Investigation of Degradation Heterogeneities in PEMFC Stack Aged Under Reformate Coupling In Situ Diagnosis, Post-Mortem Ex Situ Analyses and Multi-Physic Simulations

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Proton Exchange Membrane Fuel cells (PEMFCs) durability of stacks operated under reformate is investigated with a special focus on the heterogeneity of aging. During an aging test at constant load, the local performances were investigated in situ using a segmented circuit board and a specific CO poisoning diagnostic tool based on the transition from pure hydrogen to reformate containing carbon monoxide. The heterogeneities analyses are supported with multi-physic simulations which highlight the heterogeneous CO coverage along the anode, as well as the competition between both electrodes leading to non-monotonous current density profiles. At the end of life, electrochemical and transmission electron microscopy analyses were performed on three characteristic zones (air inlet/H2 outlet, middle and air outlet/H2 inlet) of the Membrane Electrode Assembly (MEA). These experimental investigations put in evidence that the cathode outlet aged more severely than the cathode inlet, while more CO tolerance was lost at the anode outlet. The degradation by the electrochemical Ostwald ripening mechanism of the Pt3Co nanoparticles at the cathode outlet is suspected to pollute the ionomer, leading to the observed accelerating performance losses. Finally, optimized MEAs have been designed to mitigate the suspected degradation mechanisms, and tested at stack level demonstrating a clear durability improvement.

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Manuscript submitted December 4, 2017; revised manuscript received April 6, 2018. Published April 19, 2018. This paper is part of the JES Focus Issue on Proton Exchange Membrane Fuel Cell (PEMFC) Durability.

Fuel cell based micro Combined Heat and Power systems (μCHPs) are one of the interesting options to increase energy efficiency in residential sector. Among the various fuel cell technologies, polymer electrolyte membrane (PEM) type are deeply investigated for these systems thanks to their low operating temperature, high power density, excellent dynamic response and commercial availability. Although significant progresses have been made to increase the performance of the PEMFC, durability still remains an important issue to reach the 40,000 h operating time requested for stationary application as targeted by the US department of energy.1,2

Furthermore, the main source of hydrogen is currently reformed hydrocarbons which contain traces of carbon monoxide (CO), known to be harmful to the anode. Using selective oxidation process, CO concentration can be reduced to few ppm, but at non negligible cost. Due to the CO preferential adsorption on Pt, the hydrogen oxidation reaction is inhibited on the anode, reducing drastically the performance of the fuel cell. This phenomenon is known as “CO poisoning”. It can be mitigated using air bleeding (air is introduced into the anode stream to enhance CO oxidation on the Pt surface)3 or using Pt-Ru anode catalysts which are more tolerant to CO, by promoting additional pathway for the oxidation of CO from Pt.4 Unfortunately, these two mitigation strategies can be detrimental to the PEMFC durability due to the presence of oxygen at the anode which can enhance membrane degradation and the low stability of ruthenium causing sharp degradation of fuel cell performances.5

Concerning the fuel composition, there is a standard (ISO 14687-2-2012) specifying “quality characteristics of hydrogen fuel for utilization in proton exchange membrane (PEM) fuel cell road vehicle systems” limiting CO to 0.2 μmol/mol. For the stationary applications, a draft document was also prepared (ISO 14687-3-2012), where the limiting characteristics for the reformate case are 50% minimum of hydrogen and a quite higher content of CO than for vehicles of 10 μmol/mol of CO.

Numerous publications6–12 describe degradation or durability studies aiming to correlate performance, properties and structure modifications when submitting the Membrane Electrode Assembly (MEA) to some specific aging tests. They present how performance decay rate strongly depends on the operating conditions (current or voltage load, stationary or cycling load, temperature, gas humidity) and on the degradation mechanisms affecting the fuel cell components.

If the CO poisoning has a reversible effect on performance losses, it also affects the permanent degradations of the cell which are different from those reported for stacks operated under pure hydrogen. Indeed, the presence of CO leads to a redistribution of local current density as shown for PEMFC fed with 2 ppm CO,13 affects both anode and cathode potentials,14 and can impact the cathode active layer degradation.15 Fundamental studies are also dedicated to the CO-contamination impact on the PEMFC performance or components13–15 mainly focusing on issues and conditions related to the automotive application. However, few studies address the impact of CO poisoning on PEMFC durability. Studies are most often performed at single cell level including short durability tests16 or long term test under CO-containing fuel but conducted using air bleeding.17 Indeed, reduction of the degradation in the case of ageing under reformate are mostly considered through the adaptation of the operating conditions such as air bleeding, temperature or humidity control, cleaning procedures including steps or pure hydrogen feeding to remove the CO adsorbed. More recent papers present interesting long-term durability studies with contamination issues at stack or system level but with air contaminant18 or with only non-controlled CO traces,19 thus allowing few direct comparison with studies conducted at stack level with CO content representative of a reformate stationary case.20,21 Recently, focus has also been put on the analysis of the heterogeneities of degradation thanks to local post-mortem analyses performed in different zones of the aged MEAs22,23 or thanks to in situ measurements techniques allowing direct information about local performance or electrochemical properties. Modelling and simulation have also been used extensively during the past years to investigate the performance of PEMFC.24 Indeed, numerical studies provide detail about local quantities that are difficult or even impossible to measure operando in the different components of the cell. However, few PEMFC models incorporate degradation phenomena, especially for the analysis of cells with large area.

The purpose of this work is to better understand the impact of operating under reformate with CO on the performance losses of a
fuel cell stack, focusing on the localization of all the degradation phenomena and on the correlation between the decrease in performance of the MEAs and the degradation of the electrode functional properties and microstructure. To that end, an aging test at constant load on a short stack of 8 cells with 220 cm² active area has been carried out using reformate gas and operating conditions classical for stationary applications. The evolution of the local current density during aging has been monitored in situ using a segmented circuit board. Specific tools have been developed and applied, with particularly a so-called “CO poisoning diagnostic” enabling to estimate the local CO tolerance of the MEAs and its modification during aging. In parallel, a transient two-dimensional PEMFC model that incorporates CO poisoning has been developed to simulate both anode and cathode local potentials for further interpretation of local conditions specific to operation under reformate gas in large cells. Post-mortem ex situ analyses are then added to elucidate the local mechanisms actually occurring thanks to local electrochemical properties measurements and microstructure observations. Considering the conclusions of the coupled experimental and simulation investigations optimized MEAs have been designed and tested at stack level, demonstrating a clear durability improvement.

Experimental and Simulation Tools

Test station and PEMFC stack.—The test bench is designed to provide a precise control of the operating conditions. The station has three gas lines at the fuel side in order to simulate reformed hydrogen, thus including carbon dioxide, carbon monoxide, methane and air (for air bleeding). Investigations were conducted on a short PEMFC stack of 8 cells with 220 cm² active area. Each cell is composed of one MEA and one metallic Bipolar Plate (BP). The MEAs are made of a 20μm thick reinforced Nafion HP membrane and the catalyst loadings are 0.52 mg/cm² and 0.4 mg/cm² on anode and cathode with 50% w/w PtRu/C and 52% w/w Pt/C respectively (corresponding to TKK references are TEC66V50 and TEC36V52). Gas diffusion layers are SGL 24 BC on both sides. The bipolar plates have been designed by CEA and are composed of two welded thin stamped stainless steel sheets with multi-serpentine flow fields. As described in Refs. 21, 28 and illustrated Figure 1, anode channels have five vertical passages from the inlet (top right corner of the cell) to the outlet (bottom opposite side), while cathode channels have three vertical passages from the inlet (top left corner) to the outlet (bottom opposite side), that leads to mixed co-counter flow regions.21 The coolant flow field pattern is then induced by the assembly of the anode and cathode plates. This convention is used along the paper to report the local current density measurements recorded with the segmented circuit board.

Test protocol.—The aging test has been performed under operating conditions classical for stationary applications: stack temperature of 65°C, gas pressures of 1.2 bar on both sides, stoichiometry of 1.5 for the fuel and 2 for the air, relative humidity of 85% on both sides. A fixed current of 0.5 A/cm² is applied to the stack. During the aging test the fuel used to simulate reformate hydrogen, based on the specification of the fuel processor used by our partner in their μCHP systems, is composed of 75.5% of hydrogen, 24% of carbon dioxide and 10 ppm of carbon monoxide, concentration consistent with the recommendation of the current standard for stationary applications. Electrochemical diagnostics have been performed after steps of roughly 120h.

