Evaluation of Parameters Accelerating the Aging of PEMFCs Operating under Reformate Containing Carbon Monoxide

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Development of efficient accelerated stress test protocols for polymer electrolyte membrane fuel cells (PEMFCs) is an extremely important topic closely related to FC lifetime prediction and a decrease of the FC test costs. This work is dedicated to precise investigation of the impact of various accelerating factors on a FC performance over 1000 h scale. Five identical membrane electrode assemblies with Pt-based catalysts on the cathode and PtRu-based catalyst on the anode were studied using load cycling protocols. The impact of accelerating aging stressors and their combinations, such as carbon monoxide in fuel, frequency and amplitude of current cycling and regular electrochemical diagnostics via polarization curves and cyclic voltammetry measurements was thoroughly investigated. In addition, electrochemical cell behavior under fixed and varied fuel compositions is addressed. Total and irreversible cell performance losses are quantified for different aging tests. It is shown that the importance of aging factors can change depending on a test duration. This study combines large amount of experimental electrochemical data giving quantitative ranking for the importance of factors accelerating cell aging in operation conditions close to real ones for stationary fuel cells.

Polymer electrolyte membrane fuel cells (PEMFCs) found their practical application in the field of stationary energy generation, such as large scale power supply, combined heat and power (CHP) for industry and houses, backup power tools, etc. Environmental friendly PEMFCs are characterized by high efficiency of energy conversion, relatively low operating temperatures, dynamic response, zero or very low emissions of greenhouse gases, and quiet operation without generating vibrations. The main issues still impeding large scale commercialization of PEMFC technology are high cost and limited durability, with a particularly challenging target of at least 40,000 hours for stationary applications. For these applications, when hydrogen produced on-site by reforming of natural gas is used as a fuel, this can decrease the cost compared to FCs operating under highly pure H2. However, the reformate gas contains methane (CH4) and carbon dioxide (CO2), which dilute the H2, and also carbon monoxide (CO), which poisons the catalyst at the anode. CO is indeed strongly adsorbed on the surface of the platinum (Pt) particles and deactivates the anode catalytic sites required for H2 oxidation. The impact of CO on FC performance is directly related to the concentration of CO, the exposure time to CO, the cell operation protocol and conditions such as the temperature or gas feeding features and anode catalyst types and loadings. Platinum-ruthenium bimetallic alloy (PtRu) is the most used anode catalyst for FCs operating in CO-contaminated hydrogen. On one hand, the onset of electrooxidation of CO on PtRu surfaces is observed at potentials lower than 0.4 V vs. RHE, which is beneficial. On the other hand, PtRu alloys are known to be unstable under FC operating conditions and dissolution of Ru takes place. This problem causes other issues related to restructuring of the anode catalyst, like the loss of CO tolerance thus limiting the life-time of the PEMFCs. DOE durability target for stationary FCs is 40,000 hours under realistic operating conditions. Accelerated aging procedures allows predicting a long-term performance of FC without conducting long-duration real time tests. Most of the accelerated stress test (AST) protocols developed for PEMFCs are focused on aging of particular FC components and are not adapted for durability prediction of fuel cells operating under reformate.

Accelerated protocol consisting of square-shaped load cycles with different amplitudes and frequencies under reformate (10-15 ppm CO) was applied to a 10-cell PEMFC stack. Increased frequency and amplitude of cycles along with higher CO content in fuel and flooding for one of the cells were identified as strong accelerating factors for the aging of FC stack.

In the present work, several load cycling protocols were applied at a single cell level to better understand the impact of separate elements of aging protocols on a cell performance, while limiting the stronger heterogeneities induced on the operation of membrane electrode assemblies (MEAs) in a stack. The main stressors were load cycle frequency and amplitude, intermediate electrochemical characterization and concentration of CO in reformate hydrogen. Three tests were conducted with a fixed CO concentration in fuel (10 or 26 ppm) to identify the relative impact on the performance losses of load cycles profile and anode contamination. In parallel, during the fourth test a stepwise increase of CO content from 0 to 50 ppm was employed to check the accelerating impact of high CO content. In addition, one cell was investigated under pure hydrogen to be able to separate the effect of reformate fuel gas. The main goal was to understand the impact of each stressing factor or their combination on the performance of PEMFC with Pt-based cathode and PtRu-based anode and to quantify the related performance losses over 1000 h.

