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D6.4 Final Report

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Content

1. EXECUTIVE SUMMARY

Second Act aims at improving understanding of stack degradation in order to propose solutions enabling significant lifetime improvements for µCHP systems using PEMFC (Proton Exchange Membrane Fuel Cell), operating under Hydrogen or Reformate, or DMFC (Direct Methanol) technology. The project is founded and focused on two efforts: degradation understanding and durability improvement. These efforts are oriented towards existing systems available in the project thanks to the involvement of three industry partners willing to enhance lifetime and hence competiveness for market deployment.

Application of advanced testing techniques and procedures allowed to identify specific diagnostics and to clarify with segmented cells the heterogeneities along the cells surface during ageing. Hydrogen, reformate and methanol fuelled single cell have been tested under reference (at fixed load) and load cycling conditions. PEMFC Stacks have been tested under pure hydrogen or reformate fuel, containing carbon monoxide. Effects of load or voltage profiles, of impurities and electrodes materials, mainly catalysts, have been characterized.

The presence of common degradation mechanisms feeding different fuels have been confirmed, especially in regard to cathode electrode and membrane; reversible degradation has been confirmed in all the tested conditions, whose origin is mainly attributed to water redistribution in the porous components and PtOx mechanism. Both temporary and permanent degradations and heterogeneities are considerably affected by materials. Accelerated stress tests (AST) were analysed, developed and validated for cathode degradation by platinum particles growth with particular focus on water effect, for membrane degradation by adapting the common open circuit voltage protocol, and for start-up/shut-down protocol in a PEMFC stack.

Ex-situ analyses were conducted to enhance understanding of degradation mechanisms using: fluoride ion detection, Infrared Thermography, XPS, XRD and TEM/EDX analyses and also electrochemical measurements. For DMFC, some ionomer is lost anode side but major degradation is the cathode Pt nanoparticles growth. For PEMFC, Pt, Co and Ru catalysts dissolution are main issues, along with ionomer contamination by cobalt ions, and local carbon corrosion when applying start-stops.

Much effort was put on developing and validating numerical tools for the simulation and analysis of degradation mechanisms from the MEA to the stack level, in close link with experimental investigations. Reversible mechanisms have been modelled, mainly platinum oxide formation and reduction and carbon monoxide poisoning, as well as irreversible catalyst particles dissolution. Models describing degradation mechanisms were implemented in cell models, allowing to investigate the heterogeneities and to evaluate the effect of these mechanisms on cell performance and on local operation for DMFC and PEMFC.

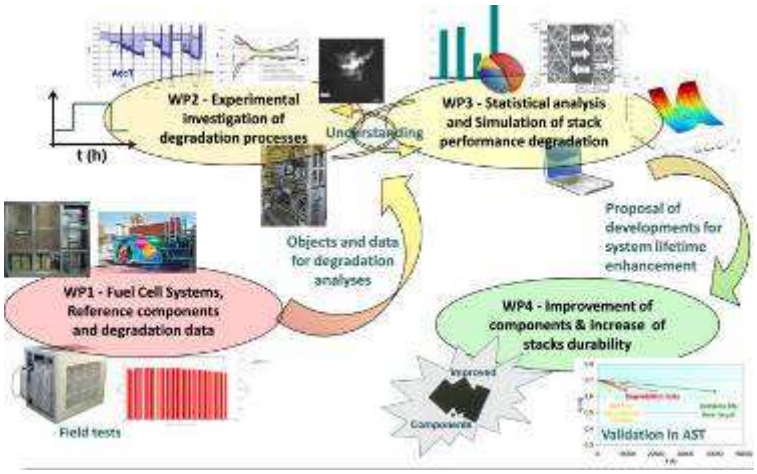
Experimental and modelling investigations of the reference MEAs highlighted several durability issues to be subject for further optimization in Second Act. The first set of MEAs have traditionally uniform electrodes, but novel catalysts and/or gas diffusion layers (GDLs). To face heterogeneities, third generation MEAs were made with graded electrodes or locally optimized cathodes and anodes, composed of a few zones with different compositions.

Thus, the main conclusion of this project is the demonstration that locally optimized electrodes and tuned operating condition and strategies, as defined based on advanced investigations of degradation coupling in-situ and ex-situ experimental analyses and modelling can actually lead to durability improvements at stack level applicable in the systems.

2. CONTEXT – OBJECTIVES

Second Act (Simulation, statistics and Experiments Coupled to develop Optimized aNd Durable µCHP systems using ACcelerated Tests) was proposed to address the topic: *"Improving understanding of cell & stack degradation mechanisms using advanced testing techniques, and developments to achieve cost reduction and lifetime enhancements for Stationary Fuel Cell power and CHP systems".*

Second Act aims at improving understanding of stack degradation in order to propose solutions enabling significant lifetime improvements for µCHP systems using PEMFC (Proton Exchange Membrane Fuel Cell), operating under Hydrogen or Reformate, or DMFC (Direct Methanol) technology. The project is founded and focused on two efforts: **degradation understanding and durability improvement**. These efforts are oriented towards existing systems available in the project thanks to the involvement of three industry partners willing to enhance lifetime and hence competiveness for market deployment.



The main double objective of Second Act is to **improve understanding of stack degradation and propose durability improvements for µCHP systems using PEMFC or DMFC.** The project aims at:

- Analysing **long term lifetime tests data from existing systems** to identify main causes for failure related to system operation and quantify performance degradation of the stacks, over the long term (at least 10,000 hrs and more than 20,000 hrs for some systems considered)
- Conducting **lifetime tests to investigate degradation** at cell and stack levels and to better understand mechanisms involved. Common degradation mechanisms in stack components (electrodes mainly) will be particularly considered to help identifying similar type of improvements on materials and processes to be implemented for lifetime extension.
- Developing, applying and **validating accelerated stress tests (AST) and specific tests representative of failures in harsh conditions** for the different Fuel Cell technologies
- Developing and applying ***in-situ* and *ex-situ* investigation techniques for better identification and local resolution of the degradation mechanisms**. Heterogeneities in degradation over the cells surface and across the stacks will be particularly tackled, with regards to local operation and local conditions (including fuel composition)

- Developing **new statistical approach and models for better understanding and description** of systems **stochastic/deterministic** degradation, **reversible/permanent** degradation and **heterogeneities** of degradation in single cells and stacks.
- **Demonstrating stack lifetime improvements** increased **tolerance to applications' relevant cycling or operating modes** (e.g. start/stop or idle), mainly through stack components modifications (in materials, components design, manufacturing processes…) for **Pure H2, Reformate PEMFC and DMFC**. For the improvements of membrane electrodes assemblies (**MEAs**) that will be particularly considered as core components, two routes will be followed, one on **raw materials and manufacturing processes** to face mainly defects and one on **structured (non-homogeneous) electrodes and gas diffusion layers (GDLs)** to face mainly degradation heterogeneities.

The overall strategy is based on degradation understanding based on lifetime tests information followed by durability improvement thanks to the exploitation of all degradation investigations. The approach is an iterative process with proposal of improvements at two periods: near mid-term and again before the end for final demonstration.

First period was thus focused on ageing investigations and degradation understanding. This understanding work has been continued until the end of the project. In parallel, the efforts during the second period have been dedicated to the proposal, selection and implementation of modified components in cells and stacks for their characterisation towards degradation, in addition to the proposal and application of operating strategies leading to final demonstration of durability improvements for different ageing conditions.

3. S & T RESULTS - FOREGROUNDS

3.1. Summary of main actions and results achieved in the first period

The activities of the first period have been conducted in three technical work packages dedicated to "specification of reference components and degradation data" (WP1), "Investigation of degradation processes" (WP2), and "Statistical analysis and simulation of stack performance degradation" (WP3).

Summary of actions and results are listed below.

WP1

- **Definition and description of systems, stacks, cells and reference components… And**
- **Preparation and delivery of reference components, cells, stacks**

The considered systems and reference samples for the three technologies (hydrogen and reformate PEM and DMFC) have been defined. An inventory has been made to define the required samples for the project partners and the components have been provided in due time for ageing tests in cells or stacks. More than 400 MEAs have been assembled in small (25 cm^2) or stack size (200 cm^2) single cells for tests at 6 partners lab, in short low power (8 cells) or higher power stacks (up to 75 cells) for tests by 3 partners on test stations or directly on real systems (incl. a 70kW power plant reaching total of 50000 hrs of operation).

In the second period of the project more samples will be supplied and tested.

- **Available degradation and durability data at systems, stacks, cells**

Three different technologies are evaluated: hydrogen and reformate PEMFC and DMFC. Previous experiences have been summarized and data have been provided as input for further understanding and statistical analysis. For pure hydrogen PEM, field tests have been performed by Nedstack for stationary industrial applications and by IRD for µCHP. Reformate PEM has been studied by CEA via AST and by ICI in real life systems. DMFC has been studied by Polimi and by IRD in long-term lab tests and via AST.

For the three technologies, the overall decay includes permanent and reversible contributions. Irreversible cathode electrochemical active surface area loss is a common cause of degradation. Then additional specific causes have been identified for each technology (contaminants, CO, catalysts modifications, systems' operation mode).

WP2

- **Planning of the whole experimental activities to ensure data statistical significance**
- **Application of advanced testing techniques and procedures**

Improved tools from new segmented cells to reformate CHP prototype and new specific diagnostics.

- **Characterization by state of art technologies**

H2, Reformate and Methanol fuelled single cell or stacks have been tested under reference, cycling or accelerated conditions. Effects of overall conditions and of particular cases such as impurities in Air or Fuel, have been characterized. Impact of operation modes such as load cycles, start-up/shut-down, flow orientation have been investigated.

Both temporary and permanent degradation are thus considerably affected by materials applied in anode catalyst layers. A main mechanism occurring cathode side in DMFC has been proposed to interpret reversible

degradation: its contribution in the reversible degradation for hydrogen PEM will be further investigated through specific experiments within Second Act.

- **Quantification of local degradation and heterogeneities effects**

Current density distribution in PEMFC and DMFC single cells and hydrogen and reformate fuelled PEMFC stacks. Heterogeneities are strongly affected by initial local conditions. Current redistribution over time is observed; it appears caused by local temporary degradation phenomena related to catalysts surface.

- **Analysis of induced failure**

Improper shut down effect on DMFC degradation has been investigated: no significant effect observed, thanks to the fast cathode potential decrease promoted by methanol presence.

Membrane pinhole effect has been characterized: it resulted to be strongly affected by pinhole position

- **Development and validation of AST for specific failure modes**

AST representative of DMFC operation has been improved, thanks to local investigation with RHE. Specific work on membrane degradation has been carried out, evidencing a beneficial role of catalysts layer presence. New AST's to analyse water effect on local ECSA loss have been proposed and preliminary adopted.

- **Ex-situ analysis of degradation mechanisms in pristine and aged samples**

Fluoride ion detection, Infrared Thermography, XPS have been carried out on aged samples to enhance degradation mechanisms understanding.

Electrochemical and Transmission Electron Microscopy analyses have been conducted on small samples extracted from MEAs aged in stacks to try and relate modifications of local properties and microstructure to local in-situ measurements obtained by segmented cells.

<u>WP3</u>

Numerical tools for the simulation of degradation mechanisms at the MEA and cell levels have been developed. First simulations have been performed and model validation is on-going. For PEMFC and DMFC reversible mechanisms are addressed. Especially in the case of DMFC, specific experiments have been proposed for the model validation and calibration. Simulations analysis and sensitivity studies will allow to propose specific experiments for the calibration and validation of the mechanisms involved in PEMFC.

Main expected outcome was to identify major performance degradation related to heterogeneous operation in a cell. The simulation performed at the MEA level for reversible degradation show a strong heterogeneous degradation through the thickness of the catalyst layer, mainly due to overvoltage variation. The first cell level simulations show heterogeneities between the inlet and the outlet of the cell. As degradation mechanism strongly depend on local condition, the degradation rate will obviously be heterogeneous over the surface of the cell.

Outcomes from WP1, WP2 and WP3 result suitable to prepare the list describing main causes for failure or performance losses to be used as a basis of first set of improvements for next period.

3.2. Summary of main actions and results achieved in the second period

During the second period, investigation activities have been conducted in the technical work packages already started from the beginning of the project "specification of reference components and degradation data" (WP1), "Investigation of degradation processes" (WP2), "Statistical analysis and simulation of stack performance degradation" (WP3) and new actions have been started and completed in the work package "durability improvements" (WP4).

Main achievements are listed below.

WP1

The activities conducted in WP1 "specification of reference components and degradation data" have been to continue delivering reference components (MEAs for cells and stacks).

WP2

- **Application of advanced testing techniques and procedures**

Novel macro-segmented cells and cell equipped with hydrogen reference electrodes have been developed and validated also at large scale for DMFC (180 cm^2), then used for durability improvements.

Current density distribution mapping in cells and stacks have been further exploited with specific ageing protocols and diagnostic tools for the proposal of locally improved components.

Diagnostic procedure to study platinum oxides formation/reduction onto the catalyst surface (PtOx mechanism identified as main cause for reversible degradation) has been further validated and used for models development.

- **Characterization by state of art technologies**

Hydrogen, reformate and methanol fuelled single cell have been tested under reference (at fixed load) and load cycling conditions. Few-cells stacks as well as higher power in PEMFC systems have also been tested under pure hydrogen or reformate fuel, containing carbon monoxide. Effects of load or voltage profiles, of impurities and electrodes materials, mainly catalysts, have been characterized.

The presence of common degradation mechanisms feeding different fuels have been confirmed, especially in regard to cathode electrode and membrane; reversible degradation has been confirmed in all the tested conditions, whose origin is mainly attributed to water redistribution in the porous components and PtOx mechanism. Both temporary and permanent degradations are considerably affected by materials applied in cathode catalyst layers.

- **Quantification of local degradation and heterogeneities effects**

Segmented cells have been used in PEMFC and DMFC single cell, as well as in hydrogen and reformate fuelled PEMFC stacks. Local conditions resulted to be strongly affected by air and fuel flows inlet conditions.

Current redistribution appears caused by local reversible phenomena (transient water content, PtOx mechanim and catalyst poisoning) and by non-reversible degradation of components (such as carbon corrosion, catalyst dissolution), depending on the ageing conditions applied.

Heterogeneity in cathode catalyst electrochemical active surface area (ECSA) loss appears to be related to severe gradient of water content and flux, catalyst poisoning, PtOx formation, that affect at local level catalyst

degradation mechanisms.
For some cases, like under reformate operation or during accelerated start-up/shut-down test, it appeared that the local degradation of the cathodes are also impacted by the composition of the anode catalyst layer. It was indeed shown that the anode operation interplays significantly in determining local cathode conditions, especially current and overpotential, and thus its degradation.

- **Development and validation of accelerated stress tests (AST) for specific failure modes**

A specific AST developed to analyse water effect on local ECSA loss have been further used and validated: water content at cathode side is confirmed to be detrimental for Pt growth mechanism; improved catalyst layers resulted insensitive to increased water content; high water content, especially liquid, is suspected to hinders GDL hydrophobicity, resulting in a worse oxygen transport at high current density.

The characterization of different MEAs (non-aged and degraded) behaviour with the common open circuit voltage (OCV) AST test has allowed to propose new insights on the impact of the electrochemical diagnostics on the membrane degradation and to define another option for the application of this protocol.

An accelerated start-up/down protocol has been applied on a PEMFC stack to demonstrate the impact of fuel starvation and reverse current mechanisms at local level and the correlation between the degradation mechanisms occurring on the cathode catalyst and the local conditions related to the design.

- **Ex-situ analysis of degradation mechanisms comparing pristine and aged samples**

Fluoride ion detection, Infrared Thermography, XPS, XRD and TEM/EDX analyses have been carried out on aged samples to enhance degradation mechanisms understanding.

Electrochemical analyses have also been conducted on small samples extracted from MEAs aged in stacks to try and correlate modifications of local properties and microstructure to local in-situ measurements obtained by segmented cells and conditions.

For aged DMFC, the ex-situ analyses have shown an increase of amount of carbon oxide in the anode likely associated with carbon corrosion and the ionomer degradation revealed by increase of carbon/ionomer ratio associated with reduction of fluorine concentration. However, the major degradation is the cathode Pt nanoparticles growth.

For aged PEMFC, an increased carbon/ionomer ratio indicating a loss of surface ionomer at the anode and cathode is observed. No anode PtRu nanoparticle degradation can clearly be revealed even if the Ru dissolution is highlighted by the Pt-Ru precipitates observed within the membrane after ageing. At the cathode side, after ageing, a thicker Pt shell surrounding the Pt_3Co nanoparticles is observed. This Pt shell increase in size is explained by the electrochemical Ostwald ripening mechanism that leads to the dissolution of the smaller Pt_3Co nanoparticles following by the Pt redeposition on the larger nanoparticles. In this mechanism the Co ions that cannot be not redeposited within the MEA lead to the ionomer contamination. Thus, the Pt_3Co cathode catalyst degradation also leads to the alteration of cathode ionomer proton conductivity.

<u>WP3</u>

Some long term ageing data on stacks have been analysed by statistical approach to try and identify causes for degradation. Results showed link between some events occurring during stack ageing and performance

decay, like stops and reversible losses. However, more data would be needed to get more relevant results on this topic and moreover, following mid-term, this aspect was not major focus for the second period.

Main efforts were put on developing and validating numerical tools for the simulation and analysis of degradation mechanisms from the MEA to the stack level, in close link with experimental investigations of WP2, as decided at mid-term. For PEMFC and DMFC reversible mechanisms have been addressed, mainly platinum oxide formation and reduction (PtOx mechanism) and carbon monoxide (CO) poisoning, as well as irreversible catalyst particles dissolution and platinum band formation in the membrane:

- Simplified platinum oxide model could be used to deeply investigate catalyst surface coverage in various conditions (gas composition and humidity) allowing to clarify reversible losses related to PtOx for all the PEMFC types investigated.
- PtOx model was also coupled to platinum particle growth model to evaluate non-reversible catalyst degradation.
- CO poisoning model allowed to describe the contamination process along the cells surface and the impact of ageing under reformate on the electrodes potentials explaining their degradations.
- More detailed description of the platinum dissolution model allowed to describe properly the Pt band formed within the membrane, providing valuable tool for post-mortem observations interpretation.

Models describing degradation mechanisms were implemented in along the channel or 2D phase cell models, allowing to investigate the heterogeneities and to evaluate the effect of these mechanisms on cell performance and on local operation for DMFC and PEMFC. These coupled models combined with experiments for their validation, actually allowed to simulate cells and stack performance including heterogeneities and reversible or non-reversible losses for several specific operation or ageing modes such as DMFC refresh procedure, ageing at fixed load under hydrogen, reformate including CO or methanol, catalyst accelerated stress test (AST), start-stops with air starvation and local defect propagation in stacks.

As a conclusion, models developed at the MEA level addressing mainly catalysts degradation mechanisms and coupled to cell models allowed to clarify the impact of local conditions on both performance and degradations and thus to contribute designing locally optimized components, as described in WP4.

<u>WP4</u>

WP4 has solely been active in the second period of Second Act (month 18-42). The starting (reference) MEAs in Second Act was defined based on well-proven precursors in the projects KeePEMAlive, Stayers and PremiumAct.

The improved understanding of degradation in LT PEMFC that was obtained in WP1-WP3 with reference MEAs has been utilised within WP4 to design two sets of improved MEAs.

Test of the reference MEAs indeed highlighted several durability issues to be subject for further optimisation in Second Act like reversible degradation that was proven to be pronounced in all steady state experiments with reference MEAs. In addition, several ageing tests using segmented cells devices at single cell or stack level confirmed strong heterogeneous degradation along the MEAs surfaces for the traditional uniform electrodes. Investigations with specific experiments and simulations allowed to correlate the mechanisms involved to the local conditions and to electrodes compositions thus allowing to propose improvements.

Reference MEAs at the beginning of Second Act were based on precursors from these three projects and were made with homogeneous electrodes using whether EWII or CEA processes. Tests with reference MEAs have been conducted in the single cells of different partners and in Nedstack or CEA designed stacks for respectively EWII and CEA MEAs to identify the degradation issues in the different conditions of interest for the systems studied in the project. Test of the reference MEAs highlighted several durability issues to be subject for further optimisation in Second Act. Particularly, reversible degradation was proven to be pronounced in all steady state experiments with reference MEAs and a major subject for optimisation.

The first set of MEA improvements (2G MEAs) were related to improved catalysts and alternative GDLs, the latter with a significant cost reduction potential. The first set of improved MEAs included ten different MEAs, in total was 273 MEAs manufactured and long-term tested both in single cells and stacks in the laboratory, the MEAs aimed for hydrogen operation was furthermore field tested in 75-cell stacks. Novel precursors particular Pt-catalyst on graphitised support proved superior stability to the baseline precursors. Significant durability improvements have been proven for the 2G MEAs. Several reference and 2G MEAs were characterised in segmented test setup at single cell and stack level that proved heterogeneous degradation along the MEAs surfaces for the traditional uniform electrodes.

The test results of these MEAs not only pin-pointed more durable catalysts, but confirmed the heterogeneous degradation that also was recorded in the reference MEAs.