In situ diagnostics.—Electrochemical characterization.—In order to investigate the global performance decay, electrochemical diagnostics have been performed after steps of roughly 120h of aging tests. Polarization curves have been performed under both pure hydrogen and reformate fuel of same composition as used for the aging test (10 ppm of CO) to investigate performance losses related to both anode and cathode degradations. Cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) have been used to evaluate the modifications of respectively anode and cathode electrochemical active surface area (ECISA) and MEA resistances caused by aging. EIS measurements have been conducted on cells and at stack level in the same operating conditions as the polarization curves. Cyclic voltammograms have been recorded at 60°C, with hydrogen and nitrogen gas pressures of 1.5 bar and relative humidity of 50% on both sides, for both anodes and cathodes of five cells (#1, 3, 4, 6 and 8) to ensure getting relevant information with verified repeatability among cells of the modifications caused by the aging test.

Local in situ diagnostics: segmented circuit board.—Local in situ diagnostics consist in the measurement of the current density and temperature distributions over the cell surface. These measurements are carried out using a printed circuit board (S++ current scan line measurement device),29 whose principle is recalled elsewhere. The card is located in the middle of the stack, between cells 4 and 5, in contact with the anodic and cathodic monopolar plates of the two adjacent cells. The card is designed according to the geometry of the cell, to cover the entire MEA surface. For the studied BP design, the current is measured on 480 (24 × 20) segments of 0.49 cm², with a resolution of 0.01 A/cm². The raw data of the cartographies are post-treated before being analyzed in order to adjust the measure of each segment to the effective area of the electric contact between the device and the plate ribs using the methodology developed for the same BP design in Refs. 28, 30. This procedure gives access to the Current Density Distribution Maps (CDDM) during the whole test.

Specific CO poisoning diagnostics.—The effect of CO poisoning on performance is commonly estimated through polarization curves performed with different fuel qualities when the stack is operated under pure hydrogen and under reformate. Record of CDDM with the segmented circuit board allows to see the impact of fuel on the heterogeneities. Under reformate fuel, the relative activity of the MEA is lower at the air inlet/fuel outlet zone, when comparing to the initial current distribution under pure hydrogen. This modification in the current distribution is attributed to the higher CO effect caused by a lowest hydrogen partial pressure in this region. The evolution of the CDDM during the transition from pure H₂ to CO polluted fuel can also be used to analyze the contamination process and its impact on
local performance. The slow kinetics of the poisoning phenomenon enables to record CDDMs with sufficient resolution during the whole contamination process, which is lasting at least few tens of minutes. In the case of aging under reformate, evolution of CDDM during the transitions from pure hydrogen to reformate fuel is used to follow the impact of aging on the MEAs’ behavior and to investigate how the local tolerance is affected.

A poisoning test has thus been proposed as a specific degradation diagnostic tool. It consists of a transition under fixed current from pure hydrogen to reformate gas with a fixed amount of CO that has been applied before and after each aging period. During this test, the cell potential decreases and the current density is redistributed over the cell area. The contamination is considered completed when the cell voltages are stabilized. The current redistribution is captured experimentally thanks to the printed circuit board. Based on the stack cell design and first CDDM analysis, three regions showing common behavior on an averaged basis have been identified: air inlet/fuel outlet zone, middle zone and air outlet/fuel inlet zone as described on Figure 2. During the transitions, the local current is averaged over these three zones of interest in order to get, in addition to the CDDMs, quantified features of the CO poisoning diagnostic.

Typical evolution of the three zones averaged current density is presented on Figure 2b for a selected transition experiment. The first identified information is that at beginning of the experiment, e.g. under pure hydrogen, the averaged current density is similar in two zones (middle and air inlet) and lower in the air outlet zone, attributed to lower cathode activity here mainly caused by lower oxygen partial pressure. The second clear feature appears after about 12 minutes with a sharp change on the current densities at air outlet and inlet zones, indicating the effect caused by the addition of CO in the fuel, enabling to clearly identify the moment when pure hydrogen is replaced by reformate. From this point, the current density starts to decrease at air outlet corresponding to the H₂ inlet, first zone obviously affected by the anode catalyst CO contamination, while the current density is slightly increased in the zone nearby to compensate and maintain at a fixed value the overall average in current density. Then the CO contamination process being progressively continued toward the fuel outlet, the relative distribution in current densities is changing, with the fuel inlet zone reaching a minimum when the CO contamination is completed for this zone and already started for the rest of the MEA surface. Around 35 minutes the current density reaches a maximum for the air inlet zone indicating that after fuel inlet and middle zones coverage, the air inlet e.g. fuel outlet complete contamination starts with local decrease of the current density in this zone while it is increasing in the two previously contaminated zones. The stabilization of these three averaged current densities indicates that the contamination process is completed over the whole MEA surface. The final relative distribution of current densities shows that the middle zone is the less modified compared to pure hydrogen relative distribution, while the air inlet e.g. fuel outlet zone presents the major relative losses, on the contrary of the air outlet e.g. fuel inlet zone.

**Post-mortem characterization.**—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 functional properties and microstructure. As the local operation conditions are not homogeneous through the MEA surface area, it is important to analyze the MEA component degradation mechanisms in different zones of the MEA surface area. Most relevant locations were determined considering the CDDM at the end of aging. Samples analyzed were located in the three main zones: air inlet, middle and air outlet. Cyclic voltammetry measurements have been performed on these samples considering small size MEAs of 2 cm² in a small single cell to evaluate the local electrochemical properties of the electrodes, particularly to help interpretation of the in situ local behavior by probing the local cathode and anode electrochemically active surface area (ECSA) losses. CVs are conducted at ambient temperature with humidified nitrogen on the targeted electrode side and humidified hydrogen on the other side, with flow rates of 500 ml/min to keep homogeneous behavior and high humidification. The voltage range for the CV was from 0.1 V to 0.6 V on the anode and 0.7 V on the cathode vs. reversible hydrogen electrode with a scan rate of 50 mV/s. ECSA was not explicitly calculated because Pt₂Co and PtRu catalysts are used instead of pure Pt, and it was considered that the assumption of an adsorption charge of 210 μC/cm² is valid only for pure Pt. Nevertheless relative comparisons of the coulombic electric charge calculated from the area of the hydrogen desorption peak and of voltammogram shapes are still fully valid. Cross-sections of MEAs taken in fresh MEA and in the air inlet and air outlet zones of an aged MEA were observed by transmission electron microscopy (TEM). For these observations, the MEA samples were embedded in epoxy resin and cut in 70–90 nm thick slices using a LEICA ultramicrotome. The observations were performed in high-angle annular dark-field/scanning TEM (HAADF/STEM) mode on a FEI Titan-Themis microscope operating at 200 kV, equipped with a spherical aberration (Cs) probe corrector and a Super-X system (4 Silicon Drift Detectors), allowing acquisitions of X-ray energy dispersive spectroscopy (X-EDS) elemental maps with a near-atomic resolution.

**Numerical tool.**—A two-dimensional (2D), transient PEMFC cell model has been developed in order to investigate heterogeneities in PEMFC with large surface area. The cell is meshed from the channel inlets to the channel outlets and through the thickness of the MEA. This model incorporates the description of CO poisoning at the anode in order to investigate its impact on the local conditions inside the cell. Since the model is transient and 2D, it is able to capture the current density evolution over the cell surface during a CO pollution event.

**Performance model.**—The cell geometry of the model is simplified to an equivalent single channel, which allows studying the main heterogeneities between gas inlet and outlet along the channel, without the computational cost associated to simulations on the real design.
In this model, the channel-rib effects are not accounted for. The modelling domain is based on nine different layers from the anode and cathode gas channels, to the entire MEA (Figure 3) including the polymer electrolyte membrane, the catalyst layers (CL), the microporous layers (MPL) and the gas diffusion layers (GDL). The different components are modeled explicitly and are connected through appropriate boundary conditions. A continuum-level approach is used to describe each component. Such a multi-physics and continuous modeling approach is becoming more and more classical for the study of PEMFC and different variants can be found in the literature, but few of them are two-dimensional including the catalyst layer thickness as well as the gas channels and, to the best of our knowledge, none are coupled with degradation mechanisms. In the present model, water is considered either in his vapor phase or as a dissolved species in the electrolyte. Liquid water is not accounted for and the model is isothermal. Oxygen, hydrogen and nitrogen concentrations are considered in the gas phase (channels and pores) and as species dissolved in the ionomer. The main physical phenomena are succinctly described below. A full description of the equations of the performance model can be found in Ref. 35. The CO poisoning mechanisms are superimposed to this performance model.