Experimental

Materials and test conditions.—The electrochemical tests have been performed on single cells using Green Light (GL-60) test station. Graphite monopolar plates with single serpentine flow field and 1 mm channel and landing dimensions were used. Anode and cathode fed gases were supplied in counter-flow. The 25 cm² MEAs were supplied by IRD Fuel Cell. The catalyst loadings were 0.3 mgPtRu/cm² and 0.1 mgCN/cm² at the anode and 0.5 mgCN/cm² at the cathode. The membrane was reinforced Nafion type and the two gas diffusion layers (GDLs) are SGL products (ref. Sigraet 35 DC). New MEA was taken for each of 5 conducted tests. The cells were fed at the anode with pure H2 or reformate H2 composed of CH4: 1.3%, CO2: 19.7%, CO: 10–50 ppm and H2: 79%. The 40% relative humidity at the cathode and 100%
Table I. Description of conditions for each test and related cell.

| Test and related cell number | Fuel gas     | CO concentration, ppm | Current density limits at load cycling, A/cm² | Duration of current density application, h | Number of electrochemical characterization procedures applied |
|-----------------------------|--------------|------------------------|-----------------------------------------------|---------------------------------------------|---------------------------------------------------------|
| Cell 1                      | H₂ pure      | 0                      | 0.4                                           | 0.065                                       | 18 6 7 (2)                                              |
| Cell 2                      | Reformate    | 10                     | 0.4                                           | 0.065                                       | 18 6 2                                                 |
| Cell 3                      | Reformate    | 26                     | 0.4                                           | 0.065                                       | 18 6 7                                                 |
| Cell 4                      | Reformate    | 0, 10, 20, 50, 10      | 0.4                                           | 0.065                                       | 18 6 2                                                 |
| Cell 5                      | Reformate    | 10                     | 0.6                                           | 0.065                                       | 1.5 0.5 6                                              |

at the anode were reached by heating the boilers at 54°C and 75°C, respectively. The gas lines were heated at 90°C to avoid water condensation. The back pressure was 1.2 bar on both sides. The air and fuel stoichiometric ratios were 2.0 and 1.2, respectively. The cell temperature was maintained at 75°C during the tests. Table I summarizes varying test conditions for each cell.

Electrochemical tests.—As seen from Table I, cells 1–4 were tested using a load cycling mimicking “day/night” operation with 24 h duration for one full cycle. This load profile was defined based on the specifications of a system aimed for electric power supply using fuel cell coupled with batteries. Figure 1a shows the current density profile applied to cells 1–4. Cell 5 was tested under more dynamic conditions.

Figure 1. Voltage profiles for the single fuel cells under aging test: cell 1 (a), cell 2 (b), cell 3 (c), cell 4 with corresponding concentration of CO in reformate gas (d) and cell 5 (e). Current density profile for cell 5 (f). Current density cycles shown for cell 1 were also used for cells 2–4. Numbers indicate measurements of polarization curves.
cycles of 2 h, the profile is presented in Figure 1f. The electrochemical characterization set consisted of 1) recording of polarization curves in reformate; 2) depolluting of MEAs tested under reformate hydrogen by 2 h operation in pure H2; 3) measuring 1 or 2 polarization curves in H2; 4) recording cyclic voltammograms. Electrochemical characterization was conducted at the beginning of test (BoT) and at the end of test (EoT) for all the cells and for cells 1, 2, 4 and 5 intermediate characterization tests were applied (Table 1). Initial performance for the cells was 0.741 ± 0.004 V at 0.4 A/cm2 and 0.694 ± 0.006 V at 0.6 A/cm2. For the cell 1 additional polarization curves were taken at 220 h and 865 h due to non-planned stops of the test bench. Voltage drops in Figure 1 correspond either to electrochemical characterization of the cells or to test bench shut-downs. At the EoT and in the course of aging tests, I-V curves were taken twice under pure H2 in order to recover reversible losses and ensure surface cleaning by complete CO desorption. Only second polarization curves were reported in this work. Polarization curves were recorded by increasing the current at 1 A/min until 37.5 A (1.5 A/cm2). All the CVs were recorded using a potentiostat Gamry ref 3000. The potentials reported are referenced to that of reversible hydrogen electrode (RHE). Cyclic voltammetry diagnostics were conducted at a scan rate of 50 mV/s in the potential range 0.90 to 0.8 V/RHE and at the same conditions as polarization curves (75°C, 40% RH on cathode and 100% RH on anode), in order to allow estimating ECSA changes before, during and after ageing. The potential upper limit was chosen to allow seeing the regions of interest, thus including at least beginning of Pt oxides formation and reduction but minimizing the impact of these electrochemical characterizations on catalyst structure. During cathode CV measurement the anode was supplied with hydrogen at flow rate of 150 sccm and served as a pseudo-reference and counter electrode. The cathode was purged with nitrogen at flow rate of 100 sccm. The single cell was turned to switch cathode and anode for the anode CV measurements following the same procedure.

