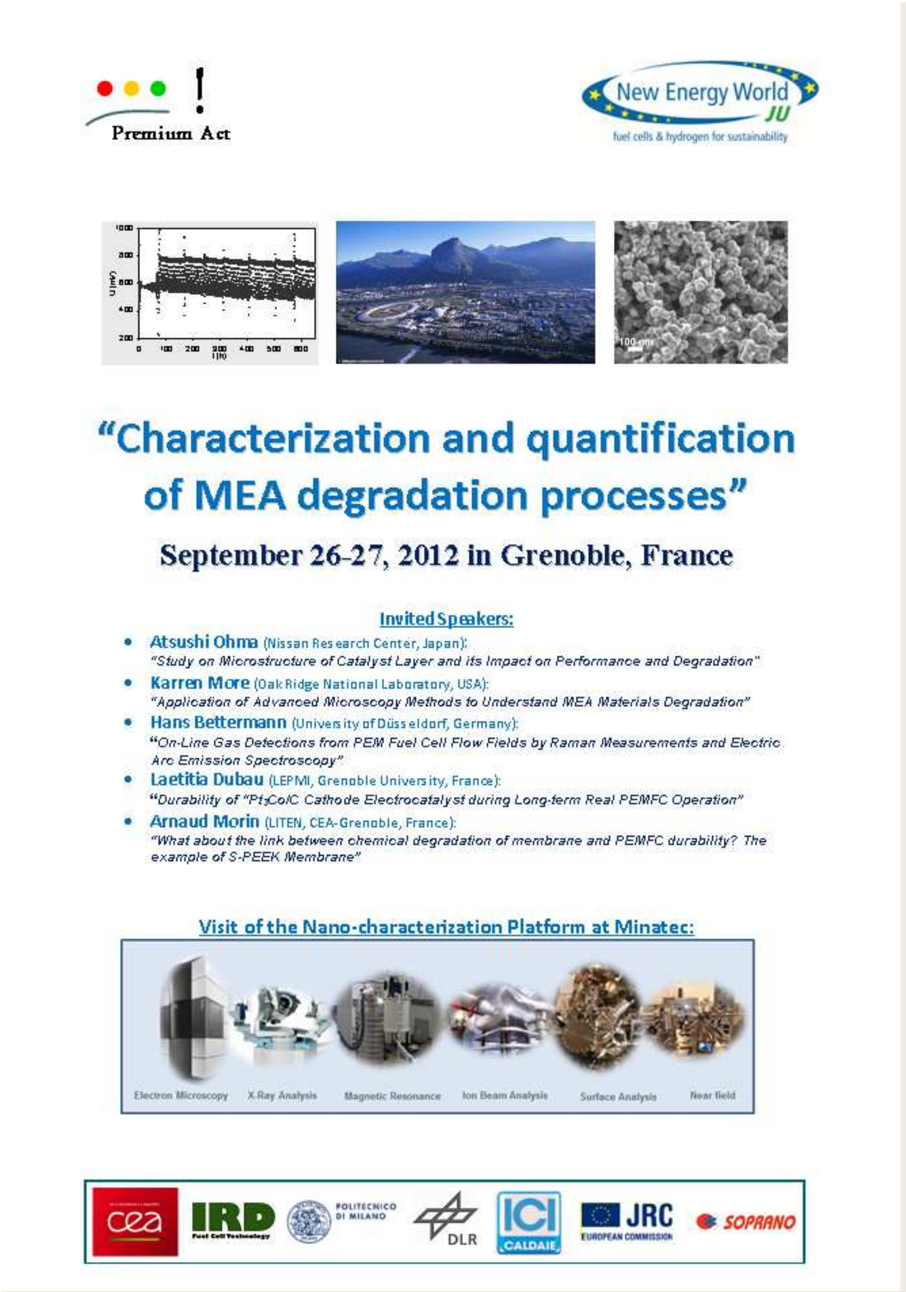


Figure 39: Premium Act Workshop announcement poster

1.5 Address of project public website and relevant contact details

http://www.mrtfuelcell.polimi.it/premiumact.html

2 4.2 USE AND DISSEMINATION OF FOREGROUND

Note of SE: Tables have been filled here but for some partners same or other information is in the tables directly up-loaded on SESAM portal

