Premium Act (n°256776)

Second period report

Publishable summary

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

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

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

For the second reporting period, the aim was to complete the investigations of MEA performance and MEA components degradation and to make use of experimental and modelling results to identify accelerating or stabilizing features among operating conditions and develop accelerated tests or operating strategies.

As for the first period, investigations have been conducted for the two fuel cell technologies, Direct Methanol and Proton Exchange Membrane Fuel Cells. Technical objectives were related to in-situ ageing tests applied following nominal reference protocols and then used to develop and validate tests allowing to accelerate the performance degradation or on the contrary to check positive impact of particular strategies. Methodology used for the development of these protocols included in-situ and ex-situ characterization of MEAs' components and modelling of the performance degradation to identify phenomena, interpret the operation and losses and understand the degradation mechanisms involved.

During the second period, specific ageing conditions have been selected and applied on reference components and also on benchmark components defined so as to present different behaviour regarding performance degradation. For both technologies, reversible and permanent degradation identified from the beginning have been further considered to allow proposing a reliable life time prediction methodology based on accelerated tests.

For DMFC, tests have been conducted in anode mode and in cell mode to clearly distinguish anode impact on reversible and permanent degradation. Thanks to deep in-situ analyses by electrochemical methods and fluids transport measurements, tuned refresh procedures have been proposed allowing to almost remove the reversible degradation, thus allowing to focus on the permanent degradation.

For PEMFC, the in-situ ageing tests following nominal conditions (reference load cycles following a day/night profile and reformate hydrogen with low CO content) allowed to confirm the common degradation mechanisms and phenomena related to cathode degradation and possibly to the membrane when particularly too high temperature is used but mainly allowed to clearly identify the ruthenium dissolution and the decrease of anode activity as the main cause for performance degradation with reformate. For PEFC, start/stops with diagnostics, air bleeding and slight increase of temperature have been validated, particularly in stack as potential positive operating methods.

Degradation analyses have been continued by mainly XPS, using a peel off method to perform chemical vertical mapping analysis from the GDL to the membrane, and transmission electron microscopy coupled with X-EDS for chemical mapping down to particles. Cathode catalyst common mechanisms with particles growth and Pt dissolution have been observed again. Main new results concern the dissolution of ruthenium that has been further analysed for both technologies. For DMFC, it seems that Ru cross-over occurs mainly at the beginning of fuel cell operation. Furthermore, the Ru can migrate to the GDLs. Additionally, the degradation of the PTFE within the gas diffusion media occurs predominantly on the anode side. For PEMFC the more interesting results concerns a new mechanism proposed with the identification of new Pt core/ Ru petals particles obtained in the membrane and allowing to conclude that Pt band catalysed Ru precipitation into the membrane. Moreover, the Ru diffusion toward the anode MPL and its precipitation into small Ru particles is also an important anode degradation mechanism that is enhanced in accelerated stress tests.

Concerning modelling, for PEMFC, the work has been focused on comparing the degradation models with dedicated experiments aiming to check the impact of oxidant or the impact of the relative humidity. Electrochemical performances (potential) and platinum surface estimation could be compared between experiments and modelling. The major influence of the gas hydration on the

cathode catalyst degradation rate has been confirmed when considering platinum dissolution. The predicted effect of the degradation on current distribution in a stack has also been qualitatively validated. However, it has not been possible to integrate also the anode catalyst pollution and degradation, and hence to simulate properly the degradation under reformate gases. For the DMFC, after working on anode catalyst during the first period, the second period has allowed to implement cathode degradation. Simulations have thus been able to confirm the trends of degradation when considering different conditions. Modelling has particularly been useful to interpret and confirm the impact of reactants and products transport or accumulation for the different ageing protocols. For the two technologies, propagation of uncertainty has been studied showing the potential impact of initial components properties on the expected degradation rates.

Thanks to in-situ and ex-situ experimental and modelling investigations, accelerating parameters have been determined and combined to design accelerated stress tests. AST are developed so as to promote main mechanisms involved in reference ageing tests. For development and validation, reference and benchmark MEAs have been used. For benchmark MEAs, the focus has been put on a parameter directly impacting on performance degradation such as the anode catalyst for PEFC and the Micro-Porous Layer for the DMFC (due to its major effect on fluid transport).