Results and Discussion

Voltage degradation over short and long term periods.—Figures 1a–1e demonstrates voltage degradation for the cells 1–5. It is noticeable that variation of voltage values at a constant current of 0.065 A/cm2 is low and similar for all the cells. The average calculated voltage losses are between 2–3% over 1000 h, which does not allow differentiation between the effects of various aging protocols applied. On the contrary, large difference in voltage is observed for the cells at maximum current densities. This is related to the fact that at 0.4 and 0.6 A/cm2 there is an increased role of ohmic and transport losses compared to 0.065 A/cm2, where mostly kinetic limitations are important. In addition, in presence of reformate hydrogen, dilution of fuel takes place along with partial coverage of anode catalysts with CO contaminant. Even low concentrations of CO (10-50 ppm) decrease considerably with time the anode active surface, originally available for hydrogen oxidation reaction, by adsorbing CO molecules thus blocking the Pt active sites for hydrogen adsorption. At higher current density the impact of pollutant is more important because the quantity of contaminant within the fuel feeding the anode is higher since the fuel stoichiometry is fixed. Therefore, larger anode surface is contaminated by CO adsorption at 0.4-0.6 A/cm2 compared to that at 0.065 A/cm2. In addition, the impact of contamination is more important because the hydrogen oxidation overvoltage is higher with a reduced active surface occupied by CO. Further, voltage values at high current densities will be used for quantification of different aging protocols effects and estimation of accelerating features.

In Figures 1c and 1d, for tests 3 and 4, oscillations of voltage appear at high current density after 700 and 500 h of the tests, respectively. The potential oscillations are attributed to the coupling of anode electro-oxidation of H2 and CO on the PtRu catalyst surface, on which adsorbed oxygen-containing species are formed more readily, i.e., at lower overpotentials.18 With the introduction of CO in the anode feed, the CO begins to build up on the surface until the catalyst anode is low and similar for all the cells. The average calculated voltage degradation for the cells 1–5. It is noticeably that variation of voltage values at a constant current of 0.065 A/cm2 is low and similar for all the cells. The average calculated voltage losses are between 2–3% over 1000 h, which does not allow differentiation between the effects of various aging protocols applied. On the contrary, large difference in voltage is observed for the cells at maximum current densities. This is related to the fact that at 0.4 and 0.6 A/cm2 there is an increased role of ohmic and transport losses compared to 0.065 A/cm2, where mostly kinetic limitations are important. In addition, in presence of reformate hydrogen, dilution of fuel takes place along with partial coverage of anode catalysts with CO contaminant. Even low concentrations of CO (10-50 ppm) decrease considerably with time the anode active surface, originally available for hydrogen oxidation reaction, by adsorbing CO molecules thus blocking the Pt active sites for hydrogen adsorption. At higher current density the impact of pollutant is more important because the quantity of contaminant within the fuel feeding the anode is higher since the fuel stoichiometry is fixed. Therefore, larger anode surface is contaminated by CO adsorption at 0.4-0.6 A/cm2 compared to that at 0.065 A/cm2. In addition, the impact of contamination is more important because the hydrogen oxidation overvoltage is higher with a reduced active surface occupied by CO. Further, voltage values at high current densities will be used for quantification of different aging protocols effects and estimation of accelerating features.

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Initial performance loss for the cells was investigated over approximately 200 h of the tests. At this time scale, polarization curves were taken for all the cells except of the cell 3 (Figure 1). Table II summarizes the cell voltage degradation. To calculate total performance losses, voltage values were taken at 0.4 A/cm2 (for the cells 1–5) and at 0.6 A/cm2 (for the cell 5) at the BoT and after ~ 200 h at the end of the cycle. For the cell 4 similar calculations were done considering periods with different CO concentrations. Thus, for estimation of degradation in pure H2 over 200 h, the difference was taken between points 1 and 2 in Figure 1d. For the period of test under 10 ppm of CO, corresponding calculations were done using values taken at points 3 and 2; then using points 4 and 3 for 20 ppm and 5 and 4 for 50 ppm. The aim of this stepwise protocol was to identify the accelerating impact of a CO content higher than nominal value of 10 ppm. To this end, the AST for the cell 4 was continued by adding other ageing periods under reformate after 1000 h (repeating the 10 ppm step). Extra-point has been added on the graphs in Figure 3 corresponding to the aging period with 10 ppm of CO conducted just after the last pure H2 period previously identified (e.g. from 1100 h to 1300 h, period VI in Figure 1). In this case, the difference between points 6 and 7 was taken to calculate a short-term voltage loss. Electrochemical performance loss over full test was extracted from the data acquired at points 6 and 1 for pure hydrogen and at points 7 and 2 for 10 ppm testing. Therefore, for this cell injection of 10–50 ppm CO in the middle of the test should be considered when comparing voltage degradations with the other cells operated with fixed fuel composition. Intermediate electrochemical characterization appeared to be efficient tool for the fuel cell refresh, here attributed by assumption to homogenization of internal water distribution and cleaning of the contaminated electrodes surface, with the total desorption of CO from the anode catalyst and the removal of platinum oxides possibly elaborated at the cathode. The cells 2, 4 and 5 indeed demonstrate an increase in the initial voltage at high current densities after each set of characterization conducted every 200 h, which is not clearly visible in Figure 1. An example of such a performance recovery is shown in more details in Figure 2 for the cell 4. Therefore, after conducting electrochemical characterization relatively low irreversible cell aging is observed, which is confirmed by polarization curve data, and minor active surface area losses. For instance, the initial voltage values at 0.4 A/cm2 for the cell 4 at the
beginning of each CO poisoning periods II-VI in Figure 1d are varied around 0.71 V as, shown in more details in Figure 2.