2.1 SECTION A (PUBLIC)

LIST OF SCIENTIFIC PUBLICATIONS (STARTING WITH THE MOST IMPORTANT ONES)

No.	Title / DOI	Main Author	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Date of publication	Relevant pages	Permanent identifiers (if applicable)	Is open access provided to this publication?	Type
1	Surface Analytical Methods for the Development of Electrochemical Components of Polymer Electrolyte Fuel Cells DOI: 10.1002/sia.5498	Pawel Gazdzicki	Surface and Interface Analysis	Not yet assigned	Wiley		2013	Not yet assigned		No	Peer-review journal
2	Surface Analytical Methods for the Development of Electrochemical Components of Polymer Electrolyte Fuel Cells DOI: 10.1149/05801.1429ecst	Indro Biswas	ECS Transactions	58	The Electrochemical Society		2013	1429 - 1444		No	Conference proceedings
3	A detailed multi-scale model for direct-methanol fuel cells I. Performance model	Thomas Jahnke					Under preparation				
4	A detailed multi-scale model for direct-methanol fuel cells II. Degradation model	Thomas Jahnke					Under preparation				
5	A Flexible Framework for Modeling Multiple Solid, Liquid and Gaseous Phases in Batteries and Fuel Cells doi: 10.1149/2.023209jes	J. P. Neidhardt	Journal of The Electrochemical Society	159	The Electrochemical Society		14/08/2012	A1528-A1542		No	Peer-review journal
1	A parametric analysis on DMFC anode degradation DOI: 10.1002/fuce.201300132	Fausto Bresciani	Fuel Cells	Not yet assigned	Wiley		2013			No	Peer-review journal
2	A physical model for DMFC anode impedance http://dx.doi.org/10.1016/j.jpowsour.2013.10.047	Matteo Zago	Journal of Power Sources	248	Elsevier		2014	1181-1190		No	Peer-review journal

3	Experimental Investigation on Methanol Crossover evolution during DMFC degradation tests http://dx.doi.org/10.1016/j.jpowsour.2013.10.032	Andrea Casalegno	Journal of Power Sources	249	Elsevier		2014	103-109		No	Peer-review journal
4	Water Transport and flooding in DMFC: Experimental and Modelling analyses http://dx.doi.org/10.1016/j.jpowsour.2012.06.022	Matteo Zago	Journal of Power Sources	217	Elsevier		2012	381-391		No	Peer-review Journal
5	A 1000 hours systematic experimental investigation on the degradation of a DMFC, part A: In Operando analyses	Fausto Bresciani	Journal of Power Sources				Under preparation			No	Peer-review Journal
6	A 1000 hours systematic experimental investigation on the degradation of a DMFC, part B: Post Mortem analyses		Journal of Power Sources				Under preparation			No	Peer-review Journal
7	A comparison of operating strategies to reduce DMFC degradation DOI: 10.1002/er.3115	Fausto Bresciani	International Journal of Energy Research	38	Wiley		2014	117-124		No	Peer-review Journal
8	Effect of anode MPL on water and methanol transport in DMFC: experimental and modeling analyses 10.1016/j.ijhydene.2014.03.147	Matteo Zago	International Journal of Hydrogen Energy	Not yet assigned	Elsevier		2014			No	Peer-review Journal
9	Water transport into PEFC gas diffusion layer: Experimental characterization of diffusion and permeation DOI: 10.1002/er.3065	Fausto Bresciani	International Journal of Energy Research	38	Wiley		2014	602-613		No	Peer-review Journal
10	Experimental Investigation on DMFC Temporary Degradation	Fausto Bresciani	Int.Journal of Hydrogen Energy				Under Review			No	Peer-review Journal
11	On the effect of Gas Diffusion Layers configuration on DMFC performance and degradation	Claudio Rabissi					Under preparation				
1	Structural and Chemical Analysis by Transmission Electron Microscopy of Pt-Ru Membrane Precipitates in Proton Exchange Membrane Fuel Cell Aged under Reformate	L. Guétaz,	Journal of Power Sources		Elsevier		To be submitted 2014			No	Peer-review Journal
2	Ageing analysis and CO tolerance of MEA fed with reformate H2 for PEMFC stationary application	P.-A. Jacques	Journal of Power Sources		Elsevier		To be submitted 2014			No	Peer-review Journal
3	Ageing studies of PEM Fuel Cells developed for reformate fuel operation in µCHP units	Sylvie Escribano	IJHE special issue (EHEC 2014)		Elsevier		to be submitted 2014			No	Peer-review Journal