Mass conservation and transport.—In the channels the total gas convection is described by the Navier-Stokes equation solved together with the mass balance of the total gas concentration. To account for gas diffusion, a mass balance for each species minus one is written, and the Stefan-Maxwell equations are considered to evaluate the diffusive fluxes. In the porous media of the anode and cathode GDLs, MPLs and CLs, the mass balance for each gas species is considered. The diffusion and convection fluxes are written together with a modified form of Stefan-Maxwell, Darcy and Knudsen equations introduced by Young and Todd. This approach allows to mathematically interpolate between the two limiting cases of pure gaseous diffusion that occurs in large pores (in the GDL) and Knudsen diffusion that occurs in very small pores (in the CL). Conservation of momentum is then expressed by a relation between the pressure gradient of the total gas and the sum of the diffusive fluxes using mean transport properties following Young and Todd’s approach. In the catalyst layer, the reactant gases (oxygen at the cathode side and hydrogen at the anode side) are supposed to dissolve in the electrolyte phase, and have to diffuse through the ionomer layer surrounding the Pt/carbon (which can be viewed as a very simplistic agglomerate model) before reaching the catalyst surface. Mass balance for the dissolved gases at the platinum surface is thus written including sources terms related to the consumption of reactants at the catalyst surface and source terms related to the reactant dissolution and diffusion in the “agglomerate”. Diffusion of the dissolved species through the membrane is also taken into account, allowing to estimate cross-over current (related to hydrogen flux from anode to cathode) and effect of oxygen at the cathode on CO poisoning.

The amount of water in the electrolyte of the CLs and in the membrane is also estimated, taking into account diffusion and electro-osmosis fluxes. Mass balance is written considering sources terms related to the water production at the catalyst surface and water absorption in the electrolyte.

Ionic and electric transport.—The ionic potential distribution is computed in both the membrane and the CLs, while the electric potential distribution is computed in the CLs and diffusion media (MPLs and GDLs). The ionic and electric potentials are obtained from the conservation of total charge, assuming electro-neutrality, steady-state and a transport of charges following Ohm’s law. The empirical law of Springer et al. is used to describe the ionic conductivity dependence to the electrolyte water content and the source terms of proton and electron in the catalyst layers are related to electrochemical reactions through Faraday’s law.

Reaction kinetics at the cathode.—At the cathode catalyst layer, the oxygen reduction reaction (ORR) is considered:

\[
\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O
\]

The classical Butler-Volmer equation is used to relate the kinetic of this reaction, to the cathode overpotential \( \eta \) via the exchange current density \( i_0 \).

\[
i = i_0 \left[ \exp \left( \frac{a_n F \eta}{RT} \right) - \exp \left( -\frac{(1 - a_n) F \eta}{RT} \right) \right]
\]

\[
i_0 = n F k_b T e^{\frac{a_n}{2}} \left( \prod_{j \neq 0} a_j^{\gamma_j} \right)^{1 - a_n} \left( \prod_{j \neq 0} a_j^{\gamma_j} \right)^{\alpha_n}
\]

where \( a \) is the specific surface area of platinum, \( \alpha \), the cathode charge transport coefficient, \( n \) the number of exchanged electron (equal to 2), \( F \) Faraday’s constant, \( R \) the universal gas constant, \( T \) the temperature, \( k_b \) and \( E \), respectively the pre-exponential factor and activation energy associated to the ORR, and \( a_j \) are the activity coefficients of the different reactants and products, \( \gamma_j \) is the stoichiometric factor of the species in the reaction and \( \gamma \) the reaction order. The overpotential is defined as the difference between the electric and ionic potentials and the equilibrium potential of the reaction which is assumed to follow Nernst’s equation.

CO poisoning model at the anode.—At the anode, HOR is decomposed into several reaction steps which are put in competition with CO poisoning. Mechanisms of CO poisoning at the anode have been largely studied, and 1D models have been reported in the literature. In this work, we consider the adsorption/desorption of CO on the catalyst surface, the electrochemical oxidation of CO, as well as the chemical oxidation of CO by dioxygen present in the anode. CO oxidation in presence of oxygen provides an additional path, allowing to remove CO from the catalyst surface at a faster rate. Dioxygen can be present at the anode because of internal air-bleeding.

Figure 3. Schematic description of the two-dimensional computational domain including fuel and air inlet/outlet in counter-flow configuration.
(oxygen cross-over through the membrane) or external air-bleeding (oxygen is added in the anode gas stream). Thus, to model CO poisoning at the anode we consider CO diffusion and convection in the anode side, as well as oxygen coming from the cathode side through the membrane. The conservation equation for the CO concentration, $C_{\text{CO}}$, is considered in the four anodic domains (a-Channel, a-GDL, a-MPL and a-CL). Since the amount of CO is very small, we assume that the diffusion follows Fick’s law and use the average gas velocity of the other gas components, $U_g$, for the convective term:

$$
\frac{\partial C_{\text{CO}}}{\partial t} + \nabla \cdot (U_g C_{\text{CO}}) - \nabla \cdot (D_{\text{CO}} \nabla C_{\text{CO}}) = S_{\text{CO}}
$$

where $\epsilon$ is the porosity of the media (equal to one in the channel), $D_{\text{CO}}$ is the diffusion coefficient of CO in the gas mixture, and $S_{\text{CO}}$ is the source term associated to the adsorption of CO on the catalyst:

$$
S_{\text{CO}} = a q_{\text{CO,ads}}
$$

where $a$ is the specific surface area of platinum and $q_{\text{CO,ads}}$ is the surface reaction rate, whose expression will be detailed hereafter. This source term is non-zero only in the anodic catalyst layer. In the surface reaction rate, whose expression will be detailed hereafter.

Regarding the boundary conditions for the CO concentration conservation equation, the concentration is imposed at the anode channel inlet based on the CO content of the inlet gas. The CO flux is zero at the membrane. The conservation equation for the CO concentration, $C_{\text{CO}}$, is considered in the four anodic domains (a-Channel, a-GDL, a-MPL and a-CL). Since the amount of CO is very small, we assume that the concentration is imposed at the anode channel inlet based on the CO content of the inlet gas. The CO flux is zero at the membrane.

$$
\rho \frac{d \theta_{\text{Pt}}} {dt} = 2q_{\text{O,ads}} - q_{\text{O-H,ox}} - q_{\text{CO-O,ox}}
$$

where $\rho$ is the molar area density of platinum site on the catalyst surface. The ratio of free Pt site is then deduced from the following relation:

$$
\theta_{\text{Pt}} = 1 - \theta_{\text{H}} - \theta_{\text{O}} - \theta_{\text{CO}}
$$

where $\theta_{\text{Pt}}$ is the site coverage ratio by oxygen, $\theta_{\text{O}}$, hydrogen, $\theta_{\text{H}}$ and carbon monoxide, $\theta_{\text{CO}}$, which depends on the kinetics of the above reactions, as follow:

$$
\frac{d \theta_{\text{Pt}}} {dt} = 2q_{\text{O,ads}} - q_{\text{O-H,ox}} - q_{\text{CO-O,ox}}
$$

Solution procedure.—The poisoning model has been developed within EuROPIUM (ElecRochemistry OPtimization Understanding Modeling). It is a multi-scale modelling framework developed at CEA for solving numerous processes relevant for PEMFC studies. The framework is based on MATLAB and Consol Multiphysics. The developed model has been solved with the Finite Elements Method, on a triangular mesh of roughly 6500 elements using quadratic Lagrange functions. To handle the large aspect ratio between the height and length of the cell, the equations are scaled in the channel direction to ensure a good quality of the meshing. The computation time for a transient computation is around 48h on a 8 cores computer.
Table I. Values of the different physical parameters associated to the CO poisoning model used in the simulations.

| Parameter                  | Value                        |
|----------------------------|------------------------------|
| \( k_{H_{ads},0} \)       | 3 m s\(^{-1}\)              |
| \( b_{H_{ads,b}} \)       | 4.18 \times 10^{11} mol m\(^{-3}\) |
| \( k_{H_{ox},0} \)        | 1 mol m\(^{-2}\) s\(^{-1}\) adjusted |
| \( k_{O_{ads},0} \)       | 6 \times 10^3 m s\(^{-1}\) adjusted |
| \( b_{O_{ads},b} \)       | 1.36 \times 10^{16} mol m\(^{-3}\) |
| \( k_{CO_{ads},0} \)      | 3 \times 10^{4} m s\(^{-1}\) adjusted |
| \( r \)                   | 39.77 kJ mol\(^{-1}\) \(\beta = 0.140\) \(H_{CO} = 0.3240\) |
| \( b_{CO_{ads},0} \)      | 11.5 \times 10^3 m s\(^{-1}\) adjusted |
| \( k_{CO_{ox},0} \)       | 3.4 \times 10^4 mol m\(^{-2}\) s\(^{-1}\) adjusted |
| \( k_{O_{ox},0} \)        | 3.28 \times 10^4 mol m\(^{-2}\) s\(^{-1}\) adjusted |
| \( k_{CO_{ox},O_{ox},0} \) | 8.3 \times 10^7 mol m\(^{-2}\) s\(^{-1}\) adjusted |
| \( \rho \)                | 4.8 \times 10^{-3} mol m\(^{-2}\) s\(^{-1}\) Eq. 26–27 |