Transient drop of voltage for the test periods under reformate compared to that one in pure H₂ in Figure 2 can be due to multiple factors including immediate response to simultaneous applying of load and reformate hydrogen, fast initial adsorption of CO on the electrode surface and fuel dilution effect. There are publications describing negative impact of CO₂ on electrochemical performance of fuel cells via catalytic reverse water-gas shift (RWGS) reaction. However, in the present work, the impact due to RWGS and to contamination of electrode with CO related to carbon support oxidation could occur but should be low because PtRu is used as anode catalyst and because tests were conducted under reformate with 10–50 ppm CO and not under H₂ with inert additives only. The fact that the cell 4 demonstrates similar performance at the beginning of each 200 h aging period under reformate allowed comparison of its performance under 10, 20 and 50 ppm of CO with the other cells having different pre-history. Dynamic data obtained from V-t curves during transients from low to high current densities in Figure 1e was used to extract total performance loss at 0.4 A/cm² for the cell 5 despite 0.6 A/cm² upper current density limit was normally applied. Irreversible voltage losses calculations were based on I-V curves data taken at 0.4 A/cm² (for the cells 1–5) and at 0.6 A/cm² (for the cell 5). Voltage values after 200 h of the test were subtracted from that recorded at the BoT.

Figure 3 demonstrates the trends obtained for total and irreversible performance losses for the cells within 200 h and 1000 h of the different aging tests. It is noticeable that in a short term scale there is a quite linear relationship between a cell voltage loss and a concentration of injected CO up to 50 ppm in Figure 3a. Cell 5 data collected at 0.6 A/cm² is out of range due to higher upper current density limit compared to the other tests. It is noticeable that total voltage loss for the cell 5 at 0.4 A/cm² is in a good agreement with other tests under reformate with 10 ppm of CO, i.e. cells 2 and 4 in Figure 3a. Voltage values after 200 h of the test were subtracted from that recorded at the BoT.

Another interesting observation is 50% growth of voltage losses for the cell 4 with 10 ppm CO from period II to period VI in Table II and Figure 3a. This means that high frequency and high amplitude protocol plays minor role for the loss of performance for the cell 5 at least within the first 200 h of the aging test. The main factor determining electrochemical behavior in this case is carbon monoxide in fuel.

Irreversible performance decay calculated from polarization curves recorded under pure H₂, gives quite low and similar values, less than 5% for all the cells (Figure 3a and Table II).

Considering a long term tests of 1000 – 1300 h in Figure 3b, it is clear that total degradation rate for the cell 3 operated in 26 ppm CO increases by 7% compared to 200 h performance analysis in Figure 3a. With further increase of CO concentration in fuel at some point a CO impurity concentration.
plateau could be reached in Figure 3b due to achieving a potential for electrochemical oxidation of CO to CO₂, as was discussed above for the oscillations observed in Figures 1c and 1d. The highest reversible and irreversible performance losses at the EoT is observed for the cell 5 at 0.4 and 0.6 A/cm² in Figure 3b, which confirms accelerated aging effect of high frequency and high amplitude cycling at 1000 h scale. The irreversible degradation values extracted from I-V curves are much lower compared to total voltage loss in presence of CO contaminant for the cells 1–5 (Figure 3b).