LIST OF DISSEMINATION ACTIVITIES (like conferences /workshops)

No.	Type of activity	Main Leader	Title	Date	Place	Type of audience	Size of audience	Countries addressed
1	Oral presentation to a scientific event (ECASIA Conference)	DLR	Surface Analytics for the Investigation of Fuel Cell Components	October 17th, 2013	Forte Village Resort, Sardinia, Italy	Researchers	~ 30	World wide
2	Poster	DLR	Methodic Aspects of XPS Investigations of Fuel Cell Components	October 17th, 2013	Forte Village Resort, Sardinia, Italy	Researchers	~100	World wide
3	Oral presentation to a scientific event (ECS Meeting)	DLR	Surface Analytical Methods for the Development of Electrochemical Components of Polymer Electrolyte Fuel Cells	October 31st, 2013	San Francisco, USA	Researchers	~40	World wide
4	Poster	DLR	A flexible framework for modeling multiple solid, liquid and gaseous phases in batteries and fuel cells	03/04/2012	Sursee, Switzerland	Researchers	~100	Worldwide
5	Poster	DLR	A mechanistic approach for modeling degradation mechanisms in direct-methanol fuel cells (DMFC)	18/05/2012	Leipzig, Germany	Researchers	~100	Germany
6	Oral presentation to a scientific event (ModVal 10)	DLR	Elementary kinetic modeling for the investigation of direct-methanol fuel cell degradation	19/03/2013	Bad Boll, Germany	Researchers	~40	Worldwide
7	Oral presentation to a scientific event (FDFC 2013)	DLR	Modeling ruthenium dissolution and platinum dissolution in direct-methanol fuel cells	17/04/2013	Karlsruhe, Germany	Researchers	~40	Worldwide
8	Oral presentation at public work shop "Characterization and quantification of MEA degradation	DLR	X-ray Photoelectron Spectroscopic Investigations of Degradation Processes in low temperature Fuel Cells	26/09/12	Grenoble, France	Researchers		Europe

	processes”							
9	Oral presentation at public work shop “Characterization and quantification of MEA degradation processes”	DLR	Current Density Measurements for in situ Studies of Aging Processes of PEMFC	26/09/12	Grenoble, France	Researchers		Europe
10	Oral presentation at public work shop “Characterization and quantification of MEA degradation processes”	DLR	FTIR and Raman Spectroscopic Investigations of Degradation Processes in PEMFC	26/09/12	Grenoble, France	Researchers		Europe
11	Poster at public work shop “Characterization and quantification of MEA degradation processes”	DLR	Chemical imaging of proton exchange fuel cell components using vibrational spectroscopy	26/09/12	Grenoble, France	Researchers		Europe
12	Poster at public work shop “Characterization and quantification of MEA degradation processes”	DLR	FTIR spectroscopy imaging of aged fuel ell components	26/09/12	Grenoble, France	Researchers		Europe
13	Poster at public work shop “Characterization and quantification of MEA degradation processes”	DLR	Ex-situ investigation of aged GDLs	26/09/12	Grenoble, France	Researchers		Europe
14	Poster or Oral (65th annual meeting ISE)	DLR	Post Mortem Analysis of Long-Term Degraded DMFC	Planned in Sep 2014	Lausanne, Swiss	Researchers		International
1	Oral presentation at Fuel Cell Advances	POLIMI	Degradation of Direct Methanol Fuel Cells: analysis of	04/04/2014	Amsterdam, France	Researchers	~ 40	Worldwide