For DMFC, it was concluded that first tried load cycles AST were not relevant enough for DMFC compared to finally selected tests based on open circuit voltage periods and air interruption For PEMFC, the identified AST should include an increase of CO content with the aim to decrease CO tolerance more rapidly and can be associated with more dynamic and higher load cycles to enhance overall performance decrease.

Validation of accelerating features has been conducted in-situ with degradation rates evaluation, and components properties measurements, but also using modeling to simulate the degradation trend or ex-situ structural characterization to confirm that similar mechanisms are involved and worse impact for strong acceleration.

The general methodology developed is based on deep initial characterization of the components properties and performance. The application of nominal ageing and then of accelerated ageing tests for short and medium durations, with modeling and experimental interpretation, enables concluding about acceleration of the applied AST.

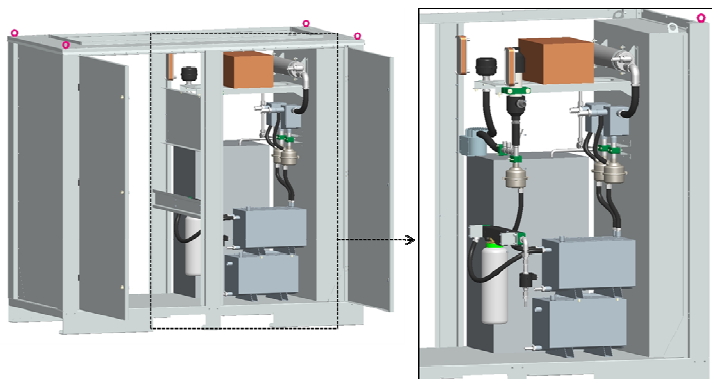**Selected illustration of SOPRANO PEMFC CHP system design adaptation:**

Figure 1: CAD view of the PEMFC-CHP SOPRANO module.

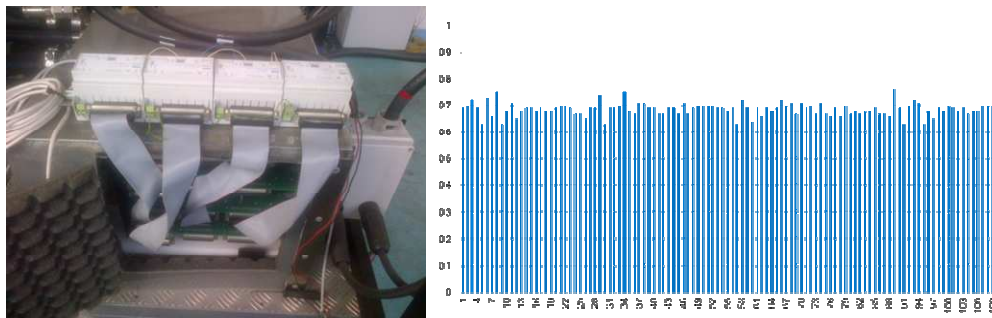## Selected illustration of ICI PEMFC system improvement:.

Figure 2: 110 single cell voltage measurement connected to one of the 4 stacks of the Sidera30 PEMFC ICI system & Voltage against the cell number in a certain moment

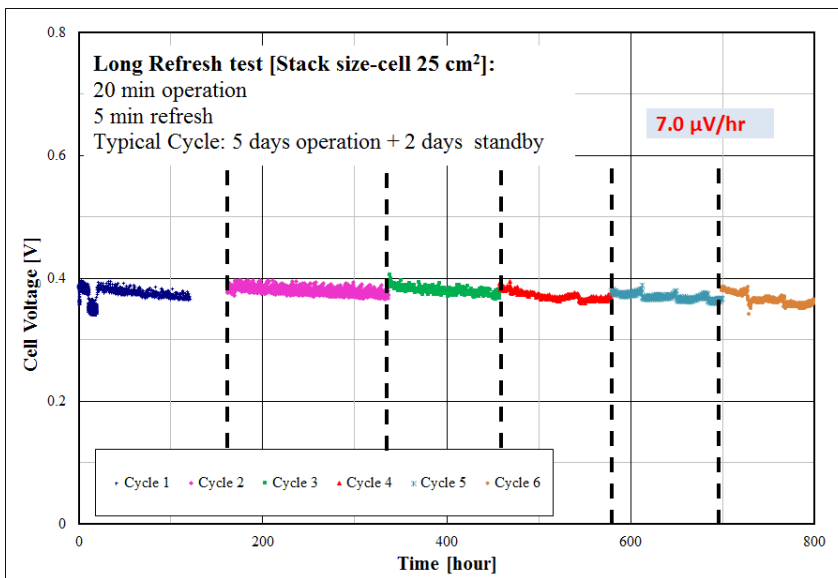## Selected illustration of DMFC operating strategy validation result (IRD):