Both cell 4 and cell 5 demonstrate slightly elevated irreversible decay when comparing to values reached by cell 1 and cell 2 for 0 ppm and 10 ppm of CO, respectively. Thus, the gaps between these two cells and the ones that can be identified here as the nominal cases (e.g. cells 1 and 2) evidenced that both aging tests applied on the cells 4 and 5 include features increasing /accelerating losses (see Figures 1a, 1b, 1d and 1e). Therefore, it can be concluded that high CO content such as 50 ppm in a fuel gas and high frequency load cycling are important factors accelerating mostly reversible voltage degradation of a single PEMFC with much lower influence on the irreversible performance decrease. This is in line with previous findings. The longer the aging test, the higher is the magnitude of impact for accelerating factors.

**In-situ cathode cyclic voltammetry measurements.**—As clear from Table I and Figure 1, electrochemical diagnostics was conducted for all the cells at the BoT and EoT and for the cells 2, 4, and 5 additionally every 200 h. Figure 4 depicts the evolution of cathode electrochemical active surface area (ECSA) via Cyclic Voltammetry (CV) diagnostic applied after initial conditioning of the cells and after about 1000 h of aging.
Smooth broad peaks related to underpotential deposition of atomic hydrogen (Hupd) are observed in the cathodic sweeps at the BoT. Cycling of the cells for ~1000 h resulted in decrease of hydrogen adsorption and desorption maxima for the cells 1–5 in Figures 4a–4e. In addition, better resolution of Hupd peaks corresponding to bigger particles or different facets of polycrystalline Pt catalyst is observed (clear peak at 0.23 V). The platinum oxide region also underwent reduction in area after aging, even though the CVs were measured only up to 0.8 V vs RHE, as seen in Figures 4a–4e. The most pronounced reduction in ECSD takes place for the cell 5, as clear from Figures 4e and 4f. This confirms an accelerating aging impact of high frequency and high amplitude load cycling on the irreversible performance drop. Diminution in cathode ECSAs was calculated by integration of hydrogen desorption area before and after conducting accelerated aging. The results are plotted in Figure 4f together with irreversible losses extracted from polarization curves at the BoT and EoT. For most of the cells the trends for irreversible voltage and ECSA losses are similar in Figure 4f except of the cell 3. It can be confirmed that at least some part of the irreversible performance decay is related to decrease of cathode ECSA for the cells 1, 2, 4 and 5. Cell 3 was particular due to its continuous aging test profile without any planned or unplanned interruptions and consequently the absence of excursion to low voltages in the course of the test in Figure 1c. Previously it was reported that multiple potential perturbations including high and low voltage operation in the course of electrochemical test has an impact on the performance of PEMFC.21,22 It is known that noble metals are subjected to transient dissolution during dynamic potential operation.23 Frequent reduction of platinum surface oxides during voltage transients to low potentials (CVs, LSVs) on positive electrode provokes Pt dissolution.24,25 Therefore, on the basis of CV measurements we hypothesize that irreversible degradation for the cell 3 is related to factors other than cathode ECSA drop. The performance of the cells 2, 4 and 5 can be compared directly since I-V and CV curves measured for double layer capacitance decrease for these cells (56% and 65%, correspondingly). This means that other factors than anode CV measurements impacted the anode catalyst evolution. In case of the cells 2 and 4 it was different concentrations of CO in reformate.

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**In-situ anode cyclic voltammetry measurements.—** Anode voltammograms recorded before and after the aging tests are shown in Figure 5. At the BoT the CV features are typical for PtRu catalyst, they are characterized by high double layer capacitance and broad Hupd peaks. After 1000 h of aging, this typical PtRu shape is preserved in the cell 1 whereas a different shape is observed in the other cells submitted to aging under reformate indicating that the catalyst surface was modified toward pure Pt. It is remarkable that the available surface area of the anodes estimated by integration of hydrogen desorption peak areas is increasing after current cycling. Thus, the increase in the anode ECSA is around 12% for the cell 1 and 52% for the cell 3, which is summarized in Figure 5f. Cells 2 and 3 show higher increase in anode active surface after the aging test compared to the cells 4 and 5 while cell 1 is the least impacted.