	Grove		temporary and permanent degradation phenomena					
2	Oral presentation at Fundamentals and Development of Fuel Cells	POLIMI	A parametric analysis on DMFC anode degradation	17/04/2013	Karlsruhe, Germany	Researchers	~ 30	Europe
3	Oral presentation at 5th European Fuel Cell Piero Lunghi Conference	POLIMI	Effects of anode MPL on DMFC mass transport phenomena and electrochemical impedance spectroscopy: experimental and modeling analyses	12/12/13	Roma, Italy	Researchers	~ 40	Worldwide
4	Oral presentation at 5th European Fuel Cell Piero Lunghi Conference	POLIMI	Experimental investigation of DMFC degradation in real operation representative conditions and during accelerated stress tests (AST)	12/12/13	Roma, Italy	Researchers	~ 40	Worldwide
5	Oral presentation at 4th European Fuel Cell Piero Lunghi Conference	POLIMI	Effects of flooding on DMFC performance: 1D+1D model development and experimental validation	15/12/11	Roma, Italy	Researchers	~ 40	Worldwide
6	Invited Lecture at 6th Forum on New Materials, CIMTEC	POLIMI	Degradation of Direct Methanol Fuel Cell: analysis of temporary and permanent phenomena and their effects on components	Planned for June 2014	Montecatini Terme, Italy	Researchers		
7	Oral presentation at public work shop "Characterization and quantification of MEA degradation processes"	POLIMI	Experimental Methodology to perform and analyse DMFC degradation tests	26/09/12	Grenoble, France	Researcher	~ 30	Europe
8	Poster at 10th Symposium for Fuel Cell and Battery Modelling and Experimental Validation	POLIMI	Preliminary physical model of DMFC anode impedance	20/03/2013	Badbol, Germany	Researcher	~ 30	

9	Poster at 11th Symposium for Fuel Cell and Battery Modelling and Experimental Validation	POLIMI	Effect of methanol concentration on DMFC anode impedance: experimental and modelling analysis	18/03/2014	Winterthur, Switzerland	Researcher	~ 30	
10	Poster at International workshop on degradation issues	POLIMI	A dynamic experimental method to perform DMFC degradation testing	22/09/2011	Thessaloniki, Greece	Researcher	~ 80	
11	Poster at 31st UIT Heat Transfer Conference	POLIMI	Water transport into PEFC Gas Diffusion Layer: experimental characterization of diffusion and permeation	26/06/2013	Como, Italy	Researcher	~ 50	
1	Workshop Oral presentation "Characterization and quantification of MEA degradation processes", September 26-27, 2012 in Grenoble, France	IRD	Degradation Studies of PEMFC	September 26-27, 2012	Grenoble, France	Researchers		International
2	Workshop Oral presentation "Characterization and quantification of MEA degradation processes", September 26-27, 2012 in Grenoble, France	IRD	Degradation Studies of DMFC	September 26-27, 2012	Grenoble, France	Researchers		International
1	Project presentation at European FCH Workshop -	CEA	PREdictive Modelling for Innovative Unit Management and ACcelerated Testing	26-27/03/2012	Grenoble, France	Researcher	~ 40	Europe

	"Materials issues for fuel cell and hydrogen technologies"		procedures of PEFC					
2	Oral presentation at ModVal 10 (10th Symposium on Fuel Cell and Battery Modelling and Experimental Validation)	CEA	PEMFC predictive modelling function of the operating mode and local conditions	19-20/03/2013	Stuttgart, Germany	Researcher		Worldwide
3	Oral presentation at FCH-JU Projects workshop - PEMFC Degradation	CEA	PEMFC Degradation under load cycles with reformate fuel	3/04/ 2013	Sintef/OSLO	Researcher	~ 30	Europe
4	Oral at FDFC 2013	CEA	Ageing of PEMFC MEAs operating under reformate fuel: performance and components degradation during load cycles	16-18/04/2013	Karlsruhe, Germany	Researchers	~ 30	Worldwide
5	Poster at FDFC 2013	CEA	PEMFC Multi-scale Modeling: Interactions between Two Dynamic Models for Fuel Cell Ageing	16-18/04/2013	Karlsruhe, Germany	Researchers	~ 30	Worldwide
6	Oral presentation at EFCF 2013	CEA - IRD	Degradation and CO tolerance studies of PEMFC aimed for reformate fuel operation in µCHP units	05/07/2013	Lucerne, Swizerland	Researchers	~ 30	Worldwide
7	Project presentation on Poster at EFC13	CEA+Consortium	Premium Act activity	15/12/11	Roma, Italy	Researchers	~ 40	Worldwide
8	Oral at EHEC 2014	CEA	Ageing studies of PEM Fuel Cells developed for reformate fuel operation in µCHP units	12-14/03/2014	Seville, Spain	Researchers	~ 50	Worldwide