Figure 3: validation test of the long refresh operating strategie performed on the single cell DMFC MEA's.

Selected illustration of PEMFC ex-situ analyses by TEM coupled with X-EDS (CEA):.

Figure 4: Precipitate Pt-rich core with a Ru-rich petals located in the membrane of a aged reformate PEMFC MEA and diagram depicting the mechanism leading to these particles located in the precipitation band

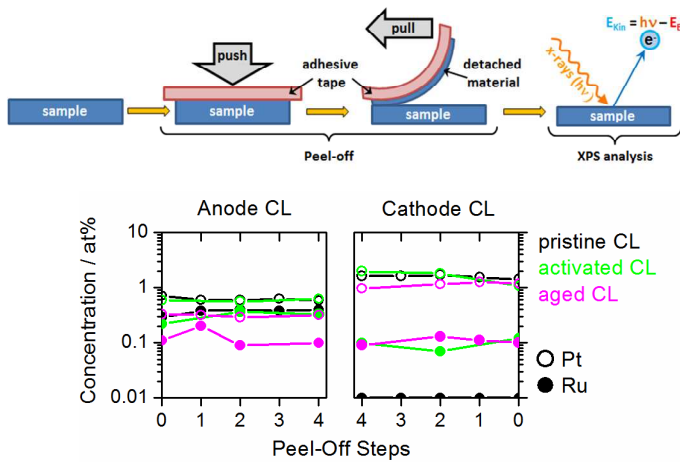**Selected illustration of DMFC ex-situ analyses by XPS (DLR):**

Figure 5: scheme of the peel-off depth profiling technique - profiles of the anode and cathode CL of the pristine, activated (30 h operation) and aged DMFC MEA (1100 h operation) showing Ru cross-over.

Selected illustration of PEMFC modelling: propagation of uncertainty (CEA).
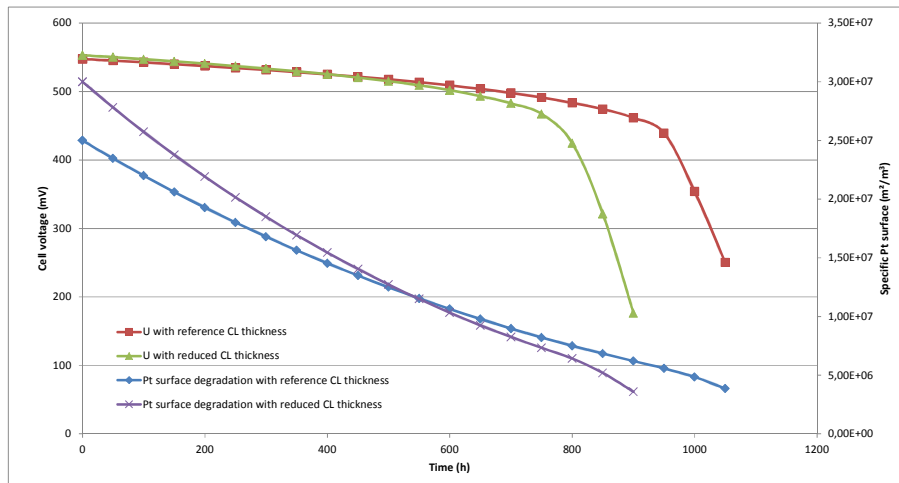