It is difficult to precisely explain the changes for the PtRu alloy anode active surface since few parallel processes take place: i) predominant leaching of Ru as a less noble metal compared to Pt and, hence, liberation of new Pt surfaces available for hydrogen adsorption and desorption, this leads to increase in ECSA and diminution of CO tolerance; ii) partial degradation of Pt particles via agglomeration and Ostwald ripening with time resulting in ECSA decrease; iii) diffusion of Pt ions from the cathode side and their reduction on anode catalyst particles by H2 flow in certain conditions.26,27 Finally, the anode active surface area at the EoT is a result of these processes. Most probably, the anode catalyst of the cells 2 and 3 has been degraded mainly by the Ru dissolution mechanism whereas the anode catalyst of the cells 4 and 5 was exposed to harsh electrochemical conditions enhancing degradation of both metals. There is no correlation between the measured anode ECSA change and irreversible voltage losses for the cells 1–5, as shown in Figure 5f. The shape of anode CV graphs changes dramatically for the cells 2–5 after conducting aging tests in Figures 1b–1e. The main features of the voltammograms after aging are decrease in double layer capacitance values, visible in the region of 0.3–0.4 V vs RHE and apparition of the peak at 0.21 V vs RHE at the anode sweep of the curves. In general, CV curves for the cells 2–5 have Pt-like shape after 1000 h of cycling in reformate, whereas for cell 1 the CV curve still presents a shape corresponding to the initial PtRu based catalyst. It should be mentioned that applying 0.8 V vs RHE as an upper cutoff voltage for the anode CVs in this work did not impacted much the anode catalyst degradation. Thus, seven electrochemical characterizations were conducted during 1200 h tests for the cells 2 and 4 (Table 1). Figure 5f demonstrates different values for double layer capacitance decrease for these cells (56% and 65%, correspondingly). This means that other factors than anode CV measurements impacted the anode catalyst evolution. In case of the cells 2 and 4 it was different concentrations of CO in reformate.

Large increase of ca. 50% in the accessible surface area of Pt in the course of potential cycling experiment (1000 cycles between 0–1.0 V and 0–1.2 V vs RHE) for PtRu alloy anode of was reported previously.28 The authors employed CO-stripping method to follow the changes in anode ECSA along with post-mortem STEM observations. It is noticeable that negative electrode ECSA estimations via Hupd peak area in the present work gave similar conclusion with ECSA assessment via CO-stripping area in the previous study.29 This means that both methods are useful to observe active area changes for PtRu electrode.

Moreover, our group reported a detailed transmission electron microscopy investigation of PtRu membrane precipitates in the cell 3.27 This study clearly showed dissolusion of Ru from the PtRu anode catalysts, its diffusion and precipitation within the anode micro-porous layer and within the membrane. Various morphologies for the PtRu deposits into the membrane were found and a mechanism for their formation was proposed. However, using a semi-quantitative X-EDS analysis in combination with TEM did not allow to observe any changes in proportions of Pt and Ru in the anode catalyst layer due to high heterogeneity of the catalyst even in the initial state. Figure 5f shows a good agreement between the results of double layer capacitance (DLC) drop measurements for the anode CV curves and irreversible voltage losses obtained from polarization curves. Therefore, DLC evolution is one of the suitable parameters to correlate PtRu anode catalyst degradation with other parameters of the cell performance contrary to ECSA evolution estimation via Hupd peaks integration. It is evident that modification of the anode active layer during current cycling test contributes to irreversible performance loss by PEMFC. This contribution is less critical compared to diminution of the cathode active surface since the kinetics of hydrogen oxidation reaction is much faster than that of oxygen reduction in pure H2. Nevertheless during operation under reformate the role of PtRu catalyst restructuring is crucial. There is a literature report describing CO-induced Pt nanoparticle surface reconstruction at saturation coverage via DFT calculations.29

**CO tolerance estimation for the anode catalyst.—** As mentioned above, the anode catalyst structure for the cells 2–5 operated under reformate was more impacted compared to the cell 1 tested in pure H2, with larger increase in double layer capacitance and Hupd region peaks characteristic of Pt catalyst observed for the cells 2–5 in Figure 5. This means that more Ru was dealloyed and dissolved from the surface of PtRu anodes in presence of reformate. This phenomenon is directly related to the overpotential initially created on the anode especially at high current densities in reformate due to significant coverage of Pt active sites by CO. If the kinetics of PtRu catalyst coverage by CO is faster than that of CO electrochemical oxidation, hydrogen evolution reaction might occur at high positive potentials. To estimate the overpotential values for the cells 2–5, polarization curves in pure H2 and in reformate taken at the EoT are presented in Figure 6. For the cell 4 the data was recorded after exposure to 50 and 10 ppm CO at points 5 and 7 in Figure 1d, correspondingly.
The I-V curves recorded in pure H₂ are very similar with some differences at the current densities > 0.4 A/cm². There are larger discrepancies for the curves obtained under reformate. In particular, OCV and kinetic region seem to be similar for the cells 2–4 while ohmic part of the polarization curves shows different cell performances. A step-like shape of the polarization curves taken under reformate for the cells 3–5 in Figure 6 is due to coverage of the active anode surface with CO. At low current densities the impact of CO is not high because there is enough Pt surface non-covered with CO for HOR. However, for each curve in Figure 6 there is a critical current density, at which dramatic voltage drop is observed. For example, it is around 150 mA/cm² for the cell 4 after 50 ppm CO. Starting from this point there is a lack of non-poisoned Pt surface for HOR. With increasing current density the potential at the anode increases to values at which adsorbed CO could be oxidized to CO₂. That is why a plateau is observed on polarization curves under reformate for the cells 3–5 in Figure 6 at total cell voltages lower than 0.5 V. The slope of this plateau is determined by ohmic drop and mass transport losses. Minimum cell voltage during I-V curve registration was 0.4 V vs RHE, that is why some curves are short. Overpotential values were calculated via subtraction of voltages at 0.4 A/cm² in pure hydrogen and in reformate for each cell. The results are summarized in Table III. The highest overpotential is found for the cell 4 operated with different fuels including a period with 50 ppm CO and slightly lower values are obtained for the cells 3 and 5. It confirms that large amounts of CO is the main stressing factor responsible for the anode performance deterioration. Comparing the data for 10 ppm CO and different cycling protocols (normal and high frequency cycling with 0.4 (cell 2) and 0.6 A/cm² (cell 5) upper current density limits, correspondingly), it is evident, that increased frequency and upper current limit