2.2 Section B (Confidential or public: confidential information marked clearly)

LIST OF APPLICATIONS FOR PATENTS, TRADEMARKS, REGISTERED DESIGNS, UTILITY MODELS, ETC.

Type of IP Rights	Confidential	Foreseen embargo date dd/mm/yyyy	Application reference(s) (e.g. EP123456)	Subject or title of application	Applicant(s) (as on the application)

OVERVIEW TABLE WITH EXPLOITABLE FOREGROUND

Type of Exploitable Foreground	Description of Exploitable Foreground	Confidential	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application	Timetable for commercial use or any other use	Patents or other IPR exploitation (licences)	Owner and Other Beneficiary(s) involved
General advancement of Knowledge	Improved understanding on how to operate the DFMC system and information on how to not operate the system, in particular based on the degradation mechanisms found and investigated in the Premium Act project. In addition IRD PEM MEA's and stacks have extensively evaluated in the project leading to significantly improved understanding of the aging under different operation strategies.			The improved understanding of degradation mechanisms in the DMFC systems has resulted in further development of operation mode based mitigation strategies and will result in changes in system components like filters, stack and MEA. The detailed analysis of the PEM MEA and stack can be exploited in terms of improved recommended operation strategies.	FC system FC techno	The DMFC system lifetime and reliability can be improved significantly with the exploitation of the results, this will require further investments to test and implement the results. When the results are implemented the DMFC systems from IRD will be become more competitive on the commercial level. With respect to the results on the PEM MEA's and stacks the result will also in time make the IRD PEM MEA's and systems more competitive.	No	IRD

ADDITIONAL TEMPLATE B2: OVERVIEW TABLE WITH EXPLOITABLE FOREGROUND

	Description of Exploitable Foreground	Explain of the Exploitable Foreground
ICI	Description of Exploitable Foreground Descrizione della conoscenze sfruttabili	Explain of the Exploitable Foreground
	System modification – new component development	Development and introduction into the system of air bleed. This component is suitable for syngas and system stabilization. It was possible to obtain higher efficiency and stabilisation of the system with consequent reduction of pay back time and service requirement.
	Utilisation and operation strategy	Software upgrade to increase the system stability and consequent increase of lifetime. Higher system efficiency and reduction of pay back time.
	Improvement in syngas production	System layout modification aimed to increase the syngas quality (low CO content) and syngas stability with consequent increase in system efficiency and system lifetime. Decrease in service requirement.

Table 1: Premium Act summary table of exploitation of results planned by industry partners (AS PROPOSED IN THE SECOND PERIOD REPORT)

Items concerned FC techno FC system Specific Application	**Results concerned** (info about ageing, op. strategy, ?)	**Type of exploitation planned** (System modifications, at components level, operating conditions, ?)	**Impact expected for the Cie** (new investments, personnel or commercial level, ?)	**Partners involved**
FC system FC techno	Improved understanding on how to operate the DFMC system and information on how to not operate the system, in particular based on the degradation mechanisms found and investigated in the Premium	The improved understanding of degradation mechanisms in the DMFC systems has resulted in further development of operation mode based mitigation strategies and will result in	The DMFC system lifetime and reliability can be improved significantly with the exploitation of the results, this will require further investments to test and implement the results. When the results are	IRD