Results and Discussion

In situ diagnostics.—Global observations.—The durability test under constant current was conducted with a long initial period (200 h) of performance under reformate for tolerance evaluation, then four periods at fixed current of approximately 120 h. The test could be conducted only during 750 h due to final strong decrease of performance during last aging period. This test does not really show reversible degradation compared to usual behavior observed under pure hydrogen.\(^{41}\) When considering previous studies conducted with the same stack design under pure hydrogen, which presented similar initial performance and mean degradation rate around 18 \(\mu V/h\) at constant current,\(^{41,28}\) such an important degradation was not expected as well as the performance degradation acceleration after 600 h. Single cell test conducted on the same type of MEA, showed similar but smoother behavior during similar time duration. In the single cell test, a constant increase in degradation of the same order of magnitude is also observed with permanent acceleration of voltage losses at high current density. The mean voltage degradation rates during the aging periods is high and always increases, here from 200, 330, 720 to 1,000 \(\mu V/h\) from 1\(^{st}\) to 4\(^{th}\) period as can be seen on Figure 4a. A rapid decrease in voltage and particularly the acceleration of this decrease with time is a major issue motivating this study. Identifying, understanding and mitigating this voltage decrease and acceleration with regard to the MEA components and stack design used are thus the focus of the experimental and modelling results discussed below.

![Figure 4](image_url)

**Figure 4.** a) Stack mean voltage evolution during ageing at fixed current under reformate and b) Polarization curves recorded under pure hydrogen (left) and under reformate including 10 ppm of CO (right) at beginning of test and after each aging step.
Comparing maps obtained under pure hydrogen or reformate with distribution is impacted by the presence of CO, as can be seen when from Pt3Co to Pt type. When comparing only beginning and end of the cathode side, modifications upon aging are less evident but the of desorption charge is about 20% for the total anodes surface. For construction mechanism described in Ref. 14. The total average loss surface containing less ruthenium than initially, possibly following re-anode catalyst structure, with additional peaks attributed to catalyst are available. Their comparison clearly shows a modification of the (EIS). For the anode side, only beginning of test and end of test CVs for the two fuels.

Electrochemical diagnostics have been performed by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). For the anode side, only beginning of test and end of test CVs are available. Their comparison clearly shows a modification of the anode catalyst structure, with additional peaks attributed to catalyst surface containing less ruthenium than initially, possibly following reconstruction mechanism described in Ref. 14. The total average loss of desorption charge is about 20% for the total anodes surface. For the cathode side, modifications upon aging are less evident but the peaks evolution tend to show some Co losses with CV shape going from Pt3Co to Pt type. When comparing only beginning and end of test, the cathodes have lost in average less than 10% of their initial active surface area. EIS measurements mainly confirmed the polarization curves and cyclic voltammetry results showing that the charge transfer and transport resistances are impacted for both fuels but that at end of test, the limitations are strongly increased for the reformate case.

**Heterogeneities evolution upon aging.**—In addition to these in situ electrochemical diagnostics giving averaged information about the MEA degradation, the current density distribution maps are analyzed to investigate the effect of aging on the heterogeneities in local activities. The CDDM have been recorded under pure hydrogen and under reformate, during aging and at different current densities during the polarization curves performed in between each durability steps. The selected results (Figure 5) present the CDDM recorded at 0.5 A/cm² during the polarization curves, for three aging times (before aging, around 600 hours of aging and end of test), under both pure hydrogen and reformate fuel including 10 ppm of CO.

The distribution of current density along the MEA surface is caused by the local conditions, particularly the position with regard to fuel and air inlets/outlets and the bipolar plate design. The distribution of current density along the MEA surface is caused by the local conditions, particularly the position with regard to fuel and air inlets/outlets and the bipolar plate design. The current density distribution is impacted by the presence of CO, as can be seen when comparing maps obtained under pure hydrogen or reformate with CO. At beginning of test, under pure hydrogen, the current density is lower in the air outlet zone, attributed to lower cathode activity here mainly caused by lower oxygen partial pressure. The current density distribution is different under reformate, with a clear shift from air inlet to air outlet, indicating a lower activity of the anode at the outlet. This modification in the current distribution is attributed to the higher CO effect caused by a lowest hydrogen partial pressure in this region.

The current density distribution evolves during the aging test, as a consequence of the local degradations and the data clearly show that the trend is different under pure hydrogen and under reformate. Main result under hydrogen is a progressive and strong decrease of operation near air outlet (hydrogen inlet). This behavior is attributed to a decrease in activity of the cathode at air outlet ending with a very poor operation at the end of aging. The average current density goes below 0.4 A/cm² for more than one third of the cell surface from fuel inlet side. This trend is probably caused by a stronger impact of the low oxygen partial pressure in this zone, compared to the impact before aging. This would be consistent with a cathode catalyst layer locally degraded enough to present much less activity toward the Oxygen Reduction Reaction after aging.

Under reformate, the trend with progressive reduction of current densities near air outlet is also clearly visible but at a lesser extent compared to pure hydrogen. The maximum of current densities is located in the middle region instead of near air inlet. In this case, there is only a slight relative increase in current densities at air inlet or hydrogen outlet. Under reformate, this effect related to the evolution of the operation cathode side is moderated, which would not be the case if the anode side had no impact due to whether relatively low or homogeneous degradation. It appears that under reformate with these aging conditions, the degradation heterogeneities are not controlled only by the cathode side. In particular, the moderation in activity losses near air inlet under reformate is attributed to the probable opposite impact of the anode side, where the CO tolerance could tend to decrease in this fuel outlet zone during aging.

The heterogeneities in current density during aging are affected but differently when considering operation under pure hydrogen or under reformate. To get more insight on the local activity of both electrodes, the results of the specific CO poisoning test are analyzed. First, the
average stack voltage evolution shows that the transition is quicker and the voltage losses are stronger with aging. Furthermore, during the transitions, the local average current density is recorded for the three zones of interest. Before aging, the three averaged current densities profiles are similar (Figure 6a). At the beginning of aging, i.e. after the first aging step, initial small differences start increasing already under pure hydrogen (before transition) with a strong relative decrease of current density profile at air outlet (Figure 6b). This first negative impact of aging is attributed to cathode catalyst initial degradation and will increase with time. When considering the current densities profiles, aging strongly increases the gap between the currents under both pure hydrogen and reformate, particularly for the inlet/outlet zones. Under pure hydrogen (beginning of transition) the standard deviation between the three zones, normalized by the mean current density, increases from 2.3% at beginning of test, to 8.8% after the first step of aging, to reach more than 16% at end of test. The other impact of aging on these features is the shift of the minimum and maximum current densities along time. For example the peak in current density for the air inlet zone (blue) is reached after 0.5 h before aging and after only 0.3 h after aging. This faster evolution shows that aging causes an...
The transient 2D PEMFC model has been used to investigate the heterogeneities inside the cell under both pure hydrogen and reformate. The goal is to have access to local physical quantities inside the cell that cannot be measured *operando*, such as local potentials or gas concentration and better discriminate between various degradation phenomena.

Since the model relies on a large number of physical parameters, a validation effort has been carried out by comparing the simulation results to the experimental data. Before considering the poisoning effect, the model has been validated under pure H\textsubscript{2} through the simulation of a polarization curve in order to optimize the various MEA physical parameters of the model. The measured current density data have not been used for this validation step. Indeed, they are 2D over the surface of the cell and given the specific design of the bipolar plates, it is not straightforward to define one “representative channel” valid for both anode and cathode overwhich the data could be averaged for direct comparison with the 1D inlet/outlet current density of the simulation.