![Graph](image-url)
of cycling leads to anode overpotential growth of more than 3 times. Moreover, this conclusion is confirmed by considering overpotential values for the cell 4 at 10 ppm CO (115 mV) and cell 5 (210 mV) in Table III. Therefore, high frequency and high amplitude load cycling leads to more pronounced CO tolerance loss compared to 200 h injections of fuels with elevated CO content. It is in line with CO tolerance degradation via polarization curves before and after aging test: voltage losses at 0.4 A/cm² are 5 times higher for the cell 5 in comparison with the cell 2 in Table III. Cells 3 and 5 gave similar overpotential at 0.4 A/cm² and close performance losses after 1000 h of aging in reformate, which may be attributed to “compensation” of high frequency cycling for cell 5 by higher concentration of CO in case of the cell 3. However, at 0.25 A/cm² the cell 3 with 26 ppm CO shows worse electrochemical characteristics, Figure 6.

Considering the cell overpotential values induced by coverage of anode active surface by CO from Table III, all of them are lower than the potential of direct anodic dissolution of Ru (0.5 V). Nevertheless, Ru dissolution was confirmed for the cells 2–5 via CV curves in Figure 5. It should be noticed that Ru is a complex element existing as Ru dissolution was confirmed for the cells 2–5 via CV curves in anode active surface by CO from Table III, all of them are lower than 0.2 V vs RHE. Ru metallic nanoparticles were found to be the most unstable electrochemically compared to RuO₂. Therefore, Ru leaching form the anode catalyst layer caused by high anode overpotential values is responsible for the PtRu particles active surface evolution in Figures 5b–5e.

Polarization curves in Figure 6 under reformate were recorded immediately after cell cycling without applying any cleaning procedures. That is why they reflect both reversible and irreversible losses of the cell associated with adsorption of CO on the anode and possibly reversible mass transport limitations. The largest part of CO can be removed by operation in pure H₂, as shown for the cell 4 (after 200 h in 50 ppm reformate, operation for 200 h in H₂ pure helped to recuperate the performance in Figure 1d). On the contrary, CV curves changes shown in Figure 5 are the evidence of irreversible anode catalyst transformations toward lower CO tolerance due to Ru loss. This fact is in good agreement with evolution of CO tolerance with time shown for the cells 2, 3 and 5 in Table III.

Based on these results, relevant features for defining AST protocols could be determined for fuel cell operating under low content of reformate and load cycling. Considering a specific system, current densities and CO concentrations higher than the nominal values are the main stressors to be combined for increasing and accelerating the performance degradation. Under reformate/air, like under hydrogen/air operation, applying load cycles can lead to the cathode catalyst degradation by well-known mechanisms such as electrochemical Ostwald ripening and dissolution with, as the main accelerating feature not related to operating conditions, the voltage amplitude allowing harsh electrochemical cycles between oxidation and reduction steps involved in these mechanisms. For the reformate case, the specificity is obviously coming from the anode side, where the weak point for the current commonly used catalyst (PtRu) is the poor stability of ruthenium. The related impact on the fuel cell operation is the loss of CO tolerance, leading to performance degradation. The two accelerating parameters identified here are both causing an increase of the anode surface potential due to the overpotential more important at high current and to the higher coverage by CO. Time spent by the anode catalyst under high CO coverage or high overpotential activates the oxidation of the ruthenium, and frequency of anode potential decrease caused by surface cleaning activates the dissolution