These results lead to design the third generation MEAs with graded (non-homogeneous) electrodes, mainly cathodes for the EWII MEAs and both anodes and cathodes for CEA MEAs, although the overall catalyst loadings were unchanged. Several types of heterogeneous electrodes and of corresponding 3G MEAs (about 12) were designed and manufactured (in total 63 MEAs) applying EWII and CEA processes for tests in single cells and in respectively Nedstack and CEA stack designs. New graded electrodes are mainly composed of a few zones (3 to 5) with different compositions, mainly varying the local catalysts loadings for the cathodes and, for some cases, also the anodes. Twelve different third generation MEAs were designed and manufactured (in total 63 MEAs manufactured and tested). The 3G MEAs with graded electrodes have been tested in single cells or stacks for prolonged time.

EWII MEAs with parabolic graded cathodes proved to degrade homogeneously over the full active area in contrast to MEAs with uniform cathodes and CEA MEAs with active layers locally modified at both anode and cathode sides also proved strong decrease in degradation rates for different conditions and ageing protocols.

The results from long-term test of these MEAs thus actually demonstrated reduced performance losses or lower degradation rates thanks to the tuned modification of the zones submitted to stronger corrosion when using reference MEAs.

In addition to components developments, different operation strategies, such as refresh and air starvation protocols have thus been proposed and demonstrated actual performance stability improvements.

Thus, the main conclusion of the project is the demonstration that locally optimized electrodes and tuned operating conditions or strategies, as defined based on advanced investigations of degradation coupling in-situ and ex-situ experimental analyses and modelling can actually lead to durability improvements at stack level applicable in the systems.

3.3. Selected technical results

Below are described some major actions conducted to analyse the degradation issues and improve durability of Membrane Electrode Assemblies in DMFC or PEMFC single cells or stacks, as done in the frame of technical WPs.

First part of this section is giving **short summary of experimental investigations**, with figures mainly illustrating in-situ and ex-situ diagnostics and characterizations, because ageing tests results are mostly shown in last section, including improvements.

In the next section are reported **modelling investigations and simulation results** with selected figures showing the validation of main degradation models.

The last section is reporting **results and figures of ageing tests showing the durability improvements reached thanks to the optimization of MEAs components or operation strategy**.

3.3.1. Summary of experimental investigations

3.3.1.1. In-situ ageing tests in single cells and stacks

Durability or ageing tests are conducted for each type of fuel (hydrogen, reformate, methanol), by the different partners using various test objects (single cells and stacks from 25 to 200 cm²).

Table 1: summarized table of test objects.

	System	Partner	Stack (200 or 20cm²)	SC test (25 or 200cm²)
Hydrogen	1.2 & 1.5 kW_{AC} 50 kW	IRD Nedstack	Nedstack CEA	Sintef DLR TUG JRC
Reformate	30 - 10 & 3kW	ICI	ICI CEA	Sintef CEA JRC
Methanol	500 / 800 W	IRD	IRD	Polimi IRD

Several types of segmented cells were used to measure the current density distribution maps within single cells or stacks.

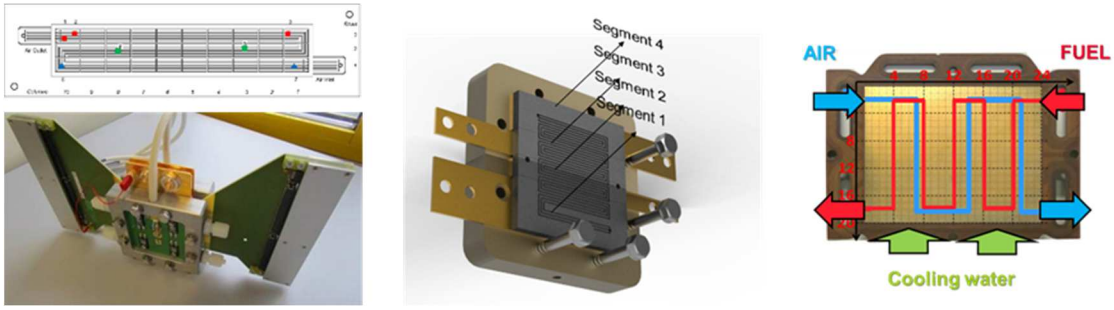


Figure 1: segmented cells used for 25 cm² single cells or 220 cm² CEA stack.

The type of tests and their main conclusions are listed below.

Durability tests of reference H2 PEMFC MEA.

The reference H2 PEMFC MEA was tested at DLR in single cell (5x5 cm2) configuration in constant load and cycling conditions. Each of the test consists of several periods of continuous operation that are interrupted by a shut-down recovery procedure in order to discriminate between reversible and irreversible degradation. Applying even short OCV transients has a refreshing effect on reversible voltage losses.

Durability test of H2 PEMFC CEA stack with reference MEA.

The objective was to analyze the evolution of the voltage over aging periods with fixed current of 100 hours. During these periods, the voltage drops with a higher degradation rates over the first ten hours (several hundreds of µV/h against approximately 100-150 µV/h over the next 90 hours); much of the performance is recovered after shutdowns and electrochemical diagnostics. In order to verify if the reversible losses could actually be limited or suppressed at lower potential, the current density was increased to 0,8 A/cm² for three periods of 100h: in this case, the average voltage shows a rise and not a decrease after the stop and the diagnostics thus confirming the removal of the reversible source of degradation.

These single cell and stack results along with also DMFC results allowed to confirm role of water distribution and also key role of platinum oxide formation/reduction in the reversible losses.

Durability testing of H2 PEMFC for full stacks in Nedstack's power plant.

This section describes continued test results of the reference samples, which started in the first reporting period. Electrochemical diagnostic testing was performed on the reference stacks to identify the influence of durability testing on the MEA components. The hydrogen crossover data is limited, the anode catalyst surface appeared unaffected by operation lifetime in the field, in contrast to the catalyst surface area on the cathode. Results suggest that the losses due to 'mass transfer' become larger over time and could be related to the changing hydrophilicity/phobicity of the MEA, thus influencing water management.

Durability test of reformate PEMFC in CEA stack.

CEA stacks made with reformate MEAs have been tested following similar reference protocols as for single cell tests under reformate fuel: at fixed current density of 0,5 A/cm² or following a load profile with steps of 0,5/1,5 hours at respectively 0,065/0,5 A/cm² as defined in Premium Act. Reformate including 24% of CO2 and 10 ppm of CO has been used as the nominal case for these ageing tests. The degradation rates estimated on the polarization curves at 0,5 A/cm² reached -75µV/h for pure hydrogen operation and -145µV/h for reformate case, after about 900 hours of cycles. So, the losses are stronger under reformate but they are lower than the rates measured during ageing test at fixed load (respectively -125 and -330µV/H for H2 and Ref.). In-situ electrochemical diagnostics showed moderate degradation of the cathode active surface area, the same for the anode side during most of the ageing but finally a stronger deterioration near the end of test. For this ageing test, post-mortem have been also conducted.

Durability test of Reformate Fuelled CHP – ICI (FC stack Nedstack S0285 & Ballard FCgen-1330).

10 kWel power - CHP system

ICI developed a 10 kWel power new CHP system with a stable CO contents during nominal operation. This new system, which replaces the 30 kWel µCHP system in order to proceed with experimental activities. The Nedstack stack S0285 was evaluated. It was possible to appreciate how the CO poisoning effect strongly affects the cells performances during the long term-test.

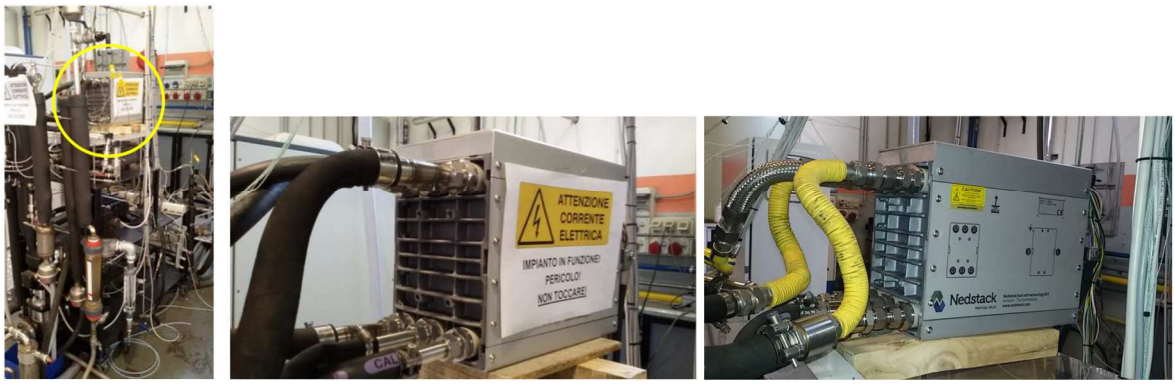


Figure 2: Nedstack FC stack S0335 – 40 cells

Development and analysis of specific accelerated stress tests.

New AST to analyse water effect on particle growth has been proposed: a suitable ast has been developed to determining the durability of cathode catalyst layer (CCL) to elucidate water content and flux influence on particle growth. With modified components, high current density region highlights a remarkably different behaviour for water ASTs compared to the reference one. Transport losses are significantly larger, leading to the hypothesis of a change in material properties, as far as GSL/MPL are concerned.

Humidity induced Platinum Agglomeration: effect of humidity and gradients have been tested on reference and new MEAs. Significant MEA improvement was possible by changing the catalyst. The improved MEA shows a better stability under standardised testing conditions but the new catalyst has shown to be more prone to humidity induced degradation.

OCV Hold Testing has been studied for Chemical Membrane Degradation Analysis: conclusion is that both dissociation of acidic ion conducting groups as well as the decomposition of the structure giving backbone may take place in parallel to obtain the given results.

Analyses of the common OCV AST in PEMFC single cell showed how the role of frequent intermediate electrochemical characterization is of high importance. It was shown that an accelerated membrane degradation protocol without intermediate electrochemical characterization could be more efficient and selective than the standardised one.

3.3.1.2. Local degradation analysis by in-situ and post-mortem ex-situ tests

Electrochemical investigation of local degradation effects of DMFC on single cells.

Several complete steady-state experimental campaigns have been performed at POLIMI, based on the performance distribution characterization (through local polarization curves and l-EIS) varying key operating

parameters such as cathode and anode stoichiometries, air saturation, flow orientation and methanol concentration. Cathode inlet area has been identified to be detrimental for the overall performance also during cell operation. Such a strong heterogeneous degradation is mostly recovered with procedures primarily intended to recovery temporary degradation (such as the full refresh), pointing out the existence of a recoverable contribution to degradation heterogeneity as well as a permanent one. Internal anode-cathode reference electrodes array has been developped: key observation here was that the standard refresh cycle procedure results in a spatially varying evolution of cathode potential over long periods, which could lead to redistribution of current density over time and, possibly, non-homogeneous degradation of MEA components.

In order to verify the validity of the results obtained with lab scale (25 cm2) DMFC mSegFC campaign, and to check the reliability of the methodology, the formerly developed hardware has been scaled up to a commercially relevant geometry (180cm²).

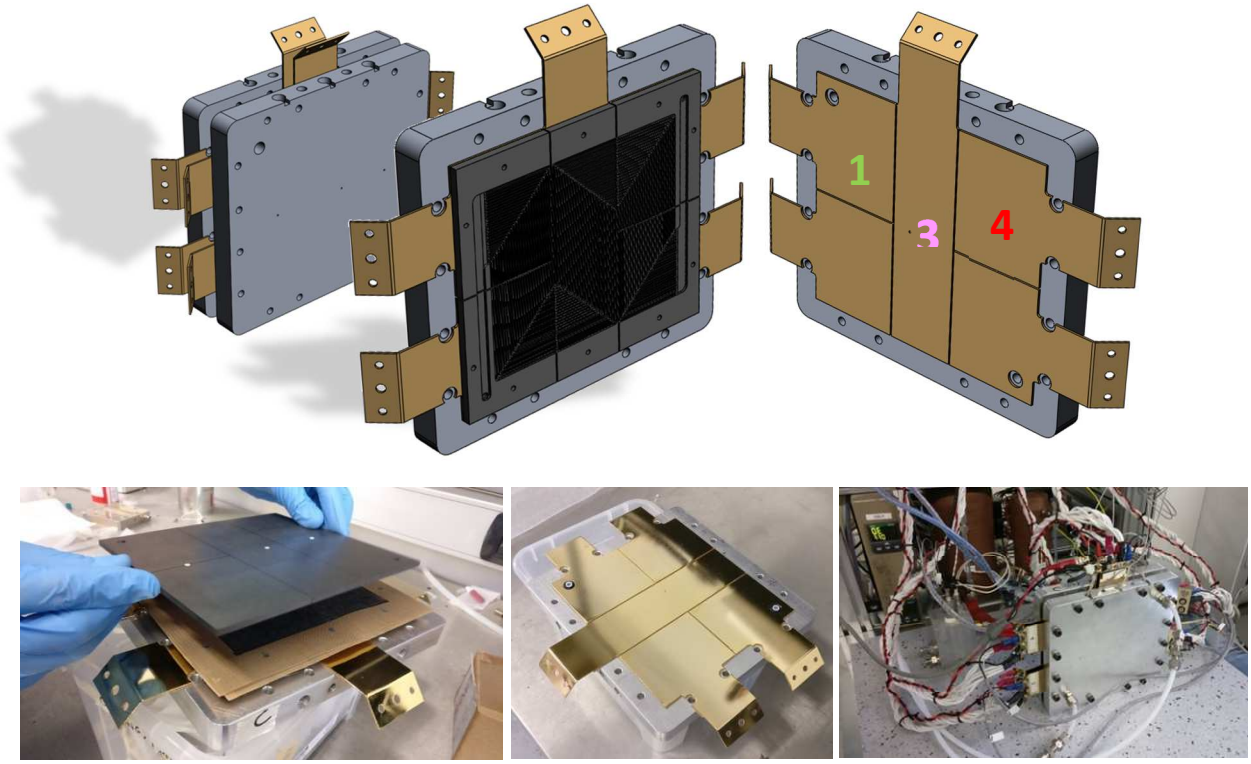


Figure 3. maxi-Segmented Fuel Cell (XSegFC) setup pictures, featuring a 5 segments macro-segmentation on 180 cm2 MEA

<u>Electrochemical investigation of local degradation effects in a PEMFC single cell.</u>

Effect of humidity on H2 PEMFC MEA performance has been studied in a single cell at DLR. Low humidity conditions represent critical operation of modified cathodes, and have to be avoided to mitigate accelerated degradation.

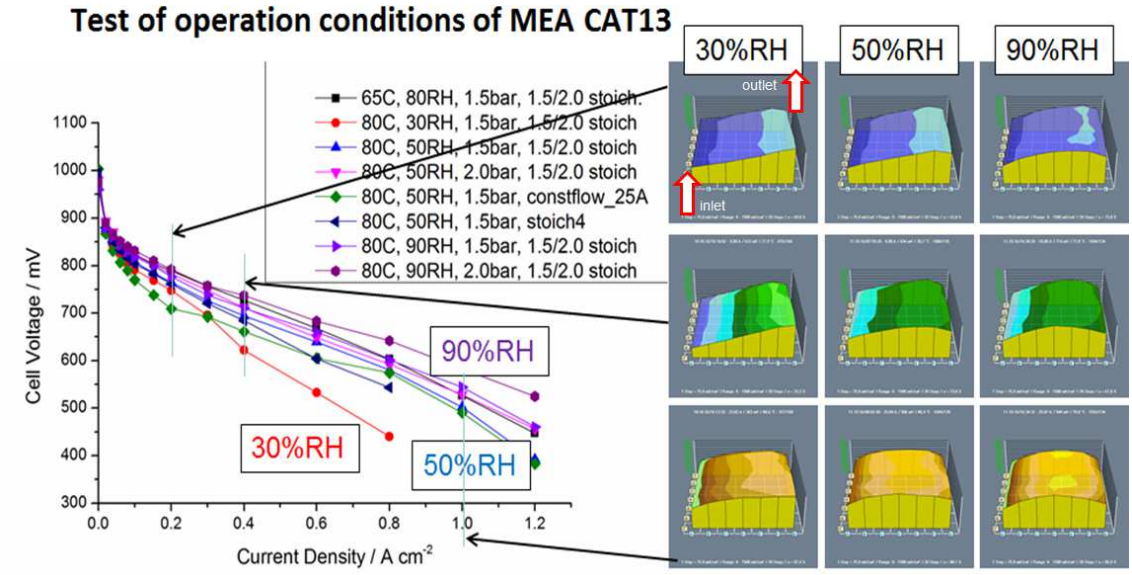


Figure 4: Performance test of H2 MEA CAT13 under different operation conditions specified in the figure. The current density distributions are measured at 30%RH, 50%RH and 90%RH at the current densities indicated by the arrows.

Electrochemical investigation of local degradation effects in PEMFC stacks.

Segmented cell analyses were also conducted using S++ devices on short stacks : 5-cell stacks with reference H2 MEA at Nedstack and 8 cells PEMFC stacks at CEA.

The current distribution is only marginally changed during aging at fixed load under pure hydrogen with both Nedstack and CEA results, while it was strongly affected during start-up shut-down protocol or during ageing under reformate. Very strong degradations occured related to the cathode catalyst layer degradation and also carbon monoxide tolerance losses when operating with reformate fuel.

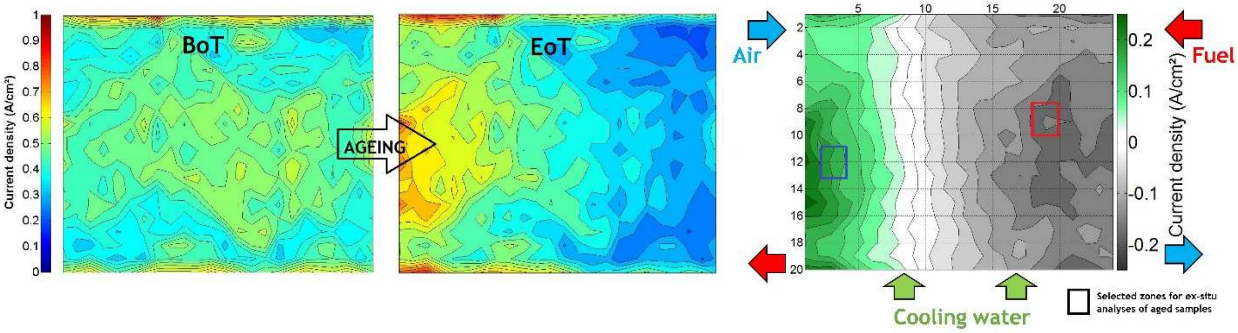


Figure 5: CDDM recorded for the MEAs aged in the short PEMFC stack under reformate and load cycles at BOT and EoT (left side) and their difference (right side) with zones identified for further ex-situ analuyses.

A CO poisoning diagnostic was developed and applied during the ageing tests showing the decrease in CO tolerance as well as an acceleration of the contamination process from H2 inlet to outlet. These effects of ageing were already noticed during the ageing test at fixed load but it appeared that they are in fact less

pronounced during the ageing under load cycles. This has been attributed to a quicker loss of CO tolerance in ageing test at fixed load.

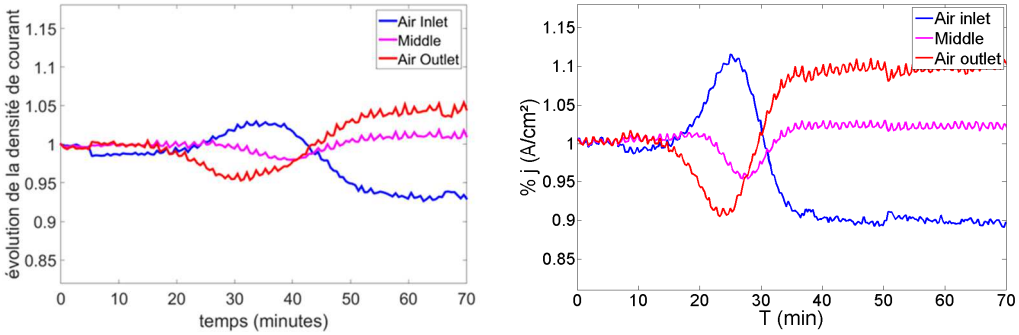


Figure 6: current density evolution for three zones of a MEA in the stack (air inlet = fuel outlet, middle, air outlet = fuel inlet) during CO poisoning test consisting in transition from pure H2 to H2 + 24% CO2 + CO 10 ppm at fixed current density of 0,5 A/cm². Tests conducted after respectively 400h and 1400h of ageing.

Post-mortem electrochemical investigations on aged MEA samples from aged PEMFC stacks.

Post-mortem analysis of aged samples have been carried out to characterize which components of the MEA have been degraded looking at the evolution of their microstructure and functional properties. For the latter, electrochemical local analyses in 2 cm² single cells were performed to complement in-situ analyses by testing small samples aged in PEMFC stack. These measurements allowed to determine the mechanisms involved locally and the correlation with the local conditions induced by the operating profile and the cell design.