To validate the CO poisoning model, the specific experimental poisoning diagnosis has been simulated with the 2D transient model and the adjusted physical parameters are reported in Table I. In the simulation, the CO poisoning is started after 10 min of simulation by switching the inlet CO concentration from 0 to 10 ppm. The obtained current densities have been averaged over the three zones defined in switching the inlet CO concentration from 0 to 10 ppm. The obtained simulation results to the experimental data. Before considering the poisoning effect, the model has been validated under pure H\textsubscript{2} through the simulation of a polarization curve in order to optimize the various MEA physical parameters of the model. The measured current density data have not been used for this validation step. Indeed, they are 2D over the surface of the cell and given the specific design of the bipolar plates, it is not straightforward to define one “representative channel” valid for both anode and cathode overwhich the data could be averaged for direct comparison with the 1D inlet/outlet current density of the simulation.

The transient 2D model gives access to the local physical quantities in the different components of the cell during the propagation of the CO front. Figure 8 presents the evolution of the anode and cathode potentials during this poisoning diagnostic. Injected at the anode inlet, the CO increases the anode potential in this zone, which leads to an increase of the cathode potential in front of this region. At the end of the transient, a higher CO coverage is obtained at the anode (Figure 9 left). The variation of the CO coverage from 94% at the inlet to 97% at the outlet means that only ~3% of platinum surface is available for the hydrogen oxidation reaction at the anode outlet while the double is available at the inlet. This ratio is coherent with the reduced anode kinetics observed at the fuel outlet. The higher CO coverage at the fuel outlet is due to the lower hydrogen partial pressure in this zone which impacts the competition between CO adsorption and hydrogen adsorption on the active sites (Figure 9).

The CO poisoning effect being higher in this region which matches with cathode inlet, it induces a redistribution of the current from cathode inlet toward cathode outlet compared to operation under pure hydrogen. This can be seen on Figure 9 right which presents the current density profiles along the channel under both pure hydrogen and reformate. The observed redistribution of current induced by the CO poisoning is coherent with the experimental CDDM observations at beginning of test presented Figure 5.

In PEMFC, the local current density results from and impacts many local conditions: activity of reactants and products which impact both the reversible potential and the exchange current density, ionic and electric potentials, temperature and electrochemically active surface area (See Butler-Volmer Equation 2 of Performance model section). Given the highly coupled nature of the involved physical phenomena, it is not trivial to predict the impact of operating conditions on local conditions and current densities. Thanks to the two-dimensional models, we have analyzed the local conditions at the origin of the observed heterogeneous current density profiles (Figure 10). Under pure hydrogen, the better performance observed at the air inlet under the operating conditions of the test are clearly driven by the higher oxygen concentration in this zone, which present the same inlet/outlet heterogeneity as the exchange current density, while the exchange current density on the anode side is totally homogeneous and the overpotentials in both electrodes are almost constant along the channel. Under reformate, the analysis is more complex since the current density results from both anode and cathode local conditions. The higher oxygen concentration at the cathode inlet induces a higher cathode exchange current density in this zone, but this time, the anode exchange current density is highly heterogeneous with maximum on the opposite side at the anode inlet because of the heterogeneous CO coverage. The overpotentials are more heterogeneous than under pure hydrogen for both electrodes with a maximum (in absolute value) at their respective outlets. These opposite trends result in a current density profile under reformate which is not monotonous (Figure 9 right).

**Post mortem analysis of the MEAs.**—Cyclic voltammetry measurements performed on selected samples of the aged MEAs show that both electrodes present lower active surface area at air outlet (Table II). This is consistent with the local operation measured in situ at end of test. For the cathode side, the ex situ CV results are particularly in good agreement with better local performance detected near air inlet under pure hydrogen, with no difference detected in averaged coulombic charge between the cathode aged samples from this zone and the fresh one. Regardless the anode, in general, more losses are noticed compared to fresh sample as for averaged data recorded at stack level. The stronger evolution of the PtRu catalyst structure occurred near hydrogen outlet, where peaks attributed to catalyst surface of pure Pt instead of PtRu can be observed Figure 11, indicating that more Ru dissolved in this zone. This result confirms that the local tolerance to CO is low and degrades with time in this zone.

In parallel, samples taken in the same MEA zones as for the electrochemical measurements, near the air inlet and outlet, were analyzed by TEM to try determining a correlation between the local performance evolution obtained in situ and the components’ microstructure and chemical composition evolution.

**Anode microstructural analyses.**—Particular attention has been given to anode microstructure via the study by HAADF/STEM and X-EDS of the evolution at atomic scale of the structure and chemical composition of PtRu nanoparticles. This study was made particularly difficult by the small size (around 2–4 nm) of the nanoparticles and their very high chemical composition heterogeneity. For example,
neighboring nanoparticles could have a composition varying between quite pure Pt to around 30 at. % of Pt, the average nanoparticle composition being around 50 at. % of Pt. Thus, TEM analyses were not able to evidence any clear PtRu nanoparticle microstructure evolution between the fresh and aged anodes. In particular no Pt enrichment could be detected at the nanoparticle surface. In addition, contrary to what could be observed in similar aged MEA in strongly degraded cases, no Ru is detected in the cathode or in the anode microporous layer. However, as observed in the similar aged MEA, Ru dissolution can be highlighted by the presence of Pt-Ru precipitates within the membrane. As suggested in Henry et al., these precipitates result from the following mechanism. The Ru dissolution at the anode is followed by the migration of Ru ions toward the cathode side through the membrane and then, their reduction by the H₂ cross-over is catalyzed on the
pre-existing Pt precipitates, this Pt precipitate band being formed by the reduction of the Pt dissolved from the cathode catalyst. In the two samples (air inlet and outlet) analyzed here, similar Pt-Ru precipitate band was observed within the membrane, the largest precipitates being located at around 6 μm far from the cathode, near the membrane reinforcement. Even if the number of precipitates appears to be similar in the two samples, the size and the Pt-Ru composition of the largest precipitates observed in the two samples are different. Precipitates approximately twice as large are observed in the air inlet zone (where the largest precipitate size is around 180 nm in diameter compared to around 80 nm in the outlet zone) whereas the Ru at.% content is five time lower in the air inlet zone (around 2%) than in the air outlet zone (around 10%). 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 in the two MEA zones. This calculation indicates that around twice more Ru is present in the largest precipitates located in the air inlet zone. Thus, the microstructural analyses of these Pt-Ru membrane precipitates are consistent with higher dissolution of the Ru suspected in the air inlet zone from the evolution of the averaged current densities profiles during the CO poisoning diagnostic showing stronger relative loss of CO tolerance and from the electrochemical analyses on the small aged samples (particularly from the shapes of the voltammograms showing Pt type peaks on anode samples aged at air inlet).

**Cathode microstructural analyses.**—Similar HAADF/STEM and X-EDS mapping analyses were performed on the Pt3Co catalyst at the cathode side. Figure 12a shows the histograms of nanoparticle size measured in the fresh and aged MEAs in the air inlet and outlet zones. The comparison of these histograms reveals a nanoparticle size increase in the aged sample with quite similar evolution between the air inlet and outlet zones. Given the large distribution of the nanoparticle diameter size, the number of 300 measured nanoparticles used to build the histograms is probably statistically too low to evidence a possibly different evolution between the two zones that could explain the difference of measured ECSA (Table II).

Furthermore, in order to determine the cathode chemical composition evolution, X-EDS analyses were performed in the fresh and 2 aged cathodes. No variation on the global composition of the cathodes is observed. However, the high resolution Pt and Co X-EDS elemental maps performed on few (between 5 and 10) nanoparticles in each cathode clearly show a more significant evolution of Pt3Co nanoparticle chemical structure in the air outlet zone. Indeed, as imaged on Figure 13a, Pt and Co X-EDS elemental maps clearly evidence in fresh MEA the 0.6 nm thick Pt shell surrounding the Pt3Co nanoparticle core. This Pt shell resulting from a Co chemical leaching during nanoparticle synthesis process was probably optimized to prevent the production of a too large amount of Co ions within the MEA during fuel cell operation, Co ions being an ionomer contaminant. The same analyses performed on Pt3Co nanoparticles in the cathode air inlet zones do not reveal a significant evolution of the Pt shell thickness that remained around 0.6 nm as measured on nanoparticles being in the size range of 8 to 18 nm (Figure 13b). On the opposite, these Pt shell surrounding Pt3Co nanoparticles of the cathode air outlet zone clearly increases in thickness until 1 nm thick (Figure 13c). This increase of thickness of the Pt shell could result from the continuously Co dissolution during fuel cell operation but more probably results from the electrochemical Ostwald ripening mechanism. Indeed during this electrochemical process illustrated in Figure 12b, atoms of the smaller nanoparticles are oxidized and produced ions migrate through the ionomer toward the larger nanoparticles where they are reduced at their surface. This process is due to the standard redox potential that for nanoparticles is negatively shifted with respect to the bulk metal proportionally to the reciprocal nanoparticle radius. The charge transfer equilibrium is maintained by the parallel electron transfer through the carbon support. Compared to pure Pt nanoparticles, the particular point for the Pt3Co nanoparticles is that because the negative Co/C standard potential prevents Co ions reduction within the MEA, only the Pt ions provided from the smaller nanoparticles are reduced at the larger nanoparticle surface. Consequently, for Pt3Co 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 Pt3Co, and in addition this mechanism leads to the contamination of the ionomer by the Co ions. The Pt redeposition on nanoparticle surface is clearly visible on Figure 12c (Pt redeposition appears brighter) and Figure 12d (Pt redeposition appears in red) where the Pt redeposition surrounding the two neighboring nanoparticles leads to their sintering. Moreover, on Figure 12a, the histogram built by subtracting the fresh cathode histogram from the aged air outlet cathode histogram clearly shows that in the air outlet cathode, after fuel cell aging, the number of nanoparticles smaller than 5 nm decreases. As for pure Pt catalysts, the Pt3Co nanoparticles smaller than 5 nm are not stable in the cathode when electrochemical Ostwald ripening mechanism largely occurs. 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 Pt₃Co catalyst should not have nanoparticles smaller than 4–5 nm.