Figure 6: Effect of the reduction of the CL thickness on the degradation rate

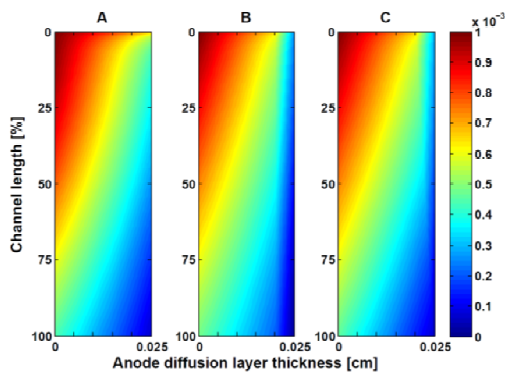**Selected illustration of DMFC modelling (POLIMI):**

Figure 7: Methanol liquid concentration across anode diffusion layer at i = 0.25 A cm-2 A) GDL of constant thickness, B) GDL+MPL of constant thickness, C) optimized GDL+MPL – Modelling result of two-phase mass transport phenomena through anode porous components.
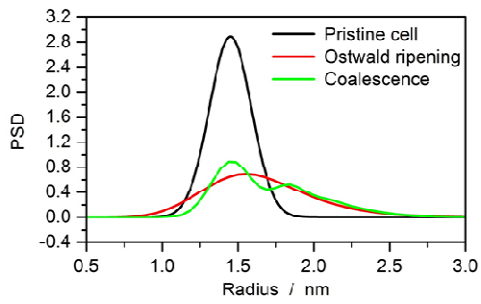
Selected illustration of DMFC modelling (DLR):

Figure 8: simulated change of particle size distribution (PSD) due to Ostwald ripening and coalescence after loss of 20% ECSA in a DMFC cathode.

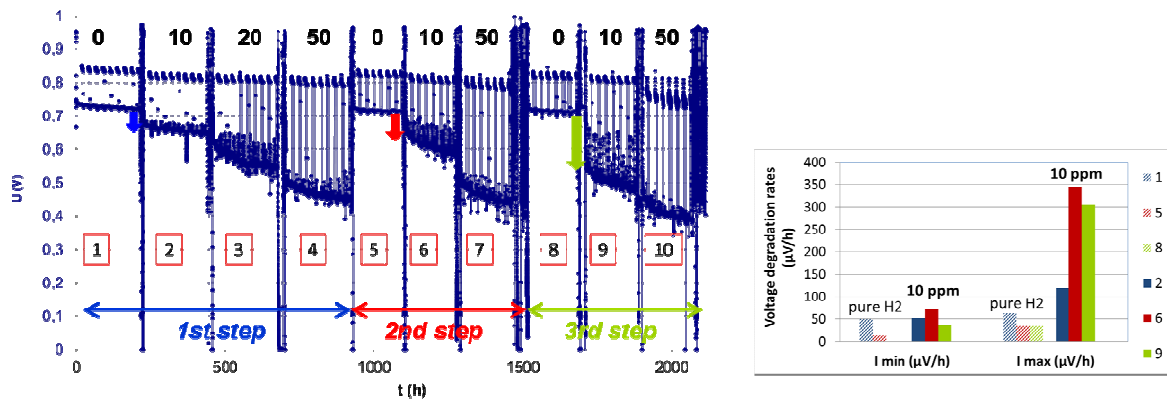## Selected illustration of PEMFC AST validation result (CEA):

Figure 9: Cell voltage along the time for a reference IRD PEMFC MEA tested under pure H2 and reformate H2 with CO contents from 10 to 50 ppm (top) and voltage degradation rates during each stage of load cycles

Selected illustration of DMFC AST and lifetime time prediction methodology result (POLMI):
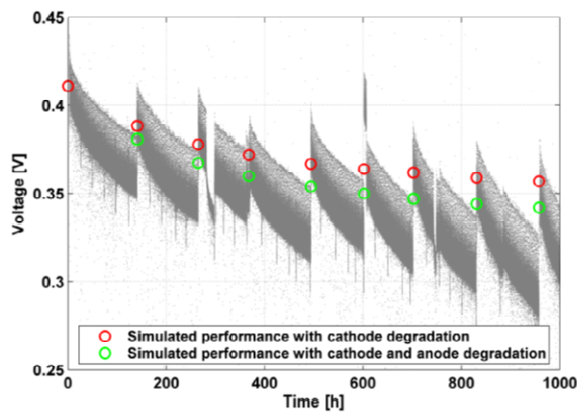

Figure 10: Simulated DMFC performance including cathode and anode ECSA reduction for reference MEA