During ageing under reformate at fixed load, the final current distribution is different when operating the degraded MEAs under pure hydrogen or under reformate including CO. It was particularly interesting to show that cyclic voltammetry results were consistent with in-situ local performance losses: electrochemical active surface area was much lower for samples near air outlet for the two eelctrodes, and the cyclic voltammogramms clearly indicated more ruthenium losses consistent with lower CO telrance measured in-situ near hydrogen outlet.

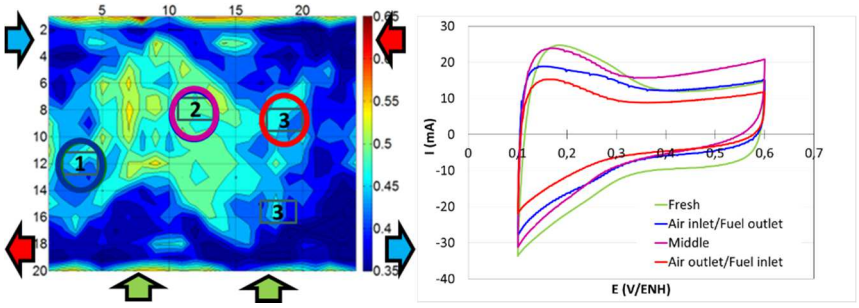


Figure 7: cyclic voltammograms on fresh and aged anode samples - Pt-type peaks appearing around 0.25 V/ENH indicating a modification from PtRu to Pt at the catalyst surface at air inlet/fuel outlet zone.

During ageing under accelerated start-up/shut down cycles, the final current distribution showed zones fully degraded and cell activity located only near hydrogen and air inlets. Thanks to performance measurements

on samples, the heterogeneities observed at end of test could be related to cathode degradation by carbon corrosion, strong in the middle of the cell, only partial near hydrogen outlet and also to in-situ local conditions, particularly oxygen partial pressure.

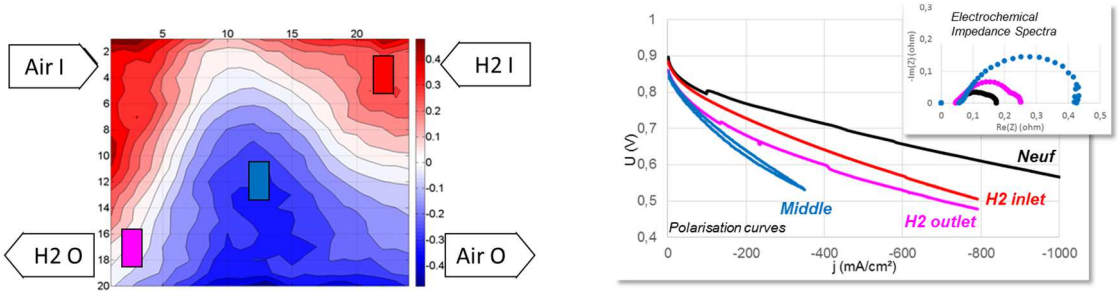


Figure 8: difference between the local current maps (in A / cm²) obtained after and before aging. After accelerated SU/SD cycles - Stack operating point: 0.5 A / cm², conditions: 60 ° C, 50/50%RH, Sto H2 / air 1.5 / 2 (left side) - Polarization curves and electrochemical impedance spectra at 0.6A / cm² obtained on samples from new MEA (black curves) or different zones of an aged MEA. Conditions 60 ° C, 1.5 bar, 50% RH (right side).

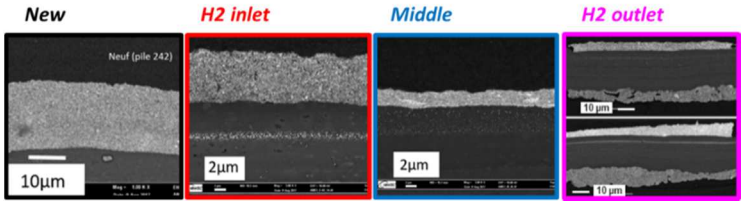


Figure 9: Scanning electron microscopy images obtained from samples from new MEA or different areas of an aged MEA. To be considered: densification of the cathode (top of the images) and platinum band in the membrane.

3.3.1.3. Ex-situ analysis of degradation mechanisms comparing pristine and aged samples

<u>Post-mortem ex-situ analyses of DMFC samples.</u>

Major degradation effects were observed with ex-situ techniques XPS, XRD, EDX, TEM in the Parabolic (non-uniform tuned electrodes with different compositions from air inlet to air outlet) and Uniform MEAs. Apparently, major effects occur in the Uniform MEA. These include: local delamination of MPL/GDL at the anode; increase of amount of carbon oxide in the anode likely associated with carbon corrosion; increase of $C_{support}$:$C_{ionomer}$ ration which indicates ionomer degradation also associated with reduction of F concentration. The major degradation observed at the Parabolic sample is Pt crystallite growth which also occurs at the Uniform sample.

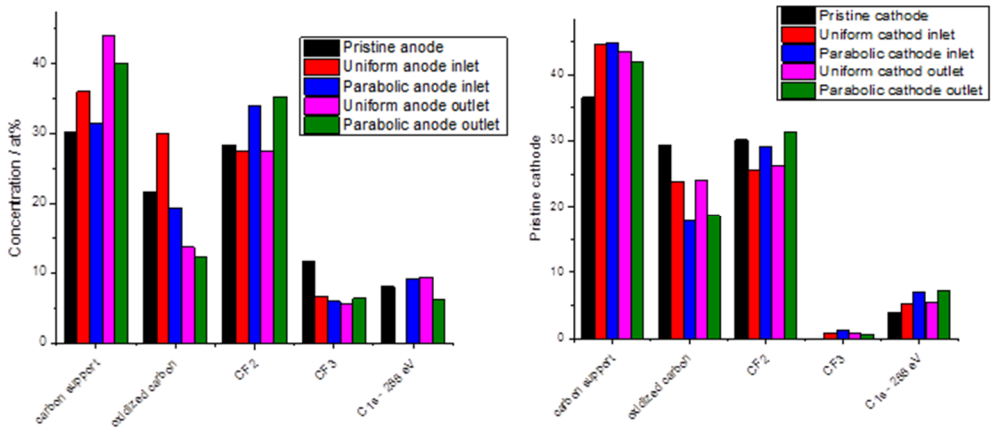


Figure 10: XPS analysis of DMFC electrodes. Atomic concentrations of C1s species identified in the analyzed DMFC samples. Left: anode; Right: cathode.

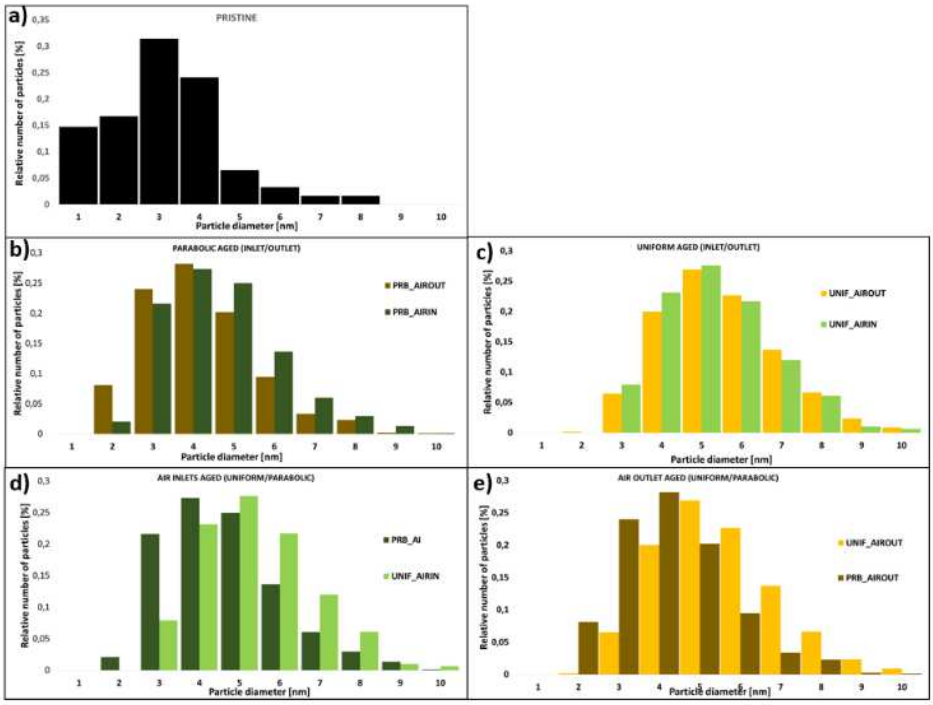


Figure 11: Nanoparticle size histogramms of a) the Pristine and aged cathode of b) Parabolic and c) Uniform MEA in the AIR IN and AIR OUT zones. d) and e) Comparaison of two aged MEA histograms analysed respectively in the AIR IN and AIR OUT zones.

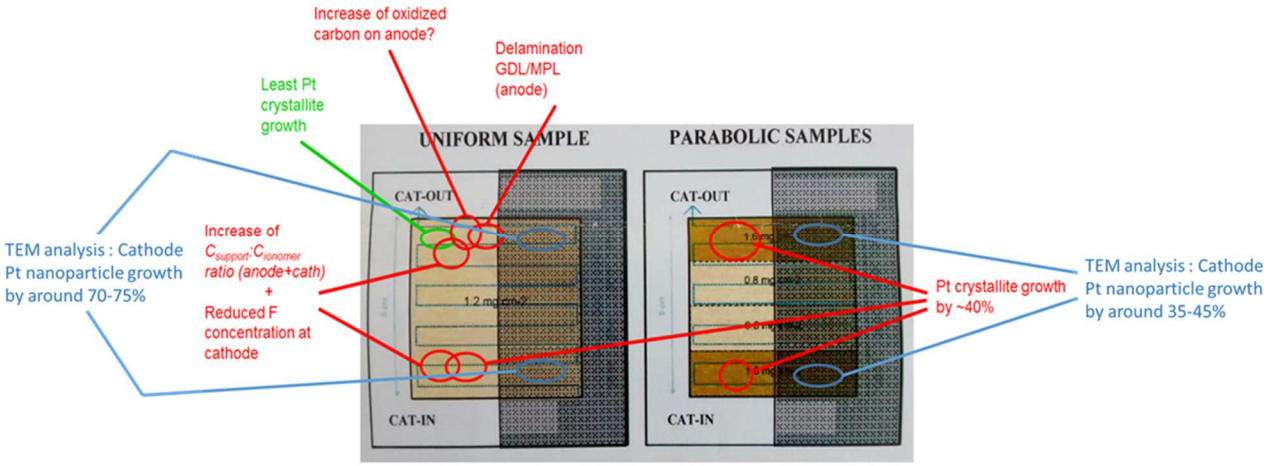


Figure 12: Summary of degradation changes observed in the Uniform and Parabolic DMFC MEAs.

Post-mortem ex-situ analyses of PEMFC samples.

Analysis of hydrogen PEMFC MEA samples after ageing in Nedstack designed stacks.

Samples are analysed after ageing under stationary conditions in a 75 cells stack: 2 cells with higher performance at end of test (25 and 26) and 2 cells with lower performance (71 and 72).

XPS results show an increased $C_{support}$:$C_{ionomer}$ ratio indicating a loss of surface ionomer at the anode and cathode for cells 71 and 72 but also for cell 26. This effect seems to be linked with a change of surface ionomer composition of these samples which exhibit a significant reduction of the CF_2:CF_3 ratio.

XRD analysis was used to study the growth of particle size, or more specifically, of crystallite size. The corresponding spectra. The relative growth is calculated for the different samples using four different Pt peaks, showing growth of about 200%.

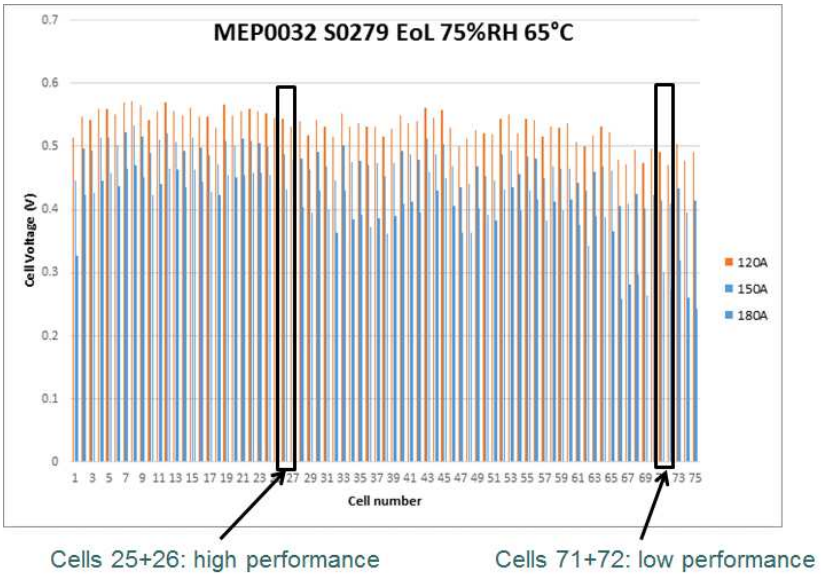


Figure 13: EOL single cell voltages of a NEDSTACK. MEAs 25, 26 and 71, 72 were analyzed in this section.

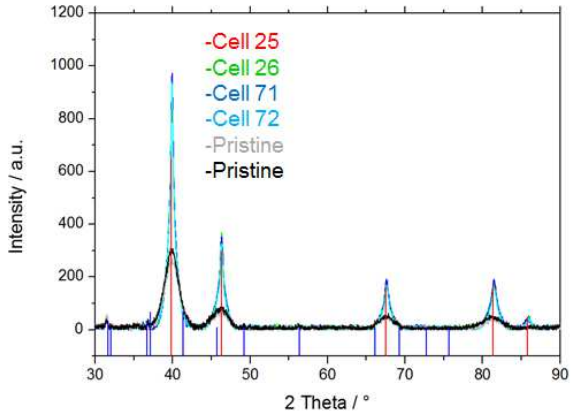


Figure 14: XRD spectra of H2 PEMFC MEAs from a stack from NEDSTACK.

Analysis of reformate PEMFC MEA samples after ageing in CEA designed stacks.

The degradation of MEAs aged at CEA in short PEMFC stacks of 8 cells were analysed by TEM: after ageing under reformate at fixed load and under load cycles, in the same zones as the ones studied by electrochemical methods, one located near the air inlet/fuel outlet zone and the second located near the air outlet/fuel inlet zone, compared to fresh sample.

Due to the strong heterogeneity PtRu particles , TEM analyses were not able to evidence any clear PtRu nanoparticle microstructure and chemical evolution between the fresh and four aged anodes. However, as observed in the similar aged MEA, Ru dissolution can be highlighted by the presence of Pt-Ru precipitates within the membrane. PtRu precipitates were observed within the membrane in the four TEM samples; the largest precipitates form a precipitate band at 6 or 8 µm far from the cathode, near the membrane reinforcement, while smaller precipitates are observed up to the anode. The membrane precipitates analyzed in the MEA aged under load cycles test are richer in Ru than the membrane precipitates analyzed in the MEA aged under stationary conditions. Considering that the quantity of Ru present in the Pt-Ru membrane precipitates is an indicator of the Ru dissolution rate of the PtRu anode catalyst, a raw calculation taking into account the volume and the composition of the largest membrane precipitates can be made. This calculation indicates that the Ru present in membrane precipitates located in the air inlet is also more than twice time larger.

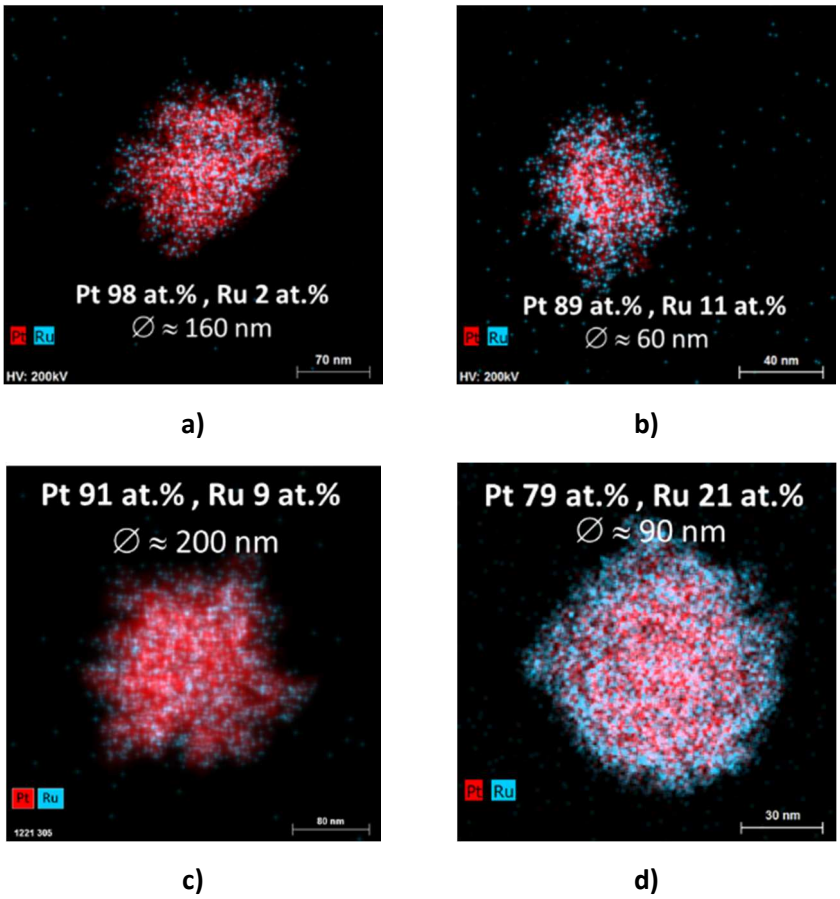


Figure 15: Pt and Ru X-EDS elemental maps of membrane precipitates observed in a) and b) MEA aged under the reference stationary durability test respectively in the air inlet and air outlet zones and in c) and d) MEA aged under the reference load cycles test respectively in the air inlet and air outlet zones.

HAADF/STEM and X-EDS mapping analyses were performed on the Pt_3Co catalyst at the cathode side. The histograms of nanoparticle size measured in the fresh and aged MEAs in the air inlet and outlet zones reveal a nanoparticle size increase in the aged samples. For the MEA aged under the stationary test quite similar evolution between the air inlet and outlet zones is observed whereas for the MEA aged under the load cycles test a larger particle size is observed in the air outlet zone. The histograms clearly suggest that nanoparticles smaller than 5 nm are not stable.

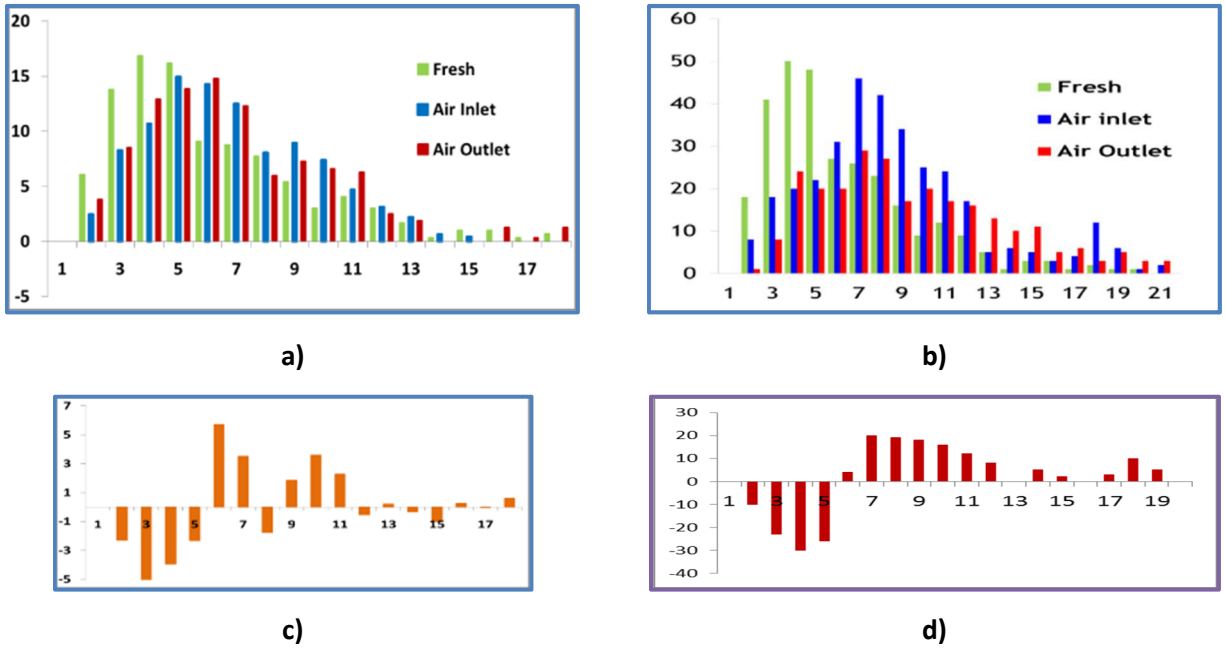


Figure 16: Histograms of the nanoparticle diameter size (in nm) a) for the MEA aged under the reference stationary durability test and b) for the MEA aged under the reference load cycles test. c) and d) histograms built from the two previous histograms by subtracting the fresh cathode histogram from the aged air outlet cathode histograms showing that nanoparticles smaller than 5 nm are not stable.