Table III. Overpotentials for the cells 2–5 extracted from polarization curves in Figure 6 and relative cell performance degradation values after aging tests calculated from corresponding polarization curves in reformate.

| Cell number | Amount of CO in reformate, ppm | Calculated cell overpotential @ 0.4 A/cm², mV | Loss of performance in reformate (BoT-EoT) @ 0.4 A/cm², % | Precise cycling test duration, h | Accelerated stress factors |
|-------------|-------------------------------|-----------------------------------------------|--------------------------------------------------------|---------------------------------|----------------------------|
| 2           | 10                            | 63                                            | 4.6                                                   | 1145                            | Reformate, cycling, CVs     |
| 3           | 26                            | 204                                           | 17.9                                                  | 1000                            | Reformate, cycling          |
| 4           | 10                            | 115                                           | 6.2*                                                   | 1282                            | Stepwise increase in CO concentration: 0, 10, 20, 50, 0, 10 (200 h each); cycling, CVs |
| 4           | 50                            | 266                                           | N/A                                                   | 934                             | Stepwise increase in CO concentration: 0, 10, 20, 50 (200 h each); cycling, CVs |
| 5           | 10                            | 210                                           | 23.0                                                   | 1070                            | Reformate, high frequency cycling, CVs |

*taken between points 3 and 7 in Figure 1d, 831 h of aging.
of the oxides. As a consequence, high frequency load cycles coupled to high CO and high maximum current density strongly promote the mechanisms causing the loss of CO tolerance thus accelerating the performance degradation.

Conclusions

Aging tests under load current cycling and various reformate fuel compositions were conducted for 5 identical fuel cells with Pt-based catalyst on the cathode and PtRu on the anode aiming at systematic investigation and quantification of impacts of different stressing factors on the electrochemical performance of the cells over about 1000 h. Test conditions representative for stationary fuel cell operation were used. The main accelerating aging parameters were i) carbon monoxide concentration in reformate, 10 ppm was taken as a nominal value; ii) amplitude and frequency of current load cycling; iii) applying regular intermediate electrochemical in-situ characterizations like polarization curves and cyclic voltammetry measurements. Considering a short term performance of the cells over 200 h, the main accelerating stressor was found to be CO concentration in fuel varied between 10 and 50 ppm for different cells. The highest total voltage decay demonstrated the cell tested with 50 ppm CO in reformate. Pre-history of cell contamination with CO and duration of test were also important for the further performance. Thus, one of the cells was tested under varying fuel compositions with injection of 0, 10, 20, 50, 10, 10 ppm CO, each for 200 h. The second period under reformate with 10 ppm CO showed two times increased voltage loss at a highest current density of 0.4 A/cm² compared to the first one. Over 1000 h test scale, two main accelerating parameters were defined. The first one is CO concentration in reformate fuel and the second one is amplitude and frequency of load cycling protocol. One of the cells was tested at elevated frequency and upper current density limit (0.6 A/cm²). It was found that total voltage losses were less important for the cell tested under 10 ppm CO using standard protocol (-9.6% at 0.4 A/cm²) compared to the cell subjected to high frequency/amplitude cycling under 10 ppm CO (-26.4% at 0.4 A/cm²). This emphasized an accelerating aging impact of a test protocol. The largest part of cell performance losses under reformate was reversible and it was retrieved by measuring polarization curves, cyclic voltammograms and electrode surface cleaning via cell operation in pure H₂. The highest irreversible voltage drop was observed for the cell tested under high frequency/amplitude protocol, which was related to the elevated cathode ECSA loss in this case. In general, accelerating aging effect of electrochemical diagnostics on cathode ECSA was evidenced by comparing the active surface area diminution for the cells characterized electrochemically every 200 h and for the one characterized only at the beginning and end of the aging test. Cell overpotentials induced by anode CO tolerance losses were estimated after 1000 h of aging tests under reformate. 50 ppm CO in reformate fuel induced the highest overpotential of 266 mV for the cell tested under varying fuel compositions. Apart from that, the most pronounced overpotential values were found for the cell tested under fuel with 26 ppm CO and standard cycling protocol (204 mV) and for the cell investigated under elevated frequency/amplitude protocol and 10 ppm CO (210 mV). It can be concluded that both CO content in fuel and a type of load cycling protocol are accelerating the cell performance losses associated with a decrease in the anode CO tolerance while intermediate electrochemical characterization leads mostly to cathode ECSA drop.

The findings of this work provide complex insight into stationary fuel cell behavior taking into account various aging stressors, their combinations and their importance in specific conditions in comparison to other cases. We believe that this detailed investigation describing the data on 5000 h of total aging time will contribute to the development of efficient accelerated stress protocols for stationary FCs.

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