TEM analysis of the aged cathodes clearly shows that the electrochemical Ostwald ripening mechanism more largely occurred in the air outlet cathode zone than in the air inlet cathode zone. This difference can explain the large cathode electrochemical performance loss recorded on CDDM in the air outlet zone. Indeed, the electrochemical Ostwald mechanism not only results in an ECSA loss but also for Pt₃Co catalyst in a thicker Pt shell surrounding the Pt₃Co nanoparticles that decreases their activity. In addition this mechanism results in large Co ion ionomer contamination that will decrease the ionomer protonic conductivity. The membrane Co ion contamination can be
Table II. Averaged coulombic electric charge on different zones of the aged MEAs (5 samples for inlet/outlet zones; 2 samples for middle zones).

|                | Fresh     | Air inlet/ Fuel outlet | Middle    | Air outlet/ Fuel inlet |
|----------------|-----------|------------------------|-----------|------------------------|
| Cathode (C)    | 0.044     | 0.044                  | 0.030     | 0.029                  |
| Anode (C)      | 0.042     | 0.028                  | 0.036     | 0.022                  |

This last point is supported by the global cathode air outlet X-EDS analysis showing no Co content decrease within the cathode. Thus in air outlet cathode zone the protonic conductivity of the ionomer is probably largely affected.

**Discussion.**—An important and unexpected loss of performance has been observed during this aging test performed under a fixed current density of 0.5 A/cm² on a PEMFC fed with reformate fuel. To try to understand the phenomena at the origin of such a different aging behavior between PEMFC fed with pure H₂ and those fed with reformate with 10 ppm of CO, we first sum up the experimental observations. The voltage drop is much stronger than under similar operating conditions with pure hydrogen and has been reproduced on a single cell test (not presented here). Furthermore, an acceleration of the degradation is observed. The analysis of the CDDMs under pure H₂ indicates a strong loss of activity at the cathode outlet, even though the total ECSA loss at the cathode is not that important (less than 10%). This ECSA loss is nevertheless more important at the cathode outlet and the modifications of the CV shape upon aging tend to show some Co losses. TEM observations on aged inlet and outlet cathode samples put in evidence an electrochemical Oswald ripening mechanism which seems to be more important at the cathode outlet given the observed thicker Pt shells surrounding Pt₃Co catalyst in this zone. This nanoparticle degradation mechanism contributes to the dissolution of Co generating Co ions which are suspected to pollute the ionomer, even though direct observation of this pollution remains tenuous. The ECSA loss is more important at the cathode outlet but does not seem strong enough to explain by itself the severe loss of performance observed at the cathode outlet. Since local performance depends not only on electrochemical activity and available surfaces of the catalysts but also on the ionic and electronic conductivities of the electrode, the contamination of the ionomer by the Co ions is strongly suspected to be the main parameter that had affected the electrode performance. This contamination, which affects transport of protons, is notably consistent with the increase in mass transport limitations observed on the polarization curves during ageing under both pure hydrogen and reformate.

**Figure 11.** 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.

highlighted by X-EDS membrane analysis where Co presence can be evidenced, however the contamination of the ionomer lying in the cathode is more challenging. This contamination was highlighted in another study in a cathode zone where a large amount of ionomer was present. In the present study only few Co was detected within the membrane that suggests that the Co ions provided by the smaller Pt₃Co nanoparticle dissolution probably remain within the cathode.

**Figure 12.** a) Nanoparticle size histograms of the fresh, air inlet and air outlet cathode, and the difference between the air outlet histogram and the fresh histogram showing that nanoparticle smaller than 5 nm are not stable. b) Scheme of the electrochemical Ostwald ripening mechanism considering Pt₃Co nanoparticles. c) and d) respectively HAADF/STEM image and Pt and Co X-EDS elemental maps highlighting the Pt redeposition between two neighboring nanoparticles leading to their sintering.
At the anode, the total ECSA loss is more important than at the cathode, probably due to the very small size of the PtRu nanoparticles and the general low Ru stability, with a modification of the anode catalyst structure from PtRu to Pt. A loss of CO tolerance at the anode is evidenced thanks to the developed specific CO poisoning diagnostic. The comparison of the CDDMs upon aging and between pure hydrogen and reformate tend to show that this loss of CO tolerance is more important at the anode outlet. This is corroborated by the local post-mortem CV measurements which indicate a dissolution of Ru at the anode outlet (consistent with loss of CO tolerance), even though more ECSA loss is observed at the fuel inlet. Observations by TEM in inlet/outlet anode regions reveal PtRu precipitates in the membrane which highlight Ru dissolution at the anode. Their chemical and microstructural analyses indicate that around twice more Ru is present in the largest precipitates located at the anode outlet that could confirm a more severe Ru dissolution in this region. In the anode outlet zone, as shown by the simulation, the larger anode potential caused by CO poisoning is probably the main cause for stronger Ru dissolution compared to anode inlet zone and this even at the quite low anode potentials reported by the simulation. Misushima et al. and Andersen et al. indeed showed that significant Ru dissolution already occurs at very low potential and increases with anode potential.

Thanks to the simulation tool, the local physical quantities (exchange current densities, reactant concentrations, local potentials, ...) in the anode and cathode have been compared for pure hydrogen or reformate including 10 ppm of CO. These simulations clearly show that the higher anode CO poisoning at anode outlet induces a redistribution of the current from cathode inlet to cathode outlet compared to operation under pure hydrogen. Consequently, the local conditions are not similar when operating under hydrogen or reformate. Our main observations are that under reformate the anode potential is higher and more heterogeneous between inlet and outlet, the current density and thus the water production is higher at the cathode outlet, where the cathode potential is the lowest.

Given all these observations, we suspect the following accelerating degradation mode. 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 toward 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 electrochemical Oswald ripening degradation mechanism by enhancing the metallic ions transport between neighboring nanoparticles. However, for PtCo catalyst, since the Co ions do not redeposit, they pollute the cathode ionomer at the outlet, leading to a decrease of the local ionomer conductivity and to a decrease of the electrode potential which should lead to a decrease in the local current by shifting it to the inlet. However, due to the heterogeneous CO coverage at the anode, even reinforced by Ru dissolution creating the loss of CO tolerance at the anode outlet upon aging, the local current density remains important at the cathode outlet. Therefore, in this configuration, the cathode is forced to work at the air outlet/fuel inlet zone where its potential is the lowest. Finally, as the necessary redistribution of the current from the cathode inlet to the cathode outlet becomes more difficult due to the cathode outlet degradation, the local performance loss of the PEMFC is accelerated.