Furthermore, in order to determine the cathode chemical composition evolution, X-EDS analyses were performed in the fresh and aged cathodes. No variation on the global composition of the cathodes is observed. However, the high resolution Pt and Co X-EDS elemental maps show a more significant evolution of Pt_3Co nanoparticle chemical structure in the air outlet zone: the Pt shell surrounding the Pt_3Co nanoparticle core resulting from a Co chemical leaching during nanoparticle synthesis process is increased by aging, mainly at air outlet.

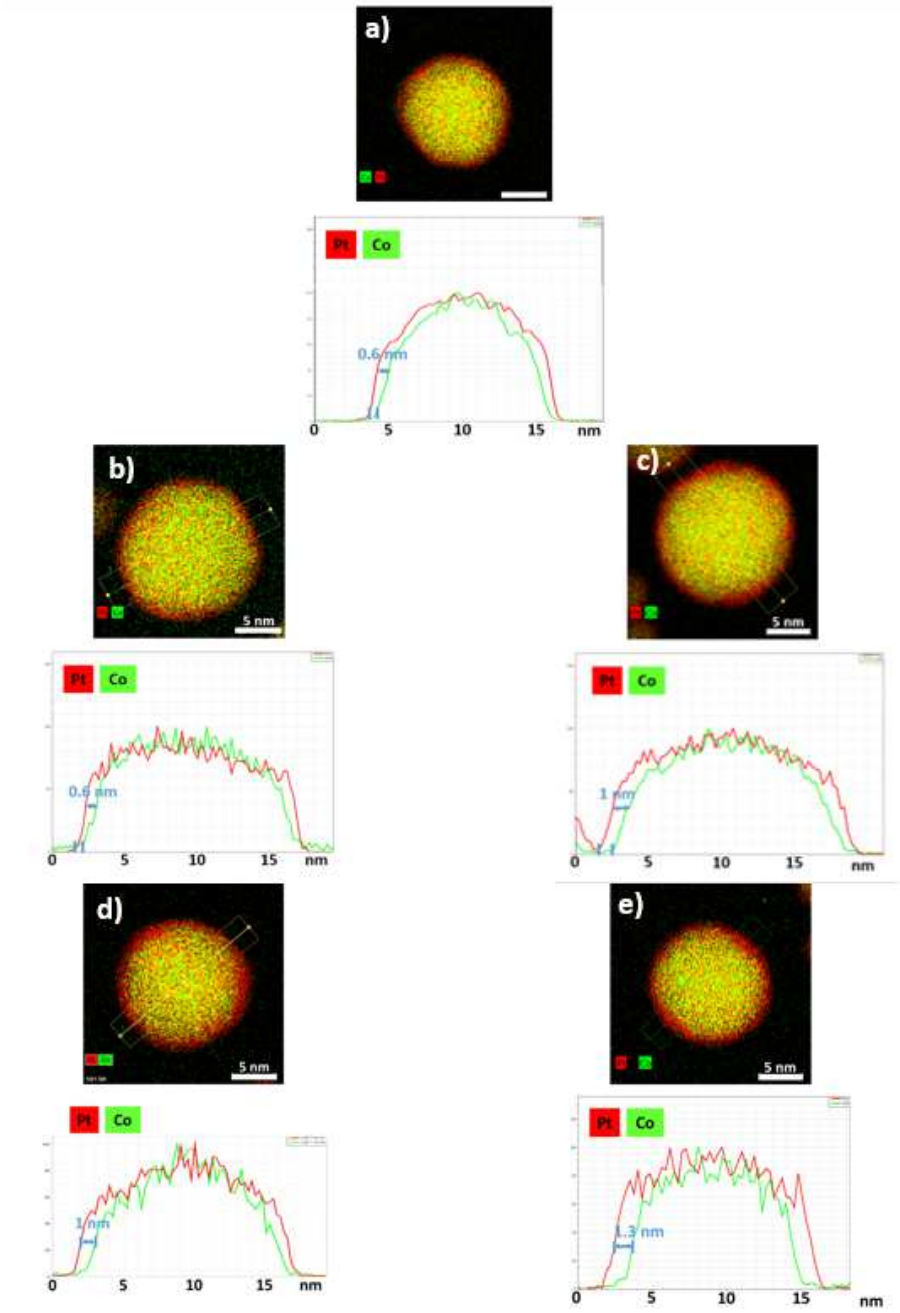


Figure 17: X-EDS Pt and Co elemental maps associated with the line-scan of the Pt (in red) and Co (in green) distribution through the nanoparticle of a) fresh cathode, b) and c) cathode aged under stationary test respectively in air inlet and air outlet zones, d) and e) cathode aged under load cycles test respectively in air inlet and air outlet zones.

Results showed an increase of thickness of the Pt shell around the Pt-Co partcicles: this could result from the continuously Co dissolution during fuel cell operation but was more probably attributed to the electrochemical Ostwald ripening mechanism, for which the smaller nanoparticles are oxidized and produced ions migrating through the ionomer toward the larger nanoparticles where Pt ions are reduced at their surface, but, because the negative Co^{2+}/Co standard potential prevents Co ions reduction within the MEA.

Consequently, for Pt_3Co catalyst, the electrochemical Ostwald ripening mechanism leads to the dissolution of smallest nanoparticles and the formation of a thicker Pt shell surrounding the larger nanoparticles. This mechanism increases their size but also decreases their activity as Pt is less active than Pt_3Co, and in addition this mechanism leads to the contamination of the ionomer by the Co ions. As the dissolution of nanoparticles smaller than 5 nm leads to the contamination of the ionomer by Co ions, more damaging than with pure Pt catalysts, an optimized robust Pt_3Co catalyst should not have nanoparticles smaller than 4-5 nm.

TEM analysis of the air inlet and air outlet of the cathodes aged under the two conditions clearly shows that the electrochemical Ostwald ripening mechanism more largely occurred in the air outlet cathode zone than in the air inlet cathode zone.

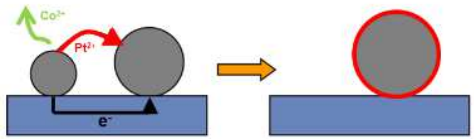


Figure 18: Scheme of the electrochemical Ostwald ripening mechanism considering Pt3Co nanoparticles. WP2 conclusive summary for the reporting period

3.3.2. Summary of modelling investigations

3.3.2.1. Modelling of reversisible and non-reversible mechanisms related to Pt based catalysts

<u>Platinum oxides formation / reduction modelling and validation (by DLR and POLIMI).</u>

The experimental activities carried out during the first period of this project confirmed that the formation of platinum oxides has a key role in the reversible degradation, as first shown with specifc experiments in DMFC single cells, then confirmed by experiments conducted on PEMFC single cells and stacks.

It was indeed highlighted in previous study (Premium Act project) that temporary degradation occurs at both anode and cathode electrodes and the most of it occurs at the cathode and can be recovered operating for short periods at low cathode potentials. This behavior suggested as a possible explanation of cathode temporary degradation in DMFC the Platinum oxides (PtOx) formation and reduction mechanism. Cathode temporary voltage decay was investigated by means of dedicated and innovative OCV tests feeding the anode with a mixture of methanol and hydrogen, in order to keep the anode potential negligible and constant in time. The effect of potential has been deeply investigated with cyclic voltammetry (CV) tests, feeding humidified hydrogen and nitrogen at anode and cathode, respectively. The CV procedure consists in holding selected potential values for different times and scanning back, forth and back again the potential at a scan rate of 25 mV/s, in order to highlight the area related to Platinum oxidation. CVs are reported for different holding potential and the corresponding active area coverage, calculated on PtOH basis, assuming a single electron transfer reaction. These results are coherent with the PtOx formation mechanism and highlight that the onset potential of PtOx formation is around 0.63 V.

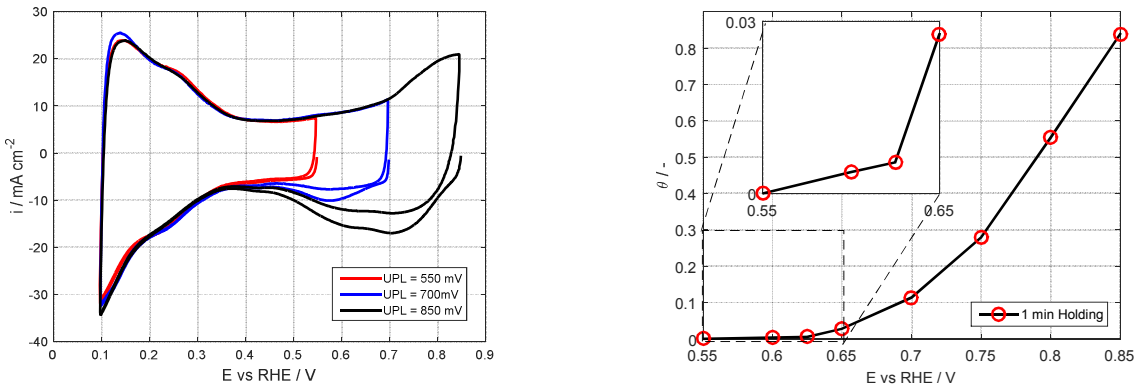


Figure 19: CVs with different holding potential and active area coverage.

The main focus was to develop a model able to describe the platinum oxide formation and reduction kinetics properly. The development of such a model is not only required to describe the reversible degradation, but also for modeling the irreversible degradation by means of platinum dissolution and particle growth, since platinum oxides affect the dissolution rates. Thus, taking into account the platinum oxide formation and reduction is crucial to correctly predict the degradation rates under transient operating conditions, e.g., during an AST with fast potential cycling.

The platinum oxide kinetics can be studied using cyclic voltammetry (CV), since the current density peaks at high potential are caused by the platinum oxide formation and reduction, respectively. Therefore, the first goal of this work was to develop a model which is able to describe the experimentally observed CVs, in order to ensure that the platinum oxide formation and reduction kinetics is described correctly. A special feature of the model is the distinction between edge and planar sites of the platinum particle. Due to their different energy, oxides will form on both sites with different kinetics.

The model has been validated with dedicated CV experiments performed at POLIMI. In these experiments the potential was hold at various values for a certain holding time. Afterwards a cathodic sweep followed by a full CV has been performed. During the hold at high potentials, the platinum oxide coverage increases, which leads to an increased current density during the following cathodic sweep.

A good agreement between simulation and experiment is achieved. The model is able to describe the effect of both, potential and holding time, on the platinum oxide formation. Furthermore, the reduction kinetics is described accurately, as the typical shape of the CVs is correctly reproduced. Therefore, the model is suitable to investigate the oxide formation and reduction during operation, e.g., to investigate the effect of the refresh procedure.

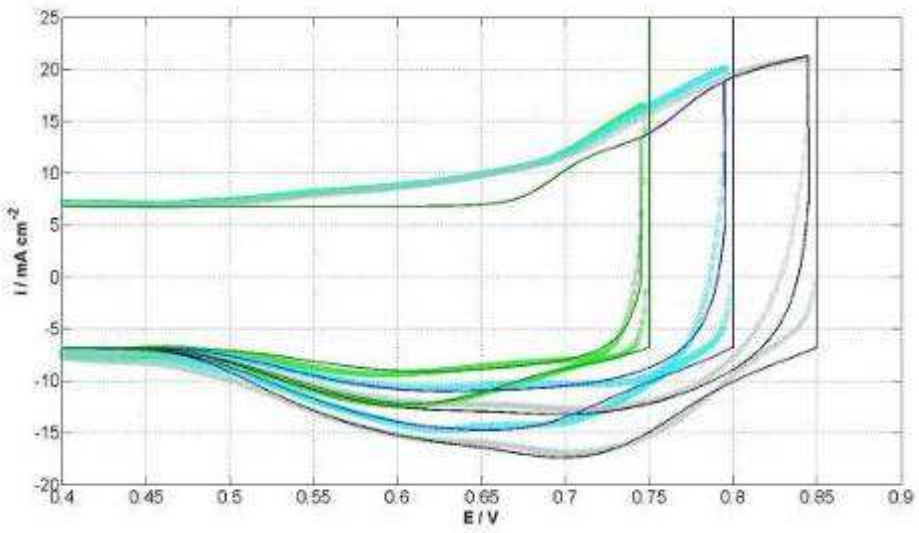


Figure 20: Comparison between CV experiment (symbols) and simulation (lines) for different holding potentials: 0.75V (green); 0.8V (blue); 0.85V (grey).

The loss of electrochemically active surface area (ECSA) on the cathode side is the main cause of irreversible performance degradation. This loss of ECSA is related to a growth in the platinum particles. On the one hand, the particle growth affects the oxide formation and reduction. On the other hand the oxide coverage also affects the particle growth. Thus, both mechanisms are strongly coupled.

The model was shown able to predict the significantly increased degradation during the AST due to the periodic reduction of the platinum oxides and the consequent increase of platinum dissolution rates.

During second period, more detailed experiments and models have been performed to enhance understading of this mechanim. In addition, these PtOx mechanisms were included into a 2D cell model in order to investigate the reversible and irreversible degradation.

Considering voltammetry measurements in inert conditions, the oxide coverage (calculated on a PtO-basis) shows a clear exponential trend as upper potential limit increases. Instead, potentiostatic experiments in inert conditions confirm that the longer is the holding time, the greater is the oxide reduction peaks. For long holding times, two dominant peaks can be recognized: they are named for the sake of simplicity α-oxide (at higher potentials) and β-oxide (at lower potentials). The presence of different oxides is further investigated developing two different potentiodynamic tests in inert conditions.

In addition, a dedicated potentiodynamic experiment *in-operando* conditions has been setup in order to evaluate the impact of Platinum oxides on PEMFC performance: different potential profiles composed by cycling and/or holding are imposed in inert conditions and then a switch to *in-operando* conditions (H_2/Air) is performed to monitor cell performance.

Finally, in order to elucidate the relation between permanent and recoverable degradation phenomena occurring at the cathode, two different Accelerated Stress Tests are proposed. The *standard*-AST consists in 30'000 potential cycles between 1 and 0.6 V at 50 mV s^{-1}, while in the so-called *beta*-AST the lower potential limit is raised to 0.7 V in order not to reduce β-oxide. The measurements evidence a reduced ECSA loss for

beta-AST compared to the *standard* one. Hence, β-oxide coverage has a negative effect in terms of recoverable performance loss, but it has a protective behavior against dissolution. During *standard*-AST, both kind of oxides are continuously formed and reduced during each cycle, which is detrimental to Platinum stability and may enhance dissolution phenomena. Thus, it is clear that Platinum oxides play a fundamental role both in performance and durability PEMFC issues, hence an optimization strategy to find the best compromise is required.

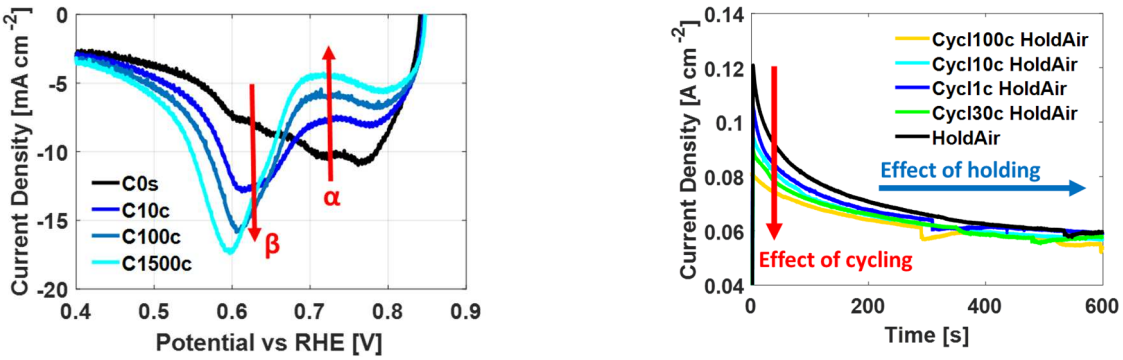


Figure 21: Linear sweep voltammetry after a variable number of cycles between 0.7 and 0.85 V (left) and effect of Cycling and Holding on PEMFC performance, measured during in-operando potentiostatic tests (right).

In the second period ***a simplified platinum oxide model*** has been derived, in order to reduce the computational cost while still being capable of describing the evolution of platinum oxide coverage. This model has been validated with dedicated CV measurements which yield the evolution of the total oxide coverage at various cathode potentials. The model is able to correctly describe the oxide evolution over the whole potential range considered in the experiments. Due to the significantly reduced computational cost, it was possible to couple this model with the detailed single cell models developed at DLR in order to investigate the effect of platinum oxide formation on cell performance for DMFC and PEMFC. Furthermore, the model was coupled with a platinum particle growth model to simulate the catalyst degradation in DMFC and PEMFC in different degradation tests.

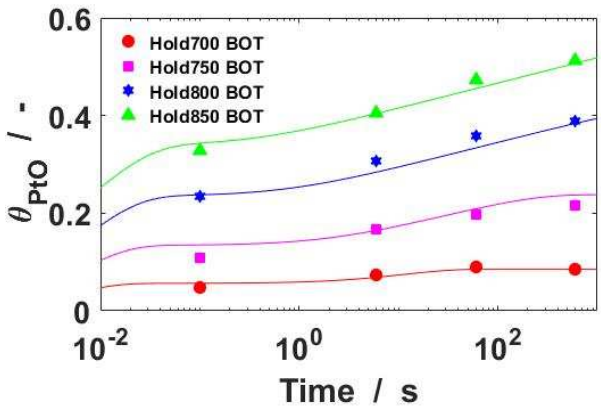


Figure 22: Comparison between experimental (symbols) and simulated (lines) coverage evolution.

Contribution from CEA on Pt dissolution and deposition inside the membrane

Platinum of the catalyst layer can dissolve but also redeposit. Dissolution or re-deposition depends on particle radius, on local electrochemical potential and on local platinum ions concentration. During this second period of the project, the 1D MEA model of CEA (presented in deliverable D3.1) has been coupled with platinum and re-deposition mechanisms module in order to analyze the platinum-band formation in the membrane.

A 1D model of the MEA in the "through thickness" direction was already available. This model computes the local ionic and electronic potentials in the MEA, taking into account ORR and HOR. The model has been improved in order to consider gases permeation through the membrane. Furthermore, a new implementation of the electrochemical equations have been developed in order to be able to compute ***mixed potentials*** in the MEA. The estimation of this "electrode" potential in the membrane is of little practical interest for the computation of the MEA performance, but becomes crucial when it comes to predict the possibility of platinum re-deposition. The developed approach allows to easily put multiple reactions in competition as well as to account for the disappearance of given species, which is not possible with the Nernst equation. The open-circuit voltage is not imposed anymore as an external parameter, but it is computed taking into account gases permeation (mainly hydrogen) through the membrane and the resulting mixed potential at the cathode.

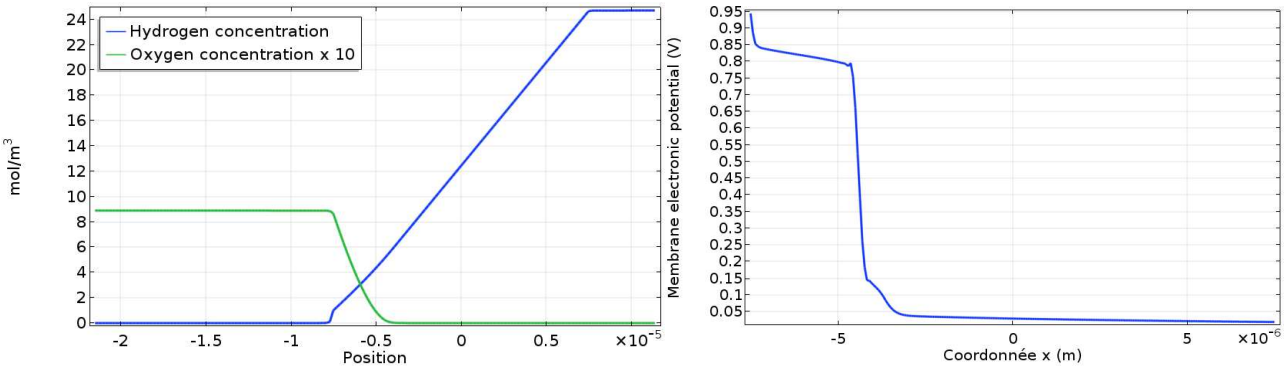


Figure 23. Left: Dissolved oxygen and hydrogen profiles in the whole MEA. Right: "electrode" potential in the membrane

This potential is also representative of the electrode potential, as at OCV the ionic potential is expected to be constant over the membrane thickness. It appears that the oxygen affects strongly the "electrode potential" in the membrane, as sharp drop appears when the oxygen concentration reaches zero. We can expect that the over-potential for the platinum dissolution or re-deposition will also be affected by this potential discontinuity.