	Act project. In addition IRD PEM MEA's and stacks have extensively evaluated in the project leading to significantly improved understanding of the aging under different operation strategies.	changes in system components like filters, stack and MEA. The detailed analysis of the PEM MEA and stack can be exploited in terms of improved recommended operation strategies.	implemented the DMFC systems from IRD will be become more competitive on the commercial level. With respect to the results on the PEM MEA's and stacks the result will also in time make the IRD PEM MEA's and systems more competitive.	
FC system	Operating strategy	System modification: Air bleed	Commercial: Increase of system efficiency	ICI
FC system	Operating strategy	Operating conditions	Commercial: increase of FC lifetime	ICI
Fuel Cell system	Increase lifetime of the stack. Make the fuel cell operation even safer	**Cell voltage monitoring.** In addition to existing systems or in a new design, measure accurately the voltage of each cell of the stack	Suitable for battery elements in a BMS (Battery Management System) or for fuel cell systems	SOPRANO
Fuel Cell system	Implement easily innovative operating strategies (Data acquisition, regulation)	**Real time process controller.** Based on a DSP (Digital Signal Processor) and analog and digital inputs/outputs, managing of the balance of plant of the fuel cell system	Suitable for any high reliability industrial application in harsh environment	SOPRANO
Fuel cell system	Save energy in power conditioning	**Isolated DC/DC converter** On the future CHP, modular 3kW high efficiency DC/DC	Topology suitable for any isolated DC/DC isolated converter with high	SOPRANO

		converter	OUTPUT/INPUT ratio	
Fuel cell system	Enhance adaptability and performance of the converter	**Digital control and regulation of DC/DC converter** Management of the CHP DC/DC converter	-Suitable for any converter topology -Control of various DC/DC converters developed at SOPRANO	SOPRANO
Fuel cell system	Premium Act project results about innovative operating strategies	**Development of a 5kW CHP**	Commercial CHP for residential houses and small offices	SOPRANO
Fuel cell system	Operative strategy to prevent performance losses due to poisoning with CO	**Innovative strategy : air bleeding** Implementation of an an additional piping line in the Balance of Plant design	Higher durability/reliability of the system during lifetime	SOPRANO
Fuel cell system	Recovery of reversible degradation of the performance	**Innovative strategy : on/off cycles** Implementation of on/off cycles in the control of the system	Higher durability/reliability of the system during lifetime	SOPRANO

3 4.3 Report on Societal Implications

3.1 B. Ethics

1. Did your project undergo an Ethics Review (and/or Screening)?	No
If Yes: have you described the progress of compliance with the relevant Ethics Review/Screening Requirements in the frame of the periodic/final reports?	
2. Please indicate whether your project involved any of the following issues :	
RESEARCH ON HUMANS	
Did the project involve children?	No
Did the project involve patients?	No
Did the project involve persons not able to consent?	No
Did the project involve adult healthy volunteers?	No
Did the project involve Human genetic material?	No
Did the project involve Human biological samples?	No
Did the project involve Human data collection?	No
RESEARCH ON HUMAN EMBRYO/FOETUS	
Did the project involve Human Embryos?	No
Did the project involve Human Foetal Tissue / Cells?	No
Did the project involve Human Embryonic Stem Cells (hESCs)?	No
Did the project on human Embryonic Stem Cells involve cells in culture?	No
Did the project on human Embryonic Stem Cells involve the derivation of cells from Embryos?	No
PRIVACY	
Did the project involve processing of genetic information or personal data (eg. health, sexual lifestyle, ethnicity, political opinion, religious or philosophical conviction)?	No
Did the project involve tracking the location or observation of people?	No
RESEARCH ON ANIMALS	

Did the project involve research on animals?	No
Were those animals transgenic small laboratory animals?	No
Were those animals transgenic farm animals?	No
Were those animals cloned farm animals?	No
Were those animals non-human primates?	No
RESEARCH INVOLVING DEVELOPING COUNTRIES	
Did the project involve the use of local resources (genetic, animal, plant etc)?	
Was the project of benefit to local community (capacity building, access to healthcare, education etc)?	
DUAL USE	
Research having direct military use	
Research having potential for terrorist abuse	

3.2 C. Workforce Statistics

3. Workforce statistics for the project: Please indicate in the table below the number of people who worked on the project (on a headcount basis).