Implementation of a modified electrode for degradation mitigation.—Considering the conclusions of the coupled experimental and simulation investigations, optimized MEAs have been designed, by varying the catalyst layers composition. Two zones have been identified with major and specific degradation phenomena. At the cathode side, it has been concluded that air outlet region operation could be affected by the contamination of the ionomer by Co ions following the promotion of the Co dissolution in this region. To prevent this phenomenon it is needed to identify a more stable catalyst regarding Co dissolution. The cathode catalyst layer has thus been modified near air outlet by replacing the initially used bi-metallic PtCo catalyst by pure Pt, while increasing slightly the loading to maintain locally similar level of catalytic activity toward Oxygen Reduction Reaction. One third of the cathode Gas Diffusion Electrode has been replaced by a GDE with same gas diffusion layer but a catalyst layer containing 50%Pt on carbon (instead of 45% PtCo) with a loading of 0.55 mgPt/cm² (instead of 0.45 mg PtCo/cm²). At the anode side, it has been concluded that fuel outlet region operation could be affected by the higher dissolution of the ruthenium due to the local highest potential, with a continuously enhanced degradation of the local CO tolerance. To compete against the initial mechanism involved, it is needed to identify more stable catalyst regarding Ru dissolution. Since PtRu catalyst is still the best solution available to
operate under CO containing reformate fuel, modification has been done by changing the catalyst loading. The anode catalyst layer has thus been modified near fuel outlet by increasing the loading in the initially used bi-metallic PtRu catalyst to improve the initial tolerance and postpone the issues related to the CO tolerance losses. One third of the anode Gas Diffusion Electrode has been replaced by a GDE with same gas diffusion layer and a catalyst layer containing 50%PtRu on carbon with a loading of 0.65 mgPtRu/cm² (instead of 0.45 mgPtRu/cm²).

These MEAs have been tested at stack level, demonstrating a clear improvement of the MEA performance stability with no acceleration of the voltage losses over the 1000 hours of aging test as can be seen Figure 14.

In addition to the global measurements showing how the modification of the electrodes composition could lead to more stable performance, their effect on the heterogeneity modifications has also been considered for further interpretation. The differences between before and after aging have been calculated for the CDDMs recorded under pure hydrogen and under reformate (Figure 15).

For the reference MEAs, the differences give same but clarified information as the CDDMs shown on Figure 5. Showing here the differences was decided for sake of clarity and to help comparison with the results obtained with the modified MEAs. So, the maps (a) and (b) confirm the heterogeneities after aging with strong performance losses at the cathode outlet for the two types of fuel and a strong relative performance gain at air inlet under pure hydrogen on the contrary of a very moderated shift of activity from middle to air inlet under reformate.

First obvious comment about the maps (c) and (d) recorded under pure H₂ and reformate respectively but with the modified MEAs is the huge difference in the evolution of heterogeneities compared to the reference case. In addition, the amplitude of current variations is similar for the two fuels. Compared to the previous MEAs, this amplitude is much lower for the pure hydrogen case, with also a surface covered by positive change or no change actually extended. Major relative losses in activity are located at the air inlet, with a more pronounced effect also extended toward the middle for the reformate case. Main difference between the two fuels cases appears at air outlet with clear current losses for the pure hydrogen case, reminding the aging effect for reference MEAs. Compared to reference case, the region of maximum increase in current densities has been shifted toward the middle and air outlet zone of the cells. While considering the previous conclusions about the link between local operation and the electrodes, here the modification of the cathode seems to have indeed actually lowered the losses near the modified zone. The beneficial effect of the new cathode composition is more important under reformate. This result shows good consistency with the phenomena suspected and described in both the experimental and modelling investigations about the damage caused to the air outlet operation with an effect accelerating the performance losses attributed particularly to Co dissolution, of course not occurring here.

With the modified MEAs, the zone now mainly degraded with regard to in situ operation is the air inlet. This new behavior is consistent with previous results obtained in an ageing study conducted with pure hydrogen only and also employing Pt₃Co, showing stronger losses near air inlet. The proposed interpretation is related to the impact of the anode side on the cathode side, with in these two latter cases, an anode operating with low limitations during ageing, thanks to respectively pure hydrogen operation or, in our case, an improved activity toward the anode reaction with the increased loading in PtRu catalyst. In our case, higher cathode activity is occurring at the air inlet zone where the oxygen partial pressure is high and the anode not preventing good operation of the MEA, thus submitting the cathode catalyst to local conditions enhancing its degradation. On the contrary

![Figure 14](image_url)

**Figure 14.** Voltage evolution for the two stacks made with reference homogeneous electrodes (Reference MEA) and with optimized electrodes (Modified MEA) (a) – Degradation rates for the two stacks (b) – Description of the modified electrodes (c).

![Figure 15](image_url)

**Figure 15.** Differences between after aging – before aging of current density distribution maps recorded at 0.5 A/cm² - left side: reference MEAs under pure hydrogen (a) or reformate (b) right side: modified MEAs under pure hydrogen (c) or reformate (d).
to what was occurring with the homogeneous reference MEAs, there is no more a reason like CO poisoning to promote so intensively the redistribution of current density toward air outlet under reformate. As a summary, the proposed explanation for the inversion in the localization of major losses with the new MEAs is that the improvement of the anode tolerance to CO prevents the protection of the cathode catalyst, whose degradation near air inlet becomes the weak point for the two fuels type. These results are thus in good agreement with what could be expected following the tuned modifications of the MEAs confirming the relevance of this type of study coupling experimental, both in situ and ex situ and modelling investigations for degradation understanding in specific cases and the proposal of mitigating solutions and durability improvement.

Conclusions

In this study a detailed analysis of degradation heterogeneities in PEMFC stack aged under reformate has been conducted. The aim was to better understand the impact of CO poisoning on the performance losses of a fuel cell stack, focusing on the localization of the degradation and on the correlation between the decrease in activity of the MEA and the degradation of the electrode functional properties and microstructure. Durability test in stationary-related operating conditions has been studied with different in situ global and local experimental techniques. An unexpected and very severe potential degradation was measured going from 200mV/Vh for the first aging block to 1,000μV/h for the last one. In situ diagnosis under pure hydrogen shows a strong decrease of current density of the cathode air outlet, while the trend is less pronounced under reformate due to the non-negligible impact of the anode degradation. These heterogeneity analyses are supported with multi-physics simulations which highlight the heterogeneous CO coverage along the anode, as well as the competition between both electrodes under reformate leading to non-monotonous current density profiles. At the end of life, electrochemical and TEM analyses were performed on three characteristic zones (air inlet, middle and air outlet) of the membrane electrode assembly to get more insight on the degradation mode. The combined analyses put in evidence heterogeneous degradations at both electrodes. More ruthenium is dissolved at the anode outlet, while an electrochemical Ostwald ripening mechanism of the Pt3Co nanoparticles at the cathode outlet is suspected to pollute the ionomer with the Co ions. Optimized MEAs have thus been designed to mitigate these suspected degradation mechanisms by varying the catalyst layer composition of both electrodes and tested at stack level demonstrating a clear durability improvement.

Acknowledgments

This work has been conducted in the frame of the project Second Act supported by the FCH JU in FP7 program. The research leading to these results has received funding from the European Union’s Seventh Framework Programme (FP7/2007–2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° 621216. Authors thank F. Micoud for his support in data treatment and answers to reviewers.

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References

1. H. R. Ellamla, I. Staffell, P. Bjujob, B. G. Pollet, and S. Pasupathi, “Current statutes of fuel cell based combined heat and power systems for residential sector,” J. Power Sources, 293, 312 (2015).

2. DOE, “http://energy.gov/eere/fuelcells/fuel-cell-technologies-office,” 2017.

3. R. Borup and J. Meyers, “Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation,” Chemical Review, 107, 3904 (2007).

4. S. Gottesfeld and J. Palford, “A new approach to the problem of carbon monoxide poisoning in fuel cells operating at low temperatures,” J. Electrochem. Soc., 135, 2651 (1988).

5. H. Sprunger, N. M. Markovic, P. Ross, and E. J. Cairns, “CO electrooxidation on well-characterized Pt-Ru alloys,” J. Phys. Chem., 98(2), 617 (1994).

6. P. A. Henry, L. Guetar, N. Pelissier, P. A. Jacques, and S. Escribano, “Structural and chemical analysis by transmission electron microscopy of PtRu membrane precipitates in proton exchange membrane fuel cell aged under reformate,” J. Power Sources, 275, 312 (2015).

7. J. D. Fairweather, D. Spennak, A. Z. Weber, D. Harvey, S. Wessel, D. S. Hussey, D. L. Jacobson, A. Yatishyusha, R. Mukundan, and R. L. Borup, “Effects of Cathode Corrosion on Through-Plane/Plane Transport in Proton Exchange Membrane Fuel Cells,” J. Electrochem. Soc., 159, 2980 (2013).

8. L. Dubau, L. Castanheira, F. Maillard, M. Chatenet, O. Lottin, G. Maranzana, J. Dillet, A. Lambric, J.-C. Perrin, E. Moukheiber, A. ElKaddouri, G. De Moor, C. Bas, L. Flandin, and N. Caqué, “A review of PEM fuel cell durability: materials degradation, local heterogeneities and aging and possible mitigation strategies,” WIREs Energy Environ., 3, 540 (2014).