Regarding the platinum dissolution and redeposition, the developed model takes into account five families of particles, as well as the impact of particle radius on the free activation enthalpies of the dissolution (oxidation) and re-deposition (reduction) reactions. The kinetics reaction are coupled with mass balance and some geometric considerations in order to compute the evolution of particles size (and resulting platinum surface) over time.

It is interesting to observe that the re-deposition of Pt does not start at the membrane boundary with the cathode, where the potential is too high due to oxygen presence, but only after around 5 µm (which corresponds to the potential drop). The deposition leads to platinum apparition in the membrane.

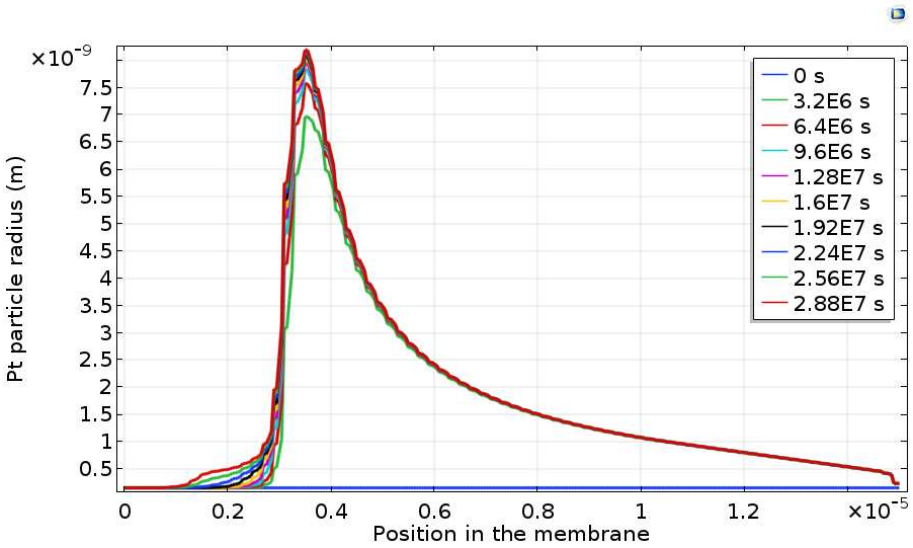


Figure 24: Platinum band formation in the membrane

The platinum "band" appears toward the cathode, approximatively at ¼ of the membrane thickness. The fact that platinum also redeposits close to the anode can be due to an overestimation of the platinum ions diffusion in the membrane. The non-linearity compared to deposition rate comes from the fact that Pt surface increases fasters in the regions where deposition rate is higher. In the simulation, platinum redeposition can also be observed in the anode, where the particle size increases over time, and then stabilizes.

Reversible degradation due to CO poisoning (by CEA).

The MEA model takes into account gas transport, heat transfer, proton and electron migration and electrolyte behaviour for the different layers of the MEA (GDL, MPL, CL and membrane). For the first period, the model has been operated in 1D through the thickness of the MEA.

A CO poisoning model is superimposed to the performance model in order to simulate reversible degradation. The reaction kinetic model for the anode is replaced by the comprehensive set of reactions proposed by Shah and al. [16]. So 7 reactions, coupling CO poisoning with hydrogen oxidation and CO oxidation are implemented: **H_2 adsorption** at the anode; H_2 electro-oxidation at the anode; **CO adsorption** (and desorption) at the anode (reduction of available Pt sites); **Electrochemical oxidation of CO** at the anode (increase of available Pt sites); Chemical oxidation of CO at the anode from oxygen cross-over, internal air-bleeding (increase of available Pt sites).

In the model, we follow: H2, O2, CO concentrations (gas phase) and surface coverage. CO2 concentration is not computed (assumed inert). Water production if taken into account but negligible compared to feeding gases hydration. The effect of feeding the cell with hydrogen mixed with CO for a given duration can be simulated.

After a stabilization time, a few ppm of CO are injected for 2 hours before switching back to pure hydrogen. Different level of CO concentration (from 5 to 60 ppm) are simulated. The simulations are performed at constant 0.7V cell potential. The effect of CO is observed on the current density.

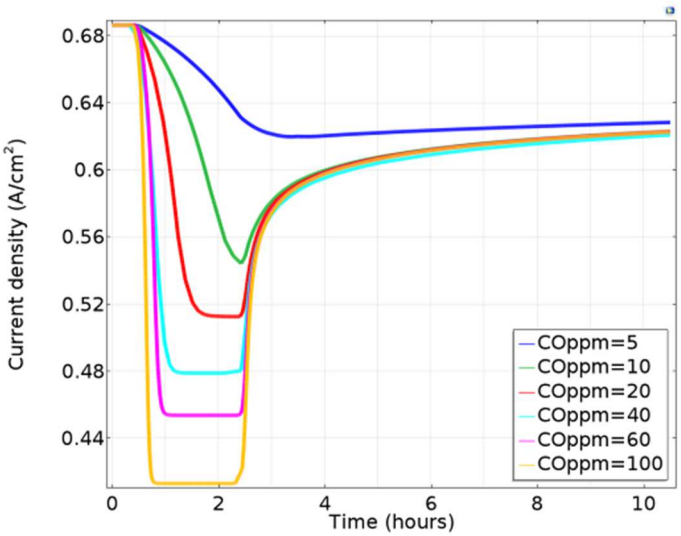


Figure 25: CO poisoning simulation

Even if not fully validated, the model gives some insight on the pollution mechanisms; progress had to be made concerning the stabilization time under CO (very fast in the model) and the performance recovery which is very slow in the model for full recovery.

The model allows also to investigate the CO pollution on the CL operation. For instance, the effect on current distribution production through the thickness of the layer can be computed. It appears that the current production is more homogeneous when feeding the cell with a few ppm of CO in the hydrogen. On the other hand, the overpential for the hydrogen oxydation is shifted homogneously all over the layer.

3.3.2.1. Implementation of degradation mechanisms in performance models and simulation of degradation and heterogeneities

The aim is to get more insight on the link between the local conditions in large cells, which depend on the operating conditions and components properties, and the observed local performance and degradations in order to provide recommendation for the design of optimized and robust components.

Single cell DMFC case (by POLIMI and DLR).

Modelling of DMFC at cell level.

A physically based DMFC cathode model has been developed in the fisrt period to simulate impedance and performance. The model describes the impact of the methanol oxidation reaction (MOR) on the cathode conditions. The current density distribution across the cathode CL has been described in OCV condition: this internal current is greater at channel inlet, where the methanol crossover through the membrane is higher.

A detailed description of cathode CL behavior is fundamental to reproduce in a representative way its potential through the electrode and along the channel, which strongly influences both temporary and permanent degradation mechanisms. The model qualitatively reproduce cathode potential along the channel for different current densities.

Then, the integration of the degradation models has been developed in order to provide insights into the heterogeneities evolution trough the MEA and along the channel.

In order to investigate the **heterogeneities in a DMFC single cell**, a two-dimensional two-phase multicomponent cell model has been implemented in the new DLR fuel cell model, allowing the simulation of flow and transport in porous media. The modelling domain is a cross-section of the DMFC single cell, including anode and cathode gas diffusion layers (GDL), catalyst layers (CL) and the membrane.

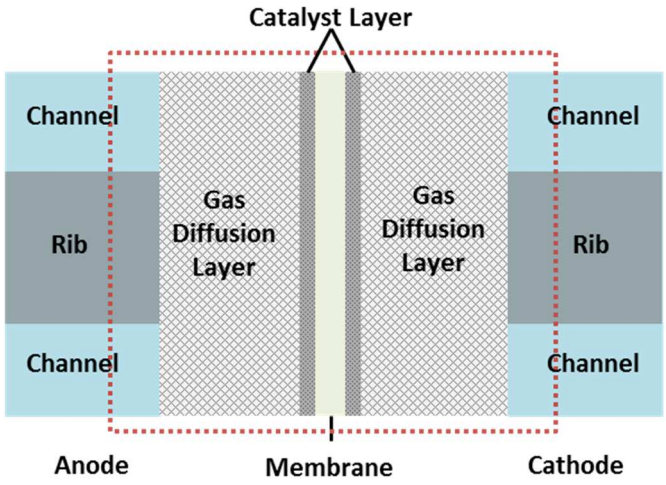


Figure 26: Modeling Domain for the DMFC Cell Model in 2D

On the anode, water, methanol and carbon dioxide are the relevant species; on the cathode, oxygen and nitrogen are additionally present in both phases. In the membrane domain diffusive transport and electroosmotic drag are considered. All three subdomains, anode GDL/CL, membrane and cathode GDL/CL, are coupled and water and methanol can crossover from one side to the other. In order to identify heterogeneities, polarization curves for different configurations (co-flow/counter-flow) with varying stoichiometry were simulated. In a co-flow configuration, cell inlet and cell outlet vary significantly in terms of saturation and concentration.

The findings show that the 2D-model is able to capture general phenomena in the DMFC and delivers reasonable results. However, it is highly dependent on the boundary conditions set for the simulations. In order to find out how the saturations and concentrations of species distribute over the channel, a model with a different setup (“along the channel”) has to be created as a next step. This “along the channel” model in 2D should incorporate a coupling of channel transport with GDL transport and be able to predict the conditions within the DMFC single cell. Reversible and irreversible degradation models shall then be integrated in this new 2D-model in order to study the effect of heterogeneities on DMFC degradation.

The 1D+1D numerical model developed within Second Act project has been further used during the second period of the project to provide ***an insight into DMFC local operation*** in order to ***design locally optimized DMFC components***. The model has been validated with respect to segmented cell data with different configations, using the counter-flow with uniform and non-uniform catalyst loadings distribution. Results allowed to propose a relevant parabolic distribution, and adapted air flow at cathode outlet to stringly reduce heterogeneities.

The promising results achieved by means of model predictions have been validated with experimental data.

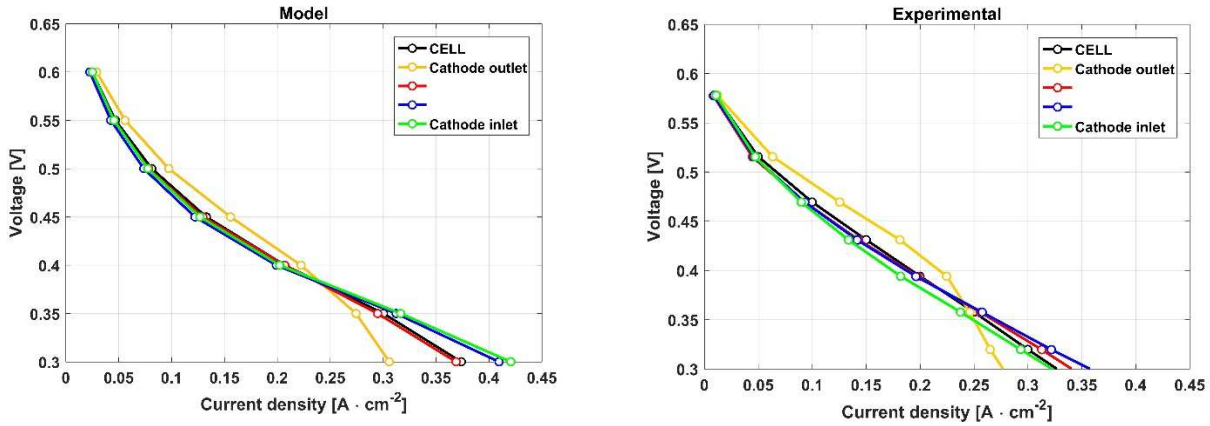


Figure 27: Simulated (left) and measured (right) local polarization curves with parabolic distribution of catalyst layer and increased airflow

In order to confirm that modeling results obtained for a 25 cm^2 DMFC can be extended to larger area, dedicated experiments have been performed on a 180 cm^2 DMFC with commercial flow fields (following EWII commercial geometry). The local polarization curves of a 180 cm^2 DMFC are consistent with the one obtained for a smaller cell: cathode inlet segment generally suffers from dehydration, while cathode outlet is usually working in limiting conditions, due to a low oxygen concentration. Moreover, cell dynamics between 25 cm^2 and 180 cm^2 DMFCs are analogous at both anode and cathode, resulting in similar Pt oxides formation and reduction mechanism. In addition, also the local evolution of cathode ECSA (expressed as percentage variation compared to the value at BoL) confirms that the trend is compatible with the same degradation mechanisms.

<u>Simulations of refresh procedure for DMFC.</u>

A physically based, ***transient 2D cell model with an along-the-channel configuration*** was developed in the DLR modeling framework NEOPARD-X in order to study ***the influence of local effects on cell performance and reversible degradation in DMFC***. The developed platinum oxide model was integrated into the 2D cell model. Galvanostatic simulations were performed.

The DMFC operation at 0.25 A/cm^2 is periodically interrupted for a refresh procedure, which is performed to recover reversible performance losses. The refresh procedure is a sequence of changing operating conditions at the cathode: First, the load is switched off, then the air flow is stopped to reduce the platinum oxide species, then air flow and current are switched on to return to the operation point. The voltage and current density evolution during this refresh procedure have been simulated.

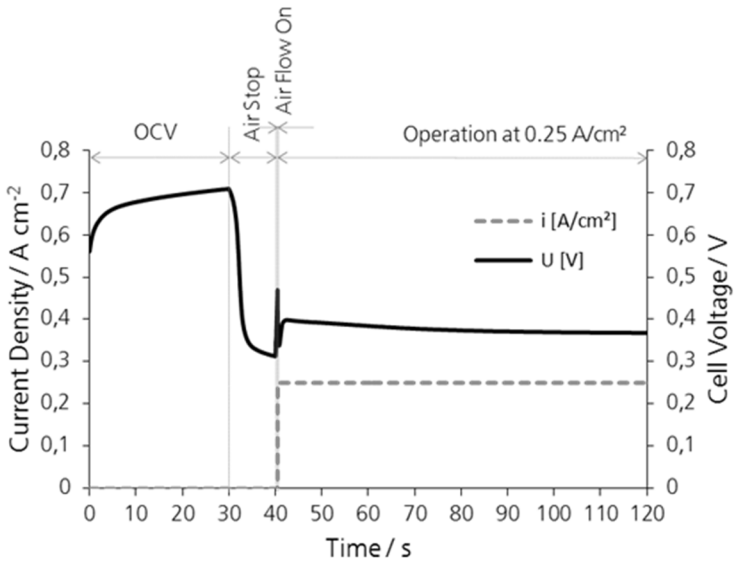


Figure 28: Simulated voltage and current density evolution during refresh procedure

The changes in the cell and especially in the cathode catalyst layer (CCL) during this refresh sequence and the initial phase of the next operating period are highly dynamic. Detailed simulations of the refresh procedure with the 2D cell model have been performed to better understand those transient effects.

During air stop, the oxygen reduction reaction (ORR) continues at the CCL-PEM interface due to methanol crossover from the anode. This leads to a full depletion of oxygen at cathode outlet, causing a drop of cathode potential and complete reduction of the platinum oxides. As soon as there is no more oxygen available, methanol accumulates in the cathode. At cathode inlet, a residual amount of oxygen remains in the CCL due to steady diffusion of air from the inlet tube into the cell. That is why the platinum oxides are only partially reduced at cathode inlet.

When the air flow is switched on, a reaction front moves through the CCL from inlet to outlet at the CL-MPL interface. Methanol, which has accumulated during the air stop, gets oxidized when the inflowing oxygen hits the CCL. This leads to strong heterogeneities in the local current densities at the initial phase of operation at 0.25 A/cm². After this initial phase, when the species concentrations in the CCL have redistributed, the cell returns to its nominal behavior at 0.25 A/cm². In the further course of operation, the formation of platinum oxides dominates the cell behavior and logarithmic voltage decay over time can be observe.

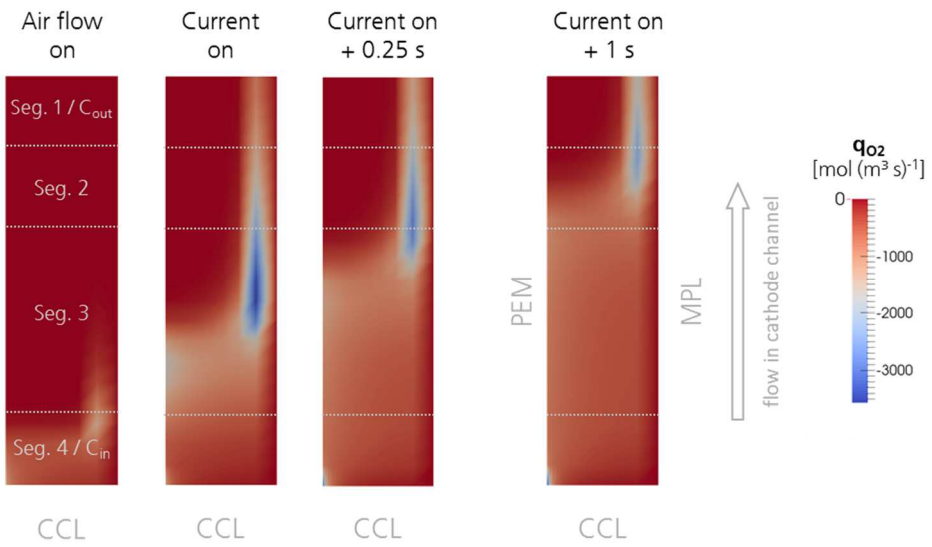


Figure 29: Oxygen reaction front in cathode CL at start of air flow and operation after refresh

Simulations of irreversible catalyst degradation for DMFC.

In order to investigate the ***irreversible catalyst degradation in DMFC***, the developed platinum oxide model has been coupled with a platinum particle growth model. Due to the complexity of the mechanisms occurring in the DMFC during transient operation, a simplified approach is followed to simulate the 500h degradation test performed at POLIMI. The platinum oxide coverages have been fixed at values which correspond to the coverages reached 5 minutes after refresh at inlet and outlet conditions respectively. With these coverages the cathode potential is hold at fixed 0.85V which corresponds to the average cathode potential at the current density 0.25A/cm² used in the degradation tests. This simplification allows simulating the catalyst degradation of the 500h degradation test in less than 20 minutes. The comparison of simulated and measured ECSA-evolution shows good agreement in the ECSA loss at inlet and outlet is achieved. In addition to the ECSA also the particle size distributions have been measured for the pristine cell and at end of the degradation test, which allows for further validation of the degradation model.

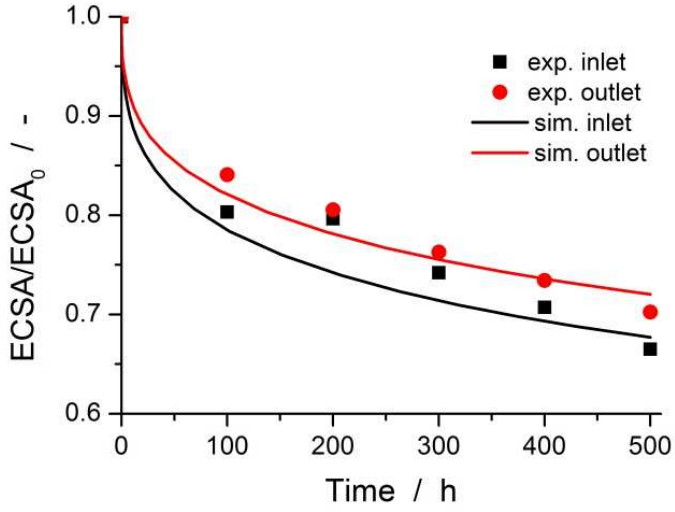


Figure 30: Comparison of simulated and measured ECSA loss during at cathode inlet and outlet during DMFC degradation test

The comparison of simulated and measured PSD at inlet and outlet shows that good agreement is achieved at the outlet, indicating that the observed ECSA loss is indeed mainly caused by the particle growth. On the other hand at the inlet the particle growth seems to be slightly overestimated by the model which indicates that another mechanism has contributed to the ECSA loss in this region of the cell.

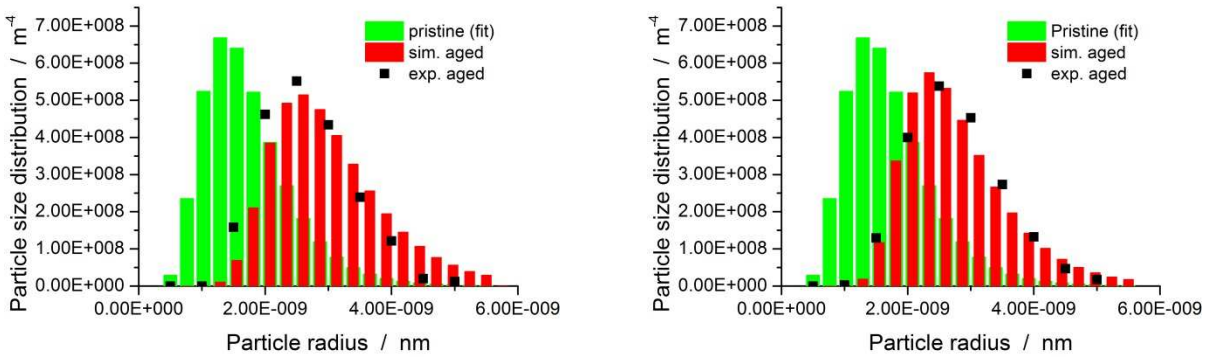


Figure 31: Comparison of simulated and measured particle size distributions at DMFC inlet (left) and outlet (right)

PEMFC case at cell and stack level (by CEA)

A 2D cell model has been developed in order to estimate the local operating conditions at the channel/MEA interface.