Type of Position	Number of Women	Number of Men
Scientific Coordinator	1	0
Work package leaders	3	5
Experienced researchers (i.e. PhD holders)	4	8
PhD student	3	0
Other	0	0

4. How many additional researchers (in companies and universities) were recruited specifically for this project?	0
Of which, indicate the number of men:	0

3.3 D. Gender Aspects

5. Did you carry out specific Gender Equality Actions under the project ?	No

6. Which of the following actions did you carry out and how effective were they?	
Design and implement an equal opportunity policy	Not Applicable
Set targets to achieve a gender balance in the workforce	Not Applicable
Organise conferences and workshops on gender	Not Applicable
Actions to improve work-life balance	Not Applicable
Other:	

7. Was there a gender dimension associated with the research content - i.e. wherever people were the focus of the research as, for example, consumers, users, patients or in trials, was the issue of gender considered and addressed?	No
If yes, please specify:	

3.4 E. Synergies with Science Education

8. Did your project involve working with students and/or school pupils (e.g. open days, participation in science festivals and events, prizes/competitions or joint projects)?	Yes
If yes, please specify:	

9. Did the project generate any science education material (e.g. kits, websites, explanatory booklets, DVDs)?	No

3.5 F. Interdisciplinarity

10. Which disciplines (see list below) are involved in your project?	
Main discipline:	1.3 Chemical sciences (chemistry, other allied subjects)
Associated discipline:	1.2 Physical sciences (astronomy and space sciences, physics and other allied subjects)
Associated discipline:	2.2 Electrical engineering, electronics [electrical engineering, electronics, communication engineering and systems, computer engineering (hardware only) and other allied subjects]

3.6 G. Engaging with Civil Society and Policy Makers

11a. Did your project engage with societal actors beyond the research community? (if 'No', go to Question 14)	No
11b. If yes, did you engage with citizens (citizens' panels / juries) or organised civil society (NGOs, patients' groups etc.)?	
11c. In doing so, did your project involve actors whose role is mainly to organise the dialogue with citizens and organised civil society (e.g. professional mediator; communication company, science museums)?	
12. Did you engage with government / public bodies or policy makers (including international organisations)	
13a. Will the project generate outputs (expertise or scientific advice) which could be used by policy makers?	

3.7 H. USE AND DISSEMINATION

14. How many Articles were published/accepted for publication in peer-reviewed journals?	0
To how many of these is open access provided?	0
How many of these are published in open access journals?	0
How many of these are published in open repositories?	0
To how many of these is open access not provided?	0
Please check all applicable reasons for not providing open access:	
publisher's licensing agreement would not permit publishing in a repository	Yes
no suitable repository available	Yes
no suitable open access journal available	No
no funds available to publish in an open access journal	No
lack of time and resources	No
lack of information on open access	Yes
If other - please specify	better knowledge of other journals
15. How many new patent applications ('priority filings') have been made? ("Technologically unique": multiple applications for the same invention in different jurisdictions should be counted as just one application of grant).	0

16. Indicate how many of the following Intellectual Property Rights were applied for (give number in each box).	
Trademark	0
Registered design	0
Other	0

17. How many spin-off companies were created / are planned as a direct result of the project?	0
Indicate the approximate number of additional jobs in these companies:	0
18. Please indicate whether your project has a potential impact on employment, in comparison with the situation before your project:	Increase in employment,
19. For your project partnership please estimate the employment effect resulting directly from your participation in Full Time Equivalent (FTE = one person working fulltime for a year) jobs:	0Difficult to estimate / not possible to quantify

3.8 I. Media and Communication to the General Public

20. As part of the project, were any of the beneficiaries professionals in communication or media relations?	No
21. As part of the project, have any beneficiaries received professional media / communication training / advice to improve communication with the general public?	No

22. Which of the following have been used to communicate information about your project to the general public, or have resulted from your project?	
Press Release	No
Media briefing	No
TV coverage / report	No
Radio coverage / report	No
Brochures /posters / flyers	Yes
DVD /Film /Multimedia	No
Coverage in specialist press	Yes
Coverage in general (non-specialist) press	No
Coverage in national press	No
Coverage in international press	No
Website for the general public / internet	Yes

Event targeting general public (festival, conference, exhibition, science café)	No
23. In which languages are the information products for the general public produced?	
Language of the coordinator	No
Other language(s)	No
English	Yes