9. J. Fairweather, B. Li, R. Mukundan, J. Fenton, and R. Borup, “In Situ and Ex Situ Characterization of Carbon Corrosion in PEMFCs,” ECS Trans., 58(1), 433 (2010).

10. L. Guetar, M. Lopez-Haro, S. Escribano, A. Morin, G. Gebel, D. Cullen, M. Kore, and R. Borup, “Catalyst-Layer ionomer imaging of fuel cells,” ECS Trans., 69(17), 455 (2015).

11. S. Ohyagi, T. Matsuda, Y. Iseki, T. Sasaki, and C. Kaito, “Effects of operating conditions on durability of polymer electrolyte membrane fuel cell Pt/cathode catalyst layer,” J. Power Sources, 196, 3743 (2011).

12. T. Morawietz, M. Handl, C. Oldani, K. A. Friedrich, and R. Hiesgen, “Quantitative in Situ Analysis of Ionomer Structure in Fuel Cell Catalytic Layers,” ACS Applied Materials and Interfaces, 8(40), 27044 (2016).

13. L. C. Pérez, P. Koski, J. Ihonen, M. J. Soussa, and A. Mendes, “Effect of fuel utilization on the carbon monoxide poisoning dynamics of Polymer Electrolyte Membrane Fuel Cells,” J. Power Sources, 258, 122 (2014).

14. T. Avanesyan, S. Dai, M. J. Kale, G. W. Graham, X. Pan, and P. Christopher, “Quantitative and atomic-scale view of CO-induced Pt nanoparticle surface reconstruction at saturation coverage via DFT calculations coupled with in situ TEM and IR.” J. Amer. Chem. Soc., 139, 4551 (2017).

15. K. Hengst, G. T. E. Pizzulo, H. C. M. Beetz, K. J. J. Mayrhofer, and C. Scheu, “Accelerated fuel cell tests of anodic Pt/Ru catalyst via identical location TEM: New aspects of degradation Behavior,” Int. J. Hydrogen Energy, 42, 25359 (2017).

16. G. Bender, M. Angelo, K. Bethune, and R. Rocheleau, “Quantitative analysis of the performance impact of low-level carbon monoxide exposure in proton exchange membrane fuel cells,” J. Power Sources, 228, 159 (2013).

17. L. Y. Sung, B. J. Hwang, K. L. Hseue, and F. H. Tsau, “Effects of anode fuel bleeding on the performance of CO-poisoned proton-exchange membrane fuel cells,” J. Power Sources, 195, 1630 (2010).

18. J. St-Pierre and M. B. V. Virji, “Cell performance distribution in a low-temperature proton exchange membrane fuel cell stack during propene contamination,” J. Appl. Electrochem., 46, 169 (2016).

19. J. Ihonen, P. Koski, V. Pulkkinen, T. Keranen, H. Karimaki, S. Auvinen, K. Nikiforow, M. Kotsiara, H. Tuiskula, and J. Viitakangas, “Operational experiences of PEMFC pilot plant using low grade hydrogen from sodium chloride production process,” Int. J. Hydrogen Energy, 42(44), 27269 (2017).

20. R. Arntrott and S. Escrivano, “Microscopic studies of a PEM fuel cell stack developed for reformate fuel operation in A,Ç,C,ÇCHP units: Development of an accelerated degradation procedure,” Int. J. Hydrogen Energy, 2015.

21. S. Foresti, G. Manzolino, and S. Escribano, “Experimental investigation of PEM fuel cells for a m-CHP system with membrane reformer,” Int. J. Hydrogen Energy, 42, 25334 (2017).

22. T. V. Reshetenko, K. Bethune, and R. Rocheleau, “Spatial proton exchange membrane fuel cell performance under carbon monoxide poisoning at a low concentration using a segmented cell system,” J. Power Sources, 218, 412 (2012).

23. Z. Qi and A. Kaufman, “Improvement of water management by a microporous sublayer for PEM fuel cells,” Journal of Power Sources, 109, 38 (2002).

24. A. A. Franco, M. Guinard, B. Barthe, and O. Lemaire, “Impact of carbon monoxide poisoning in fuel cells operating at low temperatures,” Journal of Power Sources, 212(0), 169 (2012).

25. L. Dubau, J. Durst, F. Maillard, M. Chatenet, J. Andre, and E. Rossinot, “Heterogeneities effects along large-area cell surface,” Journal of Power Sources, 316, 328 (2016).

26. L. Dubau, J.-P. Poirot-Crouveuze, M. Chandessis, J.-F. Blachot, C. Bonnau, and Y. Bultel, “Impact of heat and water management on PEM fuel cells degradation in automotive application,” Journal of Power Sources, 326, 182 (2016).

27. http://www.sphalus.com/ (2015).

28. C. Robin, M. Gerard, J. Arbigny, P. Schott, L. Jabbour, and Y. Bultel, “Development and experimental validation of a PEM fuel cell 2D-model to study heterogeneities effects along large-area cell surface,” Int. J. Hydrogen Energy, 40(32), 10211 (2015).

29. A. Z. Weber and J. Newman, “Coupled Thermal and Water Management in Polymer Electrolyte Fuel Cells,” Journal of The Electrochemical Society, 153, A2205, 2006.

30. S. Basu, C.-Y. Wang, and K. C. Chen, “Phase change in a polymer electrolyte fuel cell,” J. Electrochem. Soc., 156(6), B748 (2009).
33. C.-Y. Jung, H.-S. Shim, S.-M. Koo, S.-H. Lee, and S.-C. Yi, “Investigations of the temperature distribution in proton exchange membrane fuel cells,” *Applied Energy, 93*, 733 (2012).
34. W. J. Yang, H. Y. Wang, and Y. B. Kim, “Channel geometry optimization using a 2D fuel cell model and its verification for a polymer electrolyte membrane fuel cell,” *International Journal of Hydrogen Energy, 39*(17), 9430 (2014).
35. B. Randrianarizafy, P. Schott, M. Chandesris, M. Gerard, and Y. Bultel, “Design optimization of rib/channel patterns in a PEMFC through performance heterogeneities Modeling,” *Int. J. Hydrogen Energy*, In Press (2018).
36. J. B. Young and B. Todd, “Modelling of multi-component gas flows in capillaries and porous solids,” *International Journal of Heat and Mass Transfer, 48*(25–26), 5338 (2005).
37. T. E. Springer, T. A. Zawodzinski, and S. Gottesfeld, “Polymer Electrolyte Fuel Cell Model,” *Journal of The Electrochemical Society, 138*(8), 2334 (1991).
38. T. E. Springer, T. Rockward, T. A. Zawodzinski, and S. Gottesfeld, “Model for Polymer Electrolyte Fuel Cell Operation on Reformate Feed: Effects of CO, H2 Dilution, and High Fuel Utilization,” *J. Electrochem. Soc, 148*(1), A11 (2001).
39. J. J. Baschuk and X. Li, “Modelling CO poisoning and O2 bleeding in a PEM fuel cell anode,” *Int. J. Energy Res., 27*, 1095 (2003).
40. A. A. Shah, P. C. Sui, G.-S. Kim, and S. Ye, “A transient PEMFC model with CO poisoning and mitigation by O2 bleeding and Ru-containing catalyst,” *J. Power Sources, 166*, 1 (2007).
41. C. Robin, M. Gerard, M. Quinaud, J. d Arbigny, and Y. Bultel, “Proton exchange membrane fuel cell model for aging predictions: Simulated equivalent active surface area loss and comparisons with durability tests,” *Journal of Power Sources, 326*, 417 (2016).
42. W. J. Plieth, “Electrochemical properties of small clusters of metal atoms and their role in the surface enhanced Raman scattering,” *J. Phys. Chem.*, 86, 3166 (1982).
43. J. A. Gilbert, N. Kariuki, X. Wang, A. J. Kropf, K. Yu, D. J. Groom, P. J. Ferreira, D. Morgan, and D. J. Myers, “Pt Catalyst Degradation in Aqueous and Fuel Cell Environments studied via In-Operando Anomalous Small-Angle X-ray Scattering,” *Electrochimica Acta, 173*, 223 (2015).
44. S. Mitsushima, S. Uzuka, K. Matsuzawa, and K. Ota, “Evaluation of solubility of Ru in acidic solution,” *Electrochimica Acta, 1*, 83 (2010).
45. S. M. Andersen, L. Grahl-Madsen, and E. M. Skou, “Studies on PEM fuel cell noble metal catalyst dissolution,” *Solid State Ionics, 192*(1), 602 (2011).