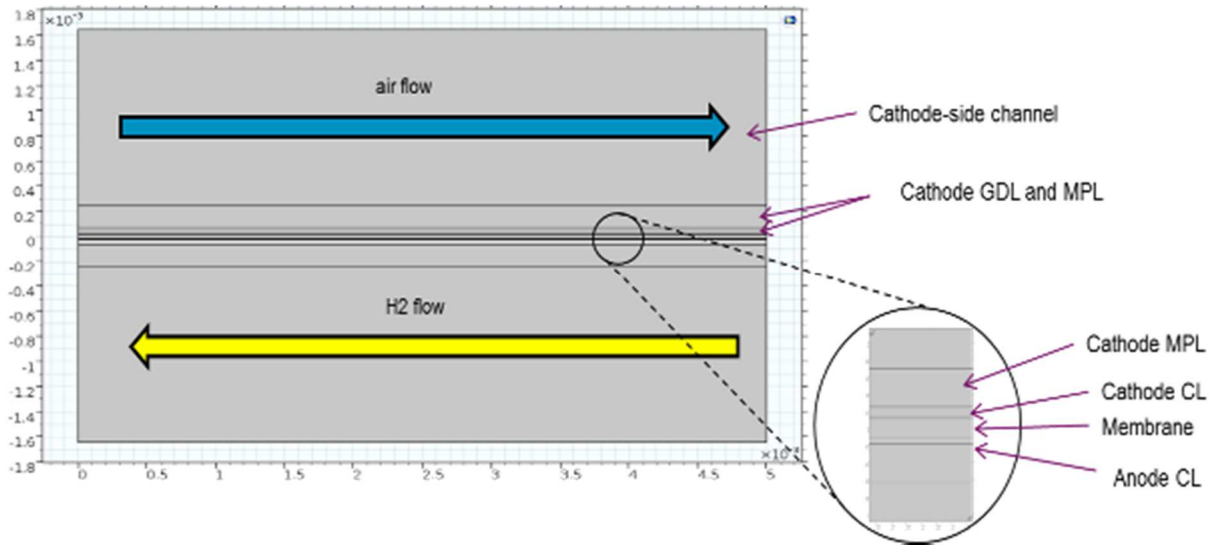


Figure 32: Cell model geometry

The model has been applied to simulate the polarization curve under Second-Act conditions. Results showed the current density profile along the channel for different current densities and the species concentrations (oxygen and vapour) in the channels and MEA. This model was then coupled with degradation mechanisms.

Parallelization of the 1D+1D DMFC single cell model, which is implemented in Matlab® environment, has been performed in order to significantly reduce the computational time, permitting the simulation of a degradation test in an isothermal stack. Once degradation models are completely developed, they will be integrated in this model to analyze heterogeneities at stack level.

PEMFC fed with reformate gas (implementation of CO poisoning model) by CEA

During this second period, the goal was to use the CO poisoning model to analyze the impact of this reversible mechanism on the heterogeneous permanent degradations of PEMFC stacks fed with reformate hydrogen. To that end, the CO poisoning module has been implemented in a transient 2D "along the channel" model to be able to capture the heterogeneous conditions inside the cell.

In order to investigate heterogeneities in PEMFC with large surface areas ***a transient physic-based 2D cell model*** has been developed. The cell geometry is simplified compared to a real cell design in the sense that only one representative channel is considered to analyze the main heterogeneities between inlet and outlet. 9 domains are considered: gas channel, GDL, MPL and CL in anode and cathode sides, plus the membrane. The model features are the same has the one of the 1D PEMFC performance model (cf. D3.1, section 4.1), and include now the Navier- Stokes equations and multicomponent transport in gas phase (N_2, O_2, H_2O, H_2 and CO) in the anode and cathode gas channels. Simulations with the Second Act operating conditions (T=65°C, 85% RH, Pa=Pc=1.2 bars, St=1.5/2) have been performed.

To validate the ***CO poisoning model***, a specific experimental poisoning diagnosis, developed during the Second Act project (See deliverable D2.4), has been used. It consists on a transition under fixed current from pure hydrogen to reformate gas with a fixed amount of CO. During this test, the cell potential decreases and the current density is redistributed over the cell area. This redistribution is captured experimentally thanks to a segmented cell (S++® type). The obtained experimental results are averaged considering 3 zones: inlet,

middle and outlet. The obtained current density maps allow to follow the progressive effect of the CO poisoning on the redistribution of the local current. This transient behavior is well captured by the developed model.

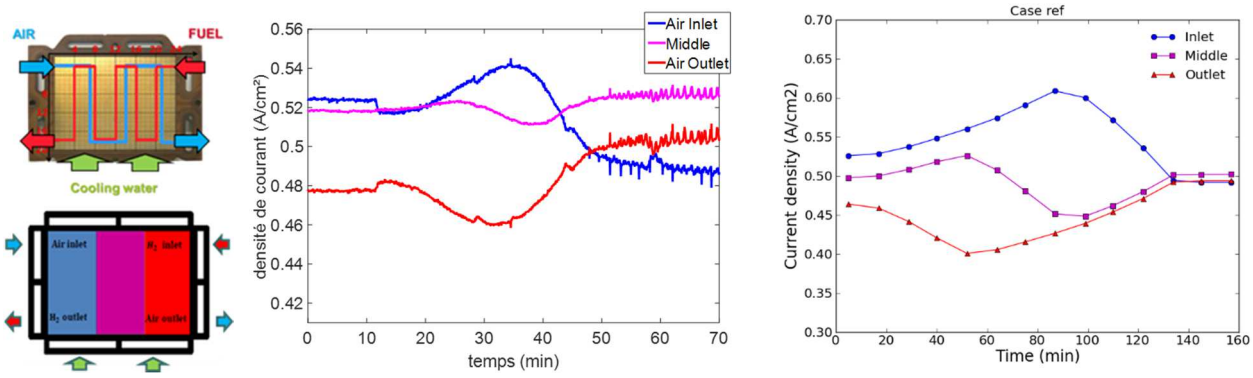


Figure 33 - Evolution of the current densities during a transition from pure hydrogen to reformate gas with 10 ppm of CO. Left: Definition of the averaging zones. Middle: Experimental results. Right: Simulation results

Furthermore, with the transient 2D model, we have access to the local physical quantities in the different compartments of the cell during the propagation of the CO front, particularly the evolution of the anode and cathode potentials during this poisoning diagnosis. The reversible loss of performance induced by the CO poisoning has a clear impact on the cell heterogeneities and this redistribution can be well understood thanks to the 2D model.

The developed model has then been used to investigate degradation heterogeneities in reformate conditions for an ageing test in short stacks of 8 large area (220 cm²) cells conducted under constant load. The simulations give further insights to analyze the ***local conditions*** between pure hydrogen and reformate with CO to try to understand the phenomena at the origin of the ***different aging behavior*** observed in stack tests in WP2 between PEMFC fed with pure H2 and those fed with reformate with ppm of CO. The analysis has also been supported with electrochemical and microscopy post-mortem analysis of the aged MEAs.

The local physical quantities (exchange current densities, concentrations, local potentials,..) in the anode and cathode for pure hydrogen or reformate with 10ppm of CO have been compared. Finally, our main conclusions are that under reformate:

- the anode potential is higher and more heterogeneous between inlet and outlet,
- the cathode potential is higher at the cathode inlet and during CO transient,
- the current density and thus the water production is higher at the cathode outlet

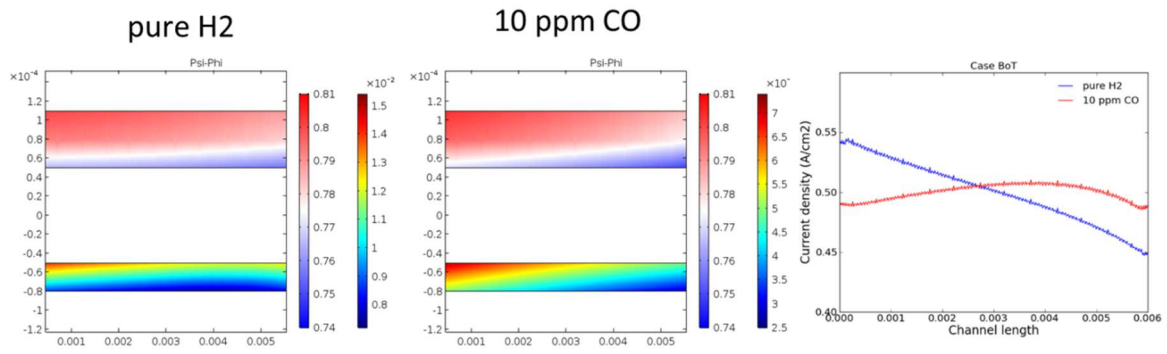


Figure 34 – Comparison of electrodes potentials (left and middle) and current density (right) under pure hydrogen and reformate with 10 ppm of CO

At the anode, the high potential at the anode outlet due to heterogeneous CO coverage promotes the Ru dissolution in this zone which increases the current density shift towards the anode inlet. Because of the CO poisoning in the anode outlet, the cathode has its highest current density at the outlet, where its potential is the lowest. This implies more local water in this zone, which promotes the Oswald degradation mechanisms. Since the Co ions do not redepose, they pollute the cathode ionomer at the outlet, increasing the local overpotential and the catalyst degradation. Given these observations, optimized MEAs have been designed, by varying the catalyst loading and its composition. These MEAs have been tested at stack level, demonstrating a clear improvement of the MEA durability.

As conclusion, coupling CO poisoning at the anode with a transient 2D performance cell model allowed to have access to the local conditions in the different compartments of the cell. Coupled to experimental local observations, they provided useful information to analyze the degradation mechanisms responsible of the strong performance decay observed in PEMFC cells fed with reformate gas and run under constant current.

<u>PEMFC fed with pure hydrogen (implementation of cathode catalyst degradation models) by DLR</u>

The ***catalyst degradation model*** developed at DLR has also been applied ***to simulate various degradation tests for PEMFC***, coupling the degradation model with ***a PEMFC transient 2D cell model*** which includes the relevant mechanisms to describe the cell behaviour.

The coupled cell model and degradation model has then be used to simulate the degradation during the ***standard catalyst degradation AST***, which consists of potential cycles between 0.6V and 1.0V with a duration of 16s per cycle. Simulating this AST is computationally demanding since it is highly dynamic. Therefore, only the first 1000 cycles of the AST performed at POLIMI have been simulated. The very fast initial drop of the ECSA is explained by the dissolution of the smallest, very unstable particles (≤1nm) which almost completely vanish within the first few cycles. Afterwards the degradation slows down due to the growth and consequent stabilization of the particles. The ECSA loss mainly occurs during the short high potential periods, because the platinum oxides have been reduced during the previous low potential periods and therefore the platinum dissolution at high potential is accelerated.

The model has also been used to ***simulate an ageing test at constant load***. The 800h PEMFC degradation test performed at DLR in which the load was hold constant at 0.5A/cm² at 65°C and 80%RH has been considered. Stronger heterogeneities with higher ECSA loss close to the membrane are obtained for the long term test, due to stronger gradients in the electrode potential and water concentration under normal operation compared to the more homogeneous distributions during the AST.

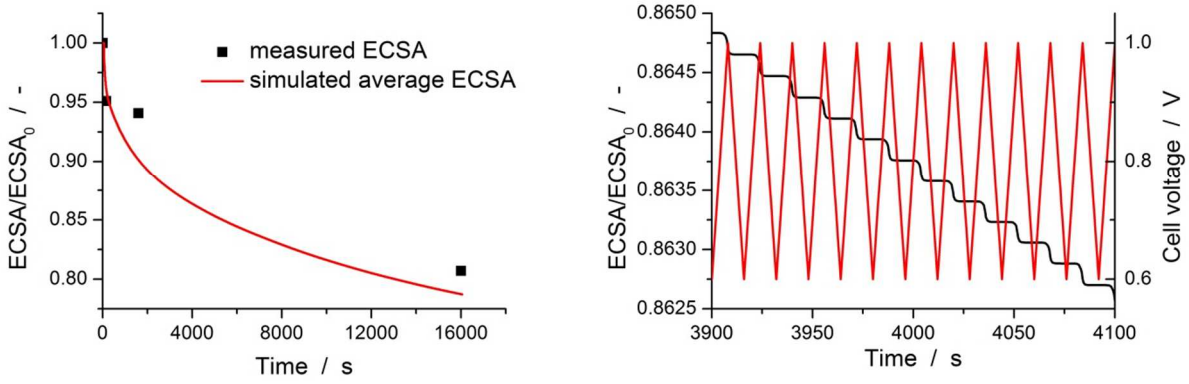


Figure 35: Comparison between measured and simulated change of ECSA during AST (left). ECSA loss mainly occurs during the high potential periods (right).

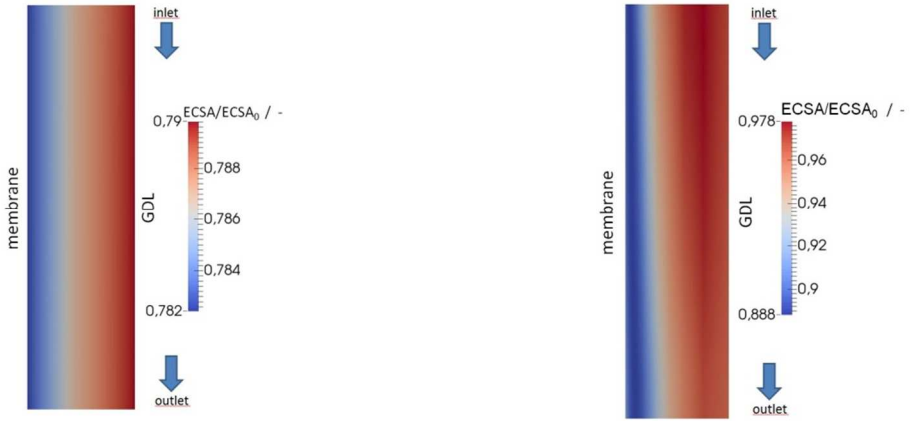


Figure 36: Simulated local ECSA after 1000 AST cycles (left) and simulated local ECSA after 800h long term test (right)

Simulation and prediction of heterogeneities at stack level

Model of PEMFC stack case by CEA.

For PEMFC, ***a multi-cell "3D" stack mode***l has been developed during the second period of the project, starting from a 2D model based on an equivalent single-cell representation. With the multi-cell model, it is possible to simulate simultaneously different cells of a stack, including their thermal and electrical coupling. After a model verification with a failure-free stack, ***two kind of defaults have been investigated***: a default in the catalyst effective surface or activity and a default in the air feeding of one cell. It has been shown that, even though the considered default can affect very strongly the considered cells, neighboring cells are only weekly affected. No long range default propagation could be observed for the considered defaults.

Model of DMFC large cell case by POLIMI.

For DMFC technology, due to the limited experimental work performed at stack level and considering that in Task 3.3 it has been demonstrated that the operation of 25 cm^2 and 180 cm^2 DMFC is similar, stack model simply reduces to parallel 25 cm^2 cell models without defaults propagation. The 1D+1D cell performance model includes all the main physical phenomena and minimizes the number of fitting parameters and computation time in order to be validated over a wide range of operating conditions, being an effective tool for components design and optimization. A detailed description of the model can be found in deliverable D3.2. During the second period of the project the model has been improved introducing in the original model an ***iterative algorithm*** that permits to solve ***counter-flow configuration*** for anode and cathode feeding. The local simulation results are then averaged in geometrical consistence with the four macro-segments of the segmented cell hardware, in order to reproduce the local results coming from the experimental activity. Moreover, since local water concentration is of crucial importance in determining cell performance, ***correlations have been developed*** and used to take into accout ***flooding and dehydration effects*** on performance.

The model simulations reproduce local experiments with acceptable accuracy. It is worth noting that it is not possible to reproduce the local polarization curves without considering dehydration and flooding effects, that play a crucial role in determining local cell performance. The model is also able to reproduce experiments varing airflow and relative umidity at cathode, further confirming that it can be used as a tool for component design and optimization.

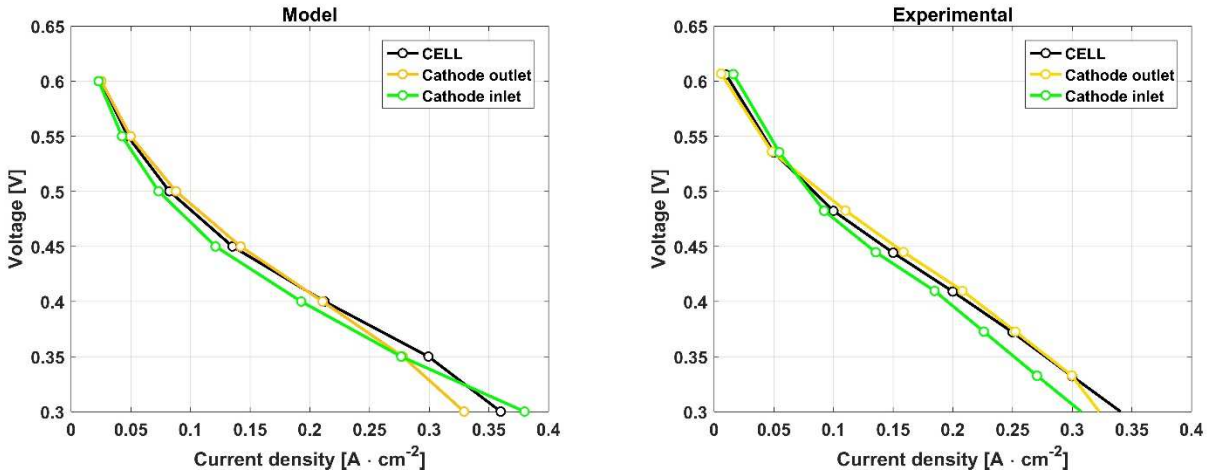


Figure 37: Comparison between simulated (left) and measured (right) local polarization curves in counter-flow.

3.3.3. Summary of durability improvements results

Two generations of improvements have been implemented on MEA level. The overall target has been to understand and in this way minimise degradation (both ir- and reversible degradation) without increasing cost. Several initiatives have been explored as described below.

For second generation MEAs, with uniform electrodes, new materials have been implemented: mainly new catalyst with more graphitised carbon support for all technologies; other GDLs for pure hydrogen operation in power stacks and at lesser extent, a novel additive (cobalt porphyrin) to anode catalyst for reformate case.

The third generation MEAs were made with selected materials and non uniform electrodes, with optimized compositions cathode side and for some cases also anode side to decrease heterogeneities and degradation rates. Reference or Improved components weer also coupled with specific operating conditions or strategy for enhanced stability.

3.3.3.1. DMFC and PEMFC single cell tests with tuned operation strategies and improved MEAs

Results obtained from single cells to stacks with the improved cathode implemented to reduce particularly reversible losses and then permanent degradation associated to the type of catalyst actually proved more stable performance for all types of fuel (DMFC and PEMFC cases). Improvement related to refresh procedures was also even more important with parabolic MEAs, locally tuned.

Effect of refresh on uniform and parabolic MEA in PEMFC single cells (25 cm²).

For PEMFC, three refresh strategies have been tested: *High-Current Refresh* not allowing a full recovery from temporary degradation losses; *Short Refresh* very quick (about 2 minutes) and more effective than the *High-Current Refresh* yet it does not recover the Beginning of Test performance; *Long Refresh* (several hours) allowing a full recovery of the Beginning of Test performance, excluding the onset of permanent losses.

Long Refresh strategy has been selected as the standard method to recover temporary degradation losses.

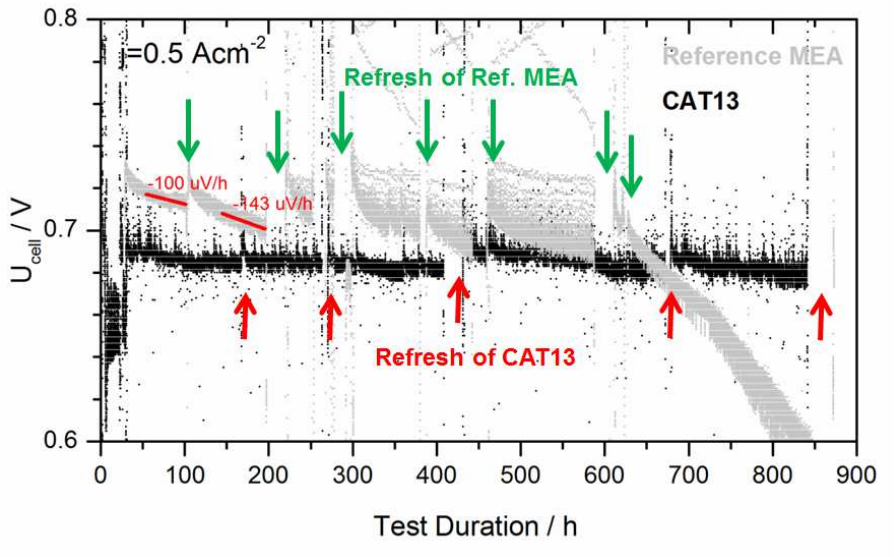


Figure 38: Comparison of durability test of reference MEA (1G) and improved MEA CAT13 (2G) performed in a 25 cm² single cell at DLR.

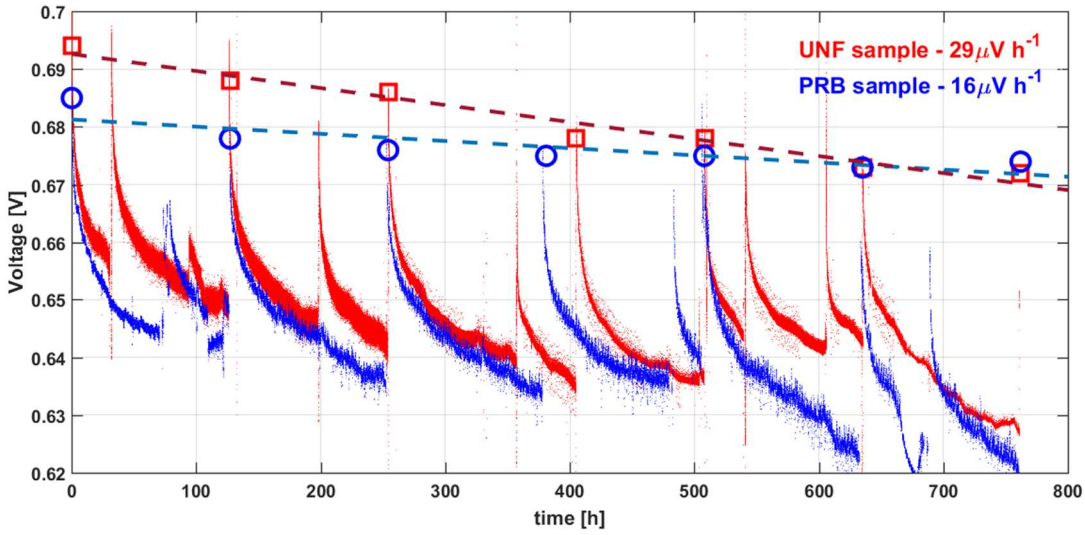


Figure 39. Voltage/Time diagram. Total test duration: 762 h at fixed current density (0.5 A/cm²). Long refresh procedure performed every 127 h. Comparison between UNF sample (blue) and PRB sample (red). Markers highlight the initial performance after long refresh.

Effect of refresh on MEA in DMFC single cells.

For DMFC, refresh strategy has been optimized for small and large single cells (with the commercial size segmented single cell specifically developed for the validation of DMFC components and local operation).

Comparison of uniform and parabolic MEA during ageing in PEMFC single cell (25 cm²)**.**

The strongly heterogeneous degradation is mostly recovered with procedures primarily intended to recover temporary degradation (such as the full refresh performed every 100 h to perform local diagnostics), pointing out the existence of a recoverable contribution to degradation heterogeneity as well as a permanent one: current decrease at cathode outlet, is compensated by current produced in the remaining areas ensuring a galvanostatic operation.

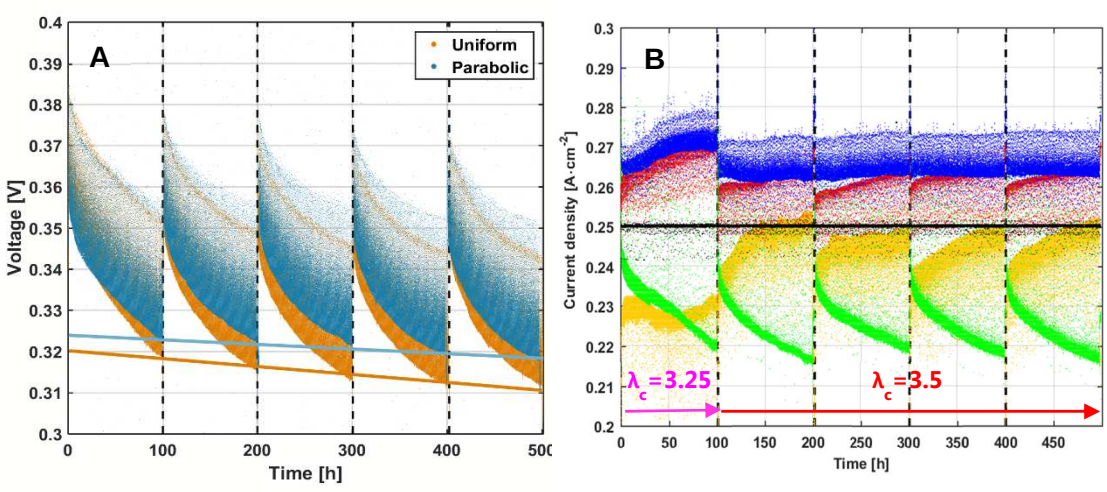


Figure 40. Voltage (A) and current density distribution (B) during 500-h degradation test for parabolic gradient MEA

Comparison of uniform and parabolic MEA during ageing in DMFC single cell (180 cm²)**.**

In the large size single cell, interruption every 100 hours are applied with the aim to recover temporary degradation and to perform the diagnostic phase. Both higher temporary and permanent degradation rates are observed, with a stronger heterogeneous operation attributed to local inhomogeneity in operating conditions enhanced by the large dimension (like in large size PEMFC cells). Concerning the whole degradation test, local current distribution undergoes deep modifications.

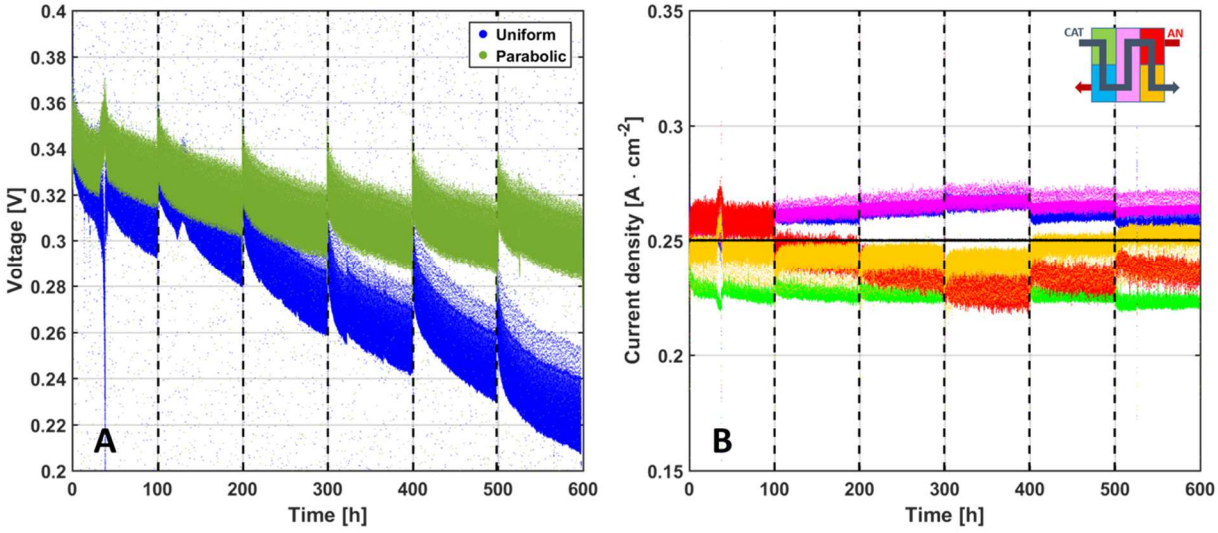


Figure 41. Voltage (A) and current density distribution (B) during 600-h degradation test for parabolic gradient mxSFC MEA

3.3.3.2. PEMFC stacks test with tuned operation strategies and improved MEAs

Performance of New MEA types in hydrogen fuelled PEMFC stacks at Nedstack

New MEAs with improved cathode material or different GDLs could be validated at stack level, confirming the gain in stability and durability for PEMFC Nedstack aged under pure hydrogen at Nedsatck and also reformate at ICI. New MEAs showed wether better performance and higher recovery at the end of ageing, or lower reversible decay under hydrogen and higher CO tolerance and endurance under reformate.

In parallel, and following conclusions of previous project Stayers, improved gaskets type were developed and manufactured in pilot and production volumes respectively for the gas and coolant gaskets for Nedstack stacks. These improved materials were tested in the Second Act full stacks that have been evaluated for durability in field tests.

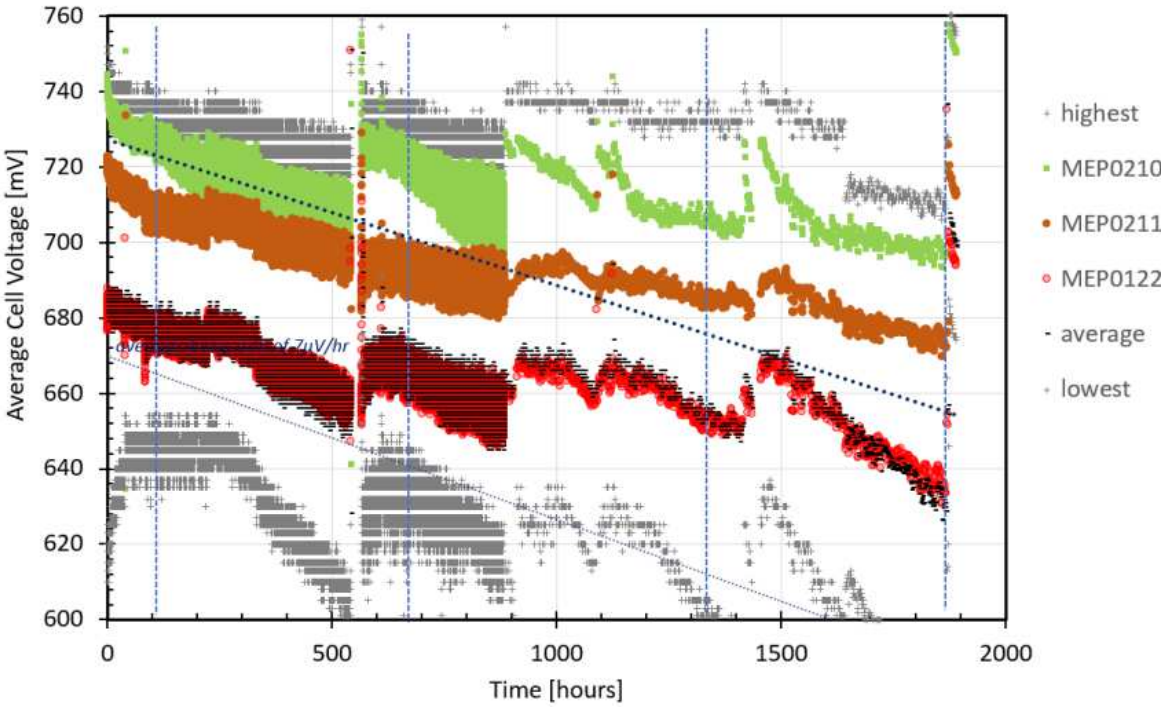


Figure 42 Operation of first improved type supplied by EWII MEP0122 and final improved types MEP0210 and -211 at Pilot plant facilities after <2khrs → MEP0210 is clearly showing a performance that is several mV in cell voltage higher and also shows a high recovery at the end. MEP0211 seems to have the lowest reversible decay.

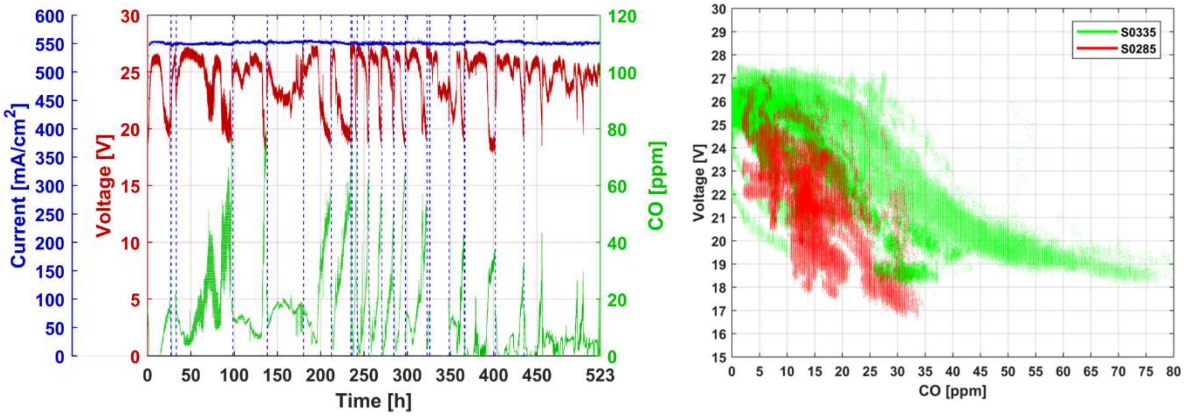


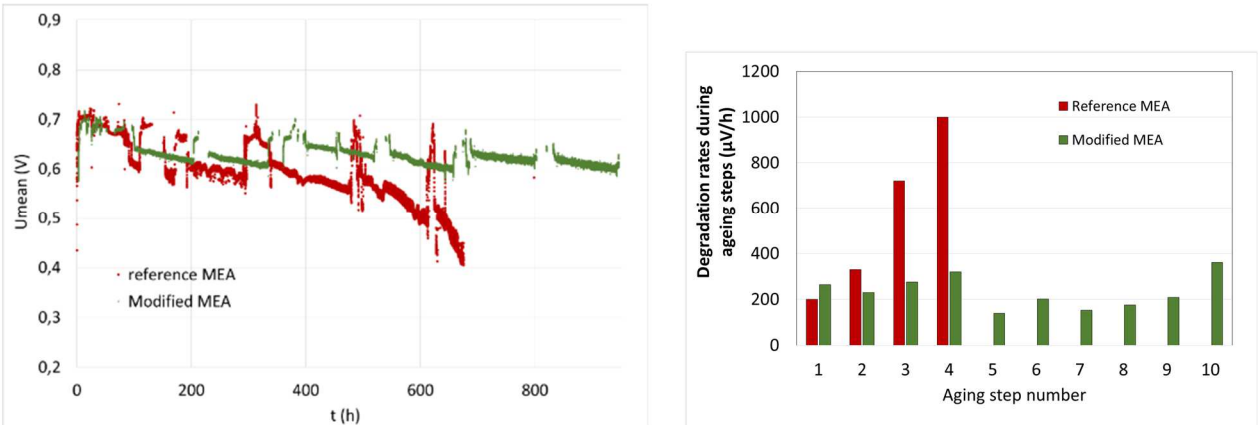
Figure 43. Nedstack S0335 voltage, current and CO trends (left) - S0285 & S0335 voltage VS. CO amount (right)

Locally improved MEAs for better durability of PEMFC stack (CEA designed 220 cm²)

After ageing in stacks under specific procedures, tuned local compositions were proposed to optimize local operation of MEAs and compensate local degradation mechanisms identified thanks to in-situ current distribution during ageing, post-mortem analyses and modelling results. MEAs were locally modified by changing in some zones both anode and cathode catalyst layers compositions.

Locally improved reformate MEAs for fixed load operation in PEMFC stack (CEA 220 cm²)

For reformate case, new MEAs were made to improve particularly their tolerance to carbon monoxide near hydrogen outlet and cathode catalyst stability towards dissolution, particularly avoinding contamination of ionomer by cobalt ions near air outlet, that were major mechanisms leading to excessive and quick performance decrease at fixed load. Results actually showed improved voltage stability allowing to more than double durability compared to the reference test with ten time lower decay rates.



a) b)

Figure 44. Voltage evolution for the two stacks made with reference homogeneous electrodes (Reference MEA) and with optimized electrodes (Locally modified MEA) (a) – Degradation rates for the two stacks (b).

Locally improved hydrogen MEAs for start-up/shut-down operation in PEMFC stack (CEA 220 cm²)

To improve endurance towards accelerated start-up/shut-down cycles, new MEAs were made to improve particularly their tolerance to carbon corrosion in the middle zone of the MEAs, where activity was totally lost. Lower platinum loading anode side and graphitized carbon cathode side were used. Results demonstrated actual improvement decreasing the losses in performance and in the electrochemical active area by five.

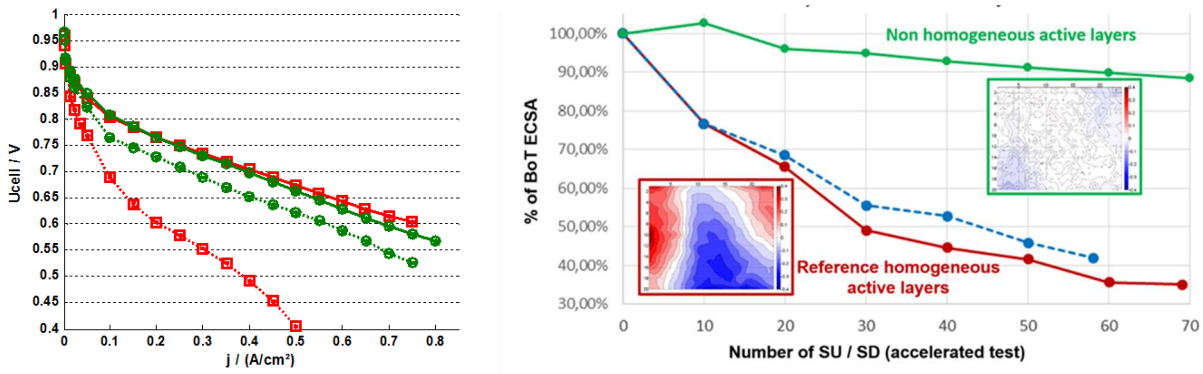


Figure 45. Initial and final polarization curves (post 70 accelerated stop-start cycles) at 60°C, 1.5 bar, RH 50/50%, Stoichiometry H_2/ air 1.5/2 (left) - Evolution of the relative decrease in surface areas for the two types of stacks with reference homogeneous MEAs (red and blue) and with locally improved MEAs (green) (right).

Hydrogen PEMFC stability improved vs. reversible losses with air starvation strategy

The selected operation strategy was to cause regular air starvation periods by reducing for short periods the air stoichiometry during the ageing. The method could actually act as prevention mean for the formation of the platinum oxides as expected. An important result of this study is to have shown that irreversible damage was not affected by 2000 hours spent under air starvation.

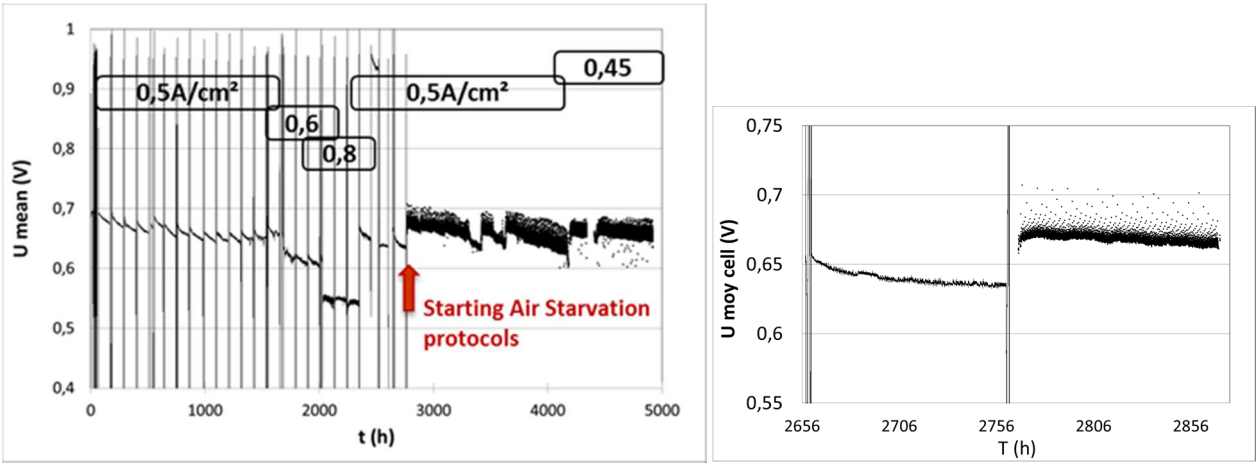


Figure 46. Evolution of the average voltage of cells on almost 5000 h during ageing steps under H2/air at fixed load (left) and passage from a step without air starvation to a step under air starvation (right) showing the slope inversion on the voltage at the beginning of the step.

3.3.4. General conclusion of the scientific and technological results

The main conclusion of the Second Act project is the demonstration that locally optimized electrodes and tuned operating conditions or strategies, as defined based on advanced investigations of degradation coupling in-situ and ex-situ experimental analyses and modelling can actually lead to durability improvements at stack level applicable in the systems.

3.3.5. Exploitation of the scientific and technological results planned

The possible exploitation of the project Second Act results is summarized for the industry partners.

EWII MEAs

Due to the Second Act project EWII has developed several new generations of MEAs. One of the improved MEAs can tolerate the gas composition that is generated by the reformer. This gas contains significant amount of CO (up to 30 ppm) that negatively affected the former type of MEA. Another very important result of Second Act is the graduated cathodes that hold a much more uniform current density and is believed to possess significantly improved durability. The Second Act work has resulted in significantly improved MEAs that show excellent performance and very low degradation rates. As for the previous generation of MEAs the new type can be manufactured in all sizes using the EWII production technology.

NEDSTACK Fuel Cell Stack

Within Second Act, NEDSTACK developed full-size 10 kWe fuel cell stacks, using two variations of EWII MEAs: pure hydrogen and reformate. The hydrogen stacks have extensively been tested by Nedstack, while the reformate stacks have been tested by Nedstack and ICI.

Several iterations of stacks were tested with pure hydrogen for durability, each time showing improved performance. The iterations produced at the end of the project are considered promising, but have only achieved limited cumulative operating time. Hence, further durability testing is required. Tests will continue and will to allow for final evaluation in the beginning of 2018.

Apart from durability tests in an industrial CHP system, stacks were also assessed for other applications and were found to be versatile, also allowing applications outside the CHP area.

Also the second iteration of reformate stacks showed to be adequate, though not performing on par with the benchmark, indicating further development in this field is required.

ICI CHP system

Within Second Act, NEDSTACK developed in conjunction with EWII (MEAs) the Full Stacks, which have been integrated into ICI CHP system. In this Full Stack module (FCS-5) LT-PEM MEAs have been implemented. The module has an output of 3 kW electrical power and is liquid cooled. The stack module is suitable for reformate from reforming of natural gas or pure hydrogen. As it could be shown within Second Act, these LT-PEM full stacks can be used for CHP applications, which are the unique selling point. The Second Act LT-PEM fuel cell module is at prototype level and needs development for stability, robustness and lifetime in CHP application. To improve the development of LT-PEM fuel cell stacks, further research projects are needed.

Thanks to the higher CO tolerance of FCS-5, the whole CHP system became more stable and able to work with reformate syngas. The CO instability caused by system perturbations (like transient between different load, natural gas pressure variation in the grid, etc.) are now better tolerate by the stack and consequentially by the whole system. This higher tolerance permits an easier control and longer operational lifetime and in the end a reduction of production cost, maintenance and operation. Further research is still necessary for the obtainment of a more competitive CHP system.

3.3.6. Dissemination

In order to openly communicate project results to the scientific community and the general public the members of the consortium provided 25 conference contributions during the second period of the project. Moreover, since mid-term review 11 articles in scientific journal have been published or submitted. Both, the conferences and the journal papers since mid- term report are listed in the following.

A common patent by EWII and Polimi was applied.

Conference and Workshop Contributions:

1. I. Profatilova, S. Escribano, L. Guétaz, D. Thoby, B. Hladys and P.-A. Jacques (CEA), *Deep insight into degradation of a PEMFC in reformate hydrogen for stationary applications,* **2017 Fuel Cell Seminar and Energy Exposition**, Long Beach, California, 07.11-09.11, **2017**.
2. A. Casalegno, A. Baricci, M. Zago (Polimi): *Experimental and Physically Based Modelling Analysis of Electrochemical Impedance in PEMFC to Interpret Performance Degradation Causes;* **232nd ECS Meeting 2017**, 5.10.2017, National Habor, MD, USA
3. T. Jahnke, G. Futter, A. Latz (DLR), *„A transient 2D PEMFC model to investigate cell performance and degradation",* **647. WE-Heraeus-Seminar***,* 02.07.-05.07.**2017***,* Bad Honnef, Germany
4. A. Baricci (Polimi), M. Zago (Polimi), T. Jahnke (DLR), A. Casalegno (Polimi): *Effect of Platinum Oxides on reversible and irreversible degradation in Polymer Electrolyte Fuel Cells;* **6th European PEFC & Electrolyser forum**, 4-7.07.**2017**, Lucerne, Switzerland
5. C. Rabissi (Polimi), M. Zago (Polimi), M. Odgaard (EWII), L. Grahl-Madsen (EWII), A. Casalegno (Polimi): *Improved durability in DMFC: local optimization of catalyst layers*; **6th European PEFC & Electrolyser forum**, 4-7.07.**2017**, Lucerne, Switzerland
6. S. Escribano, F. Micoud, A. Finkler, H. Lafôret, L. Guetaz & M. Chandesris (CEA), *Impact of the operation modes on the reversible and non-reversible degradation mechanisms of a PEMFC,* **6th European PEFC & Electrolyser forum**, Lucerne, Switzerland, 04.07-07.07, **2017**
7. T. Jahnke, G. Futter, A. Latz (DLR), *„A transient 2D PEMFC model to investigate cell performance and degradation",* **20th Topical Meeting of the International Society of Electrochemistry***,* 19.03-22.03.**2017**, Buenos Aires, Argentina
8. M.-D. Baum (DLR), C. Rabissi (Polimi), A. Casalegno (Polimi), A. Latz (DLR) and T. Jahnke (DLR): *Analysis of local heterogeneities and their effect on DMFC performance with a physical 2D cell model;* **14th**

Symposium on Fuel Cell and Battery Modelling and Experimental Validation; 02.03. – 03.03.**2017**; Karlsruhe, Germany

9. C. Rabissi, A. Casalegno, M. Zago (Polimi): L*ocal degradation analysis in DMFC*, **SECOND-ACT PUBLIC WORKSHOP ON DURABILITY ISSUES IN PEMDC AND DMFC (@FDFC 2017)**, 31.01.**2017**, Stuttgart, Germany
10. S. Escribano (CEA), *Investigation of PEMFC degradation during ageing tests on stack under pure hydrogen or reformate,* **Second Act Workshop**, Stuttgart, Germany, 30.01, **2017**
11. M. Chandesris & L. Guétaz (CEA), *Simulation and characterization of degradation mechanisms for PEMFC electrodes aged under reformate*, **Second Act Workshop**, , Stuttgart, Germany, 30.01, **2017**.
12. M.-D. Baum (DLR), C. Rabissi (Polimi), A. Casalegno (Polimi), A. Latz (DLR) and T. Jahnke (DLR): *Identification of local heterogeneities in direct methanol fuel cells with a physical 2D model;* **7th International Conference on Fundamentals and Development of Fuel Cells**; 30.01. – 03.02.**2017**; Stuttgart, Germany
13. M. Chandesris, L. Guetaz, P. Schott & S. Escribano (CEA), *A transient 2D PEMFC cell model to investigate degradation heterogeneities in reformate conditions* **7th international conference on Fundamentals and Development of Fuel Cells, FDFC**, Stuttgart, Germany, 31.01.-02.02, **2017**
14. S. Escribano, A. Finkler, M. Chandesris, L. Guétaz (CEA)*; Local Investigations of Membrane Electrode Assemblies' Degradation During and After Ageing in PEMFC Stacks Operated Under Reformate;* **7th International Conference on Fundamentals And Developments of Fuel Cells (FDFC)**, Stuttgart, Germany, 31.01.-02.02.**2017**.
15. **P. Gazdzicki**, J. Mitzel, A. Dreizler, M. Schulze, K. A. Friedrich, *Degradation of PEMFC at low loadings*, **7th International Conference on Fundamentals And Developments of Fuel Cells (FDFC),** Stuttgart, Germany, 31.01.-02.02.**2017.**
16. M.-D. Baum, A. Latz , T. Jahnke (DLR): *Understanding heterogeneities in DirectMethanol Fuel Cells – A modelling approach;* **13th Symposium on Modeling & Experimental Validation of Fuel Cells, Batteries & Electrolysers**, 22.03.-23.03.**2016**; Lausanne, Switzerland
17. M. Chandesris, L. Guetaz, P. Schott, J.-P. Poirot-Crouvezier & S. Escribano (CEA) *Investigation of degradation heterogeneities in PEMFC stacks combining local in-situ measurements, post-mortem analysis and multiphysic simulation* **67th Annual Meeting of the Int. Soc. Electrochemistry, ISE,** The Hague, Netherland, 21.08-26.08, **2016**
18. S. Escribano, A. Finkler, M. Chandesris, L. Guétaz (CEA), *Further understanding of PEMFC stack degradation thanks to in situ local measurements* **Fuel Cells Gordon Research Conference,** Stone Hill College, North Easton, USA, 07.08-12.8, **2016**
19. **P. Gazdzicki**, M. Schulze, K. A. Friedrich, *Durability Testing of Polymer Electrolyte Fuel Cells Under Stationary and Automotive Conditions*, 229th ECS Meeting, San Diego, USA (06/**2016**)

20. A. Casalegno, A. Baricci, M. Zago (Polimi): *Coupling experiments and models to interpret degradation in polymer electrolyte fuel cell*; **THERMEC 2016 International Conference on Processing & Manufacturing of Advanced Materials Processing, Fabrication, Properties, Applications,** 30.05.**2016**, Graz, Austria

21. I. Profatilova, S. Escribano, L. Guétaz, B. Hladys and P.-A. Jacques (CEA), *Towards cheaper fuel: degradation of a PEMFC in reformate hydrogen,* **EMN Meeting on Fuel Cells**, Energy Materials and Nanotechnology, Jeju Island, South Korea, 23.05-27.05, **2016**

22. C. Rabissi, M. Zago, A. Casalegno (Polimi): *Investigation of localized temporary and permanent degradation in PEMFC;* **FUEL CELLS SCIENCE AND TECHNOLOGY (FUCE) 2016,** 13-14.04.2016, Glasgow, United Kingdom

23. M. Chandesris & P. Schott (CEA), T. Jahnke & M.-D. Baum (DLR), T. A. Aarhaug (SINTEF), M. Zago & A. Casalegno (Polimi), *Investigation of permanent and reversible degradations in PEMFC and DMFC stationary applications using statistical and modelling tools,* **13th Symposium on fuel cell and battery modeling and experimental validation, Modval13**, Lausanne, EPFL, 22.03-23.03, **2016**

24. C. Rabissi (Polimi), J. L. Bonde (EWII), E. Brightman, G. Hinds and A. Casalegno (Polimi): *Novel macro-Segmented Fuel Cell approach to investigation of localized degradation in PEMFCs***, EUROPEAN FUEL CELL (EFC) 2015**, 16-18.12.2015, Napoli, Italy

25. M. Zago, A. Baricci, A. Casalegno (Polimi): *Physical modelling of cathode impedance in low temperature fuel cells,* **EUROPEAN FUEL CELL (EFC) 2015**, 16-18.12.2015, Napoli, Italy

Articles in scientific journals:

1. *Marion Chandesris, Laure Guétaz, Pascal Schott and Sylvie Escribano (CEA) "Investigation of degradations heterogeneities in PEMFC stack aged under reformate coupling in situ diagnosis, post-mortem ex situ analyses and multi-physic simulations" (submitted to JES dec. **2017**)*
2. *I. Profatilova, P. A. Jacques, D. Thoby and S. Escribano (CEA, LITEN): Impact of Electrochemical Pre-Treatment Step on Accelerated Ageing of Membrane Under Ocv Protocol in Polymer Electrolyte Membrane Fuel Cell, (Submitted to ECS trans, Dec **2017**)*
3. *Claudio Rabissi (Polimi), E. Brightman, G. Hinds, A. Casalegno (Polimi), Mitigating temporary degradation of direct methanol fuel cell via operando measurement of localised cathode potential. International Journal Of Hydrogen Energy; (submitted **2017**)*
4. *Thomas Jahnke (DLR), Matteo Zago (Polimi), Andrea Casalegno (Polimi), Wolfgang G. Bessler, Arnulf Latz- A transient multi-scale model for direct methanol fuel cells, Electrochimica Acta (**2017**) 232, pp. 215-225*
5. *Bodner M, Schenk A, Salaberger D, Rami M, Hochenauer C, Hacker V.: Air Starvation Induced Degradation in Polymer Electrolyte Fuel Cells. Fuel Cells. **2017** Feb 2;17(1):18-26. Available from, DOI: 10.1002/fuce.201600132*

6. *Matteo Zago (Polimi), Andrea Bisello (Polimi), Andrea Baricci (Polimi), Claudio Rabissi (Polimi), Edward Brightman, Gareth Hinds, Andrea Casalegno (Polimi) On the actual cathode mixed potential in direct methanol fuel cells, Journal of Power Sources (**2016**) 325, pp 714-722*
7. *Bodner M, Rami M, Marius B, Schenk A, Hacker V.: Determining Membrane Degradation in Polymer Electrolyte Fuel Cells by Effluent Water Analysis. ECS transactions. **2016** Sep 23;75(14):703-706. Available from, DOI: 10.1149/07514.0703ecst*
8. *Bodner M, Schenk A, Marius B, Rami M, Hacker V.: Air Starvation Accelerated Stress Tests in Polymer Electrolyte Fuel Cells. ECS transactions. **2016** Sep 23; 75(14):769-776. Available from, DOI: 10.1149/07514.0769ecst*
9. *Bodner M, Cermenek B, Hacker V.The effect of platinum electrocatalyst on membrane degradation in polymer electrolyte fuel cells.* Membranes ***2015***, 5*(4), 888-902*
10. *Merit Bodner; Christoph Hochenauer; Viktor Hacker (TU Graz), Effect of pinhole location on degradation in polymer electrolyte fuel cells. Journal of Power Sources (**2015**) 295, S. 336 – 348*
11. *Bodner M, Hofer A, Hacker V.: H2 generation from alkaline elctrolyzer. Wiley interdisciplinary reviews / Energy and enviroment [Electr. Res.]. **2015**; (4):365- 381. Available from: 10.1002/wene.150*

Internal workshop:

In order to share results obtained in the SecondAct related to fuel cell degradation mechanisms and processes and to discuss these results with experts and stakeholders an internal workshop on “Durability Issues in PEMFC and DMFC” was organized on 19th May 2016 in Milan, Italy, with POLIMI acting as the local organizer. Thereby both technologies, PEMFC and DMFC, are of interest since they are affected by common issues. Moreover, contributions focusing on stationary as well as on automotive applications have been planned. All invited participants have been encouraged to share their results as presentations and discuss them in the frame of the workshop. The workshop was targeted at 4 talks by SecondAct partners and 8 talks by invited speakers to be given during a single day. 27 people from Europe participated in the workshop, see D5.4. The Programme is provided in Figure 47.

Internal Workshop on Durability Issues in PEMFC and DMFC

Politecnico di Milano, Department of Energy, Room 0.09, building BL25, via Lambruschini 4, Milan, Italy

19th May 2016

Program

Time	Title	Speaker
09:00 – 09:15	**Arrival**	
09:15 – 09:30	Welcome	S. Escribano
09:30 – 09:55	Stationary PEM degradation	S. Escribano (CEA)
09:55 – 10:20	Improved Lifetime of Automotive Application Fuel Cells with ultra-low Pt-loading - IMPACT	K .A. Friedrich (DLR)
10:25 – 10:50	Lifetime investigation of automotive fuel cell stacks - results from FCH-JU AutostackCORE	A. Kabza (ZSW)
10:50 – 11:20	**Coffee Break**	
11:20 – 11:45	Modelling of GDL structure and degradation	J. Pauchet (CEA)
11:45 – 12:10	Increasing of lifetime of stationary PEM systems by prognostics and control	F. Zenith (Sintef)
12:10 – 12:35	Degradation of PEM electrolyzers	M. Carmo (FZ Jülich)
12:35 – 13:35	**Lunch**	
13:35 – 14:00	Harmonization of testing protocols	G. Tsotridis (JRC)
14:00 – 14:25	Segmented cell analysis of stack degradation	C. VanAken (Nedstack)
14:25 – 14:50	Segmented single fuel cells for degradation detection	M. Bodner (TU Graz)
14:50 – 15:20	**Coffee Break**	
15:20 – 15:55	Pt-alloy cathode catalysts for PEM fuel cells: preparation, performance and degradation	I. Gatto (CNR-ITAE)
15:55 – 16:15	Degradation issues of DMFC	A. Casalegno (Politecnico di Milano)
16:15 – 16:40	Prediction of fuel cell lifetime by a multi-scale and multi-physics approach: which targets are achieved and which challenges ahead	M. Chandesris (CEA)
16:40 – 17:00	Closing Remarks	S. Escribano (CEA)

Figure 47: Programme of SecondAct internal workshop

International workshop:

A goal agreed in the frame of SecondAct's dissemination activity was to share results on problems related to degradation of low temperature fuel cells and limitation of their lifetime. Thereby both technologies, PEMFC and DMFC, are of interest since they are affected by common issues.

In this context an international public workshop on Durability Issues in PEMFC and DMFC was organized by the SecondAct consortium on 30th January 2017 in the conference room "Reutlingen" in "Haus der Wirtschaft" in the center of Stuttgart, Germany. Moreover, contributions focusing on stationary as well as

on automotive applications have been considered. All invited participants have been encouraged to share their results as presentations and discuss them in the frame of the workshop.

In order to address a broad audience and to assure a high number of participants the workshop was organized in Stuttgart in the frame of the international FDFC conference taking place in "Haus der Wirtschaft" as well. The workshop was scheduled one day before the official start of the conference. DLR was responsible for the local organization. The workshop was attended by 26 participants, see D5.5. The Programme is provided in Figure 48**.**

Public Workshop on Durability Issues in PEMFC and DMFC

Monday, 30th January 2017

Haus der Wirtschaft (Conference Room Reutlingen), Willi-Bleicher-Straße 19, 70174 Stuttgart, Germany

	Time	Speaker	Topic
	12:30-13:30	***Light Lunch***	
Session 1	13:30-13:40	Sylvie Escribano (CEA)	Second Act Introduction
	13:40-14:10	Sylvie Escribano (CEA)	Investigation of PEMFC degradation during ageing tests under pure Hydrogen or Reformate
	14:10-14:40	Marion Chandesris (CEA)	Simulation and characterization of degradation mechanisms for PEMFC electrodes aged under reformate
	14:40-15:05	Viktor Hacker (TU Graz)	Localisation of Inhomogeneous Degradation Effects in PEFCs
	15:05-15:30	Pawel Gazdzicki (DLR)	Degradation behavior of PEMFC
	15:30-16:00	***Coffee Break***	
Session 2	16:00-16:30	Radenka Maric (University of Connecticut)	Degradation of the low Pt loading cathode and possible mitigation strategy
	16:30-17:00	Claudio Rabissi (Polimi)	Local degradation analysis in DMFC
	17:00-17:30	Rodolfo Taccani (University of Trieste)	Degradation analysis of HTPEM subjected to different ageing tests
	17:30-18:00	Jens Mitzel (DLR)	Stack-Test Project

The workshop is public and free of charge. Please register at the workshop website: http://smodell.besl-eventservice.de/L2oC6PkY6MWP/

The workshop is organized by the **Second Act** consortium (FCH JU Grant No. 621216) and is associated with the **FDFC conference**. DLR is responsible for the local organization.

Workshop contacts:
Pawel Gazdzicki (DLR, dissemination leader)
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Sylvie Escribano (CEA, project coordinator)
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Figure 48: Programme of SecondAct international workshop.

Contact to other EU projects and National projects (M1-M36)

The SecondAct consortium interacts with past and on-going EU projects that focus in MEA durability improvement to exchange ideas and profit from on-going developments. A List of EU-projects that cooperate with SecondAct are listed in the following.

Table 2: List of projects cooperating with SecondAct

PremiumAct	**Knowledge on methodology and protocols for degradation testing for H2PEM, Reformate PEM and DMFC**
Keepemalive	Knowledge on methodology and protocols for degradation testing of PEMFC for stationary applications
Stayers	Knowledge on methodology and protocols for degradation testing of PEMFC for stationary applications
Pumamind	Methodology and knowledge for fuel cell development Interactions about the degradation models and mechanisms
Matisse	Joint development of segmented cell analyses by common partners (Nedstack and CEA) Contribution to Second Act first internal workshop (May 2016) - Nedstack S++® Results
Impact	Knowledge on discrimination of reversible/irreversible degradation Contribution to Second Act international workshop (held the 30th of January 2017 in conjunction to the 7th FDFC conference which took place in Stuttgart) P. Gazdzicki (DLR) – Degradation behavior of PEMFC
Stack Test	Recommendations on tests and data processing Contribution to Second Act international workshop (held the 30th of January 2017 in conjunction to the 7th FDFC conference which took place in Stuttgart) Jenz Mitzel (DLR) - Stack test – Development of tests and procedure to evaluate performance and durability
Hycora	Exchange about methods and analyses of fuel contaminants impact

Moreover, the Second Act consortium collaborates with the EU harmonization activities related to fuel cell testing.

Second Act partners are involved in the IEA Advanced Fuel Cells implementing agreement, Annex 31 (Polymer Electrolyte Fuel Cells) and Annex 35 (Fuel Cells for Portable Applications).

Specifically, CEA and TUG are members and can disseminate key aspects of Second Act in IEA workshops. Findings were disseminated by TU Graz in Annex 34 (Fuel Cells for Transportation) in Nov. 2015.