

Effect of accelerated ageing tests on PBI HTPEM fuel cells performance degradation

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ABSTRACT

The study presented in this paper aims to evaluate the performance degradation of Polybenzimidazole (PBI) based High Temperature PEM (HTPEM) fuel cells subjected to different ageing tests, according to a methodology already used by the authors. Three HTPEM Membrane Electrode Assemblies (MEAs) were characterized before and after different aging tests and performance compared. The three MEAs have been named MEA C, MEA D and MEA E. MEA C was subjected to 100,000 triangular sweep cycles between Open Circuit Voltage (OCV) and 0.5 A/cm² with 2 s of permanence at OCV at each cycle. MEA D and MEA E were subjected to 440 h of operation at constant load of 0.22 A/cm². In order to assess the cell performance, polarization curves, Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) were recorded during the ageing tests. Degradation rates have been obtained for MEA C (44 μ V/h), for MEA D (30 μ V/h) and for MEA E (29 μ V/h). ECSA (Electrochemical Surface Area) has been calculated for the three MEAs showing a reduction of approximately 50% for MEA C and of approximately 30% for MEA D and MEA E. Polarization curves during aging tests confirm that load cycling is more detrimental. A comparison with data obtained by the authors in a previous research seems to confirm the repeatability of the test protocol used.

Introduction

Polybenzimidazole (PBI) based High Temperature Polymer Electrolyte Membrane (HTPEM) fuel cells (FC) represent a possible option to Nafion based PEM FC, especially for micro Combined Heat and Power (CHP) applications. The development of High Temperature (up to 200 °C) PEM fuel cells has introduced some improvements regarding operation with fuels such as Natural Gas (NG) and Liquefied Petroleum Gas (LPG): HTPEM fuel cells, thanks to their high CO tolerance, need minor purification processes in reformers and simpler, thus less expensive, systems [1].

HTPEM FCs in addition to their higher CO tolerance show other advantages [2,3,4] such as: simplification of the heat recovery system, higher reactants diffusion rate and the possibility to use alternative catalysts.

However, the main limiting factors that hamper commercialization of HTPEM are: cost, operational lifetime and performance degradation. Regarding performance degradation, PBI membranes demonstrated a good lifetime under steady state operation, reaching up to 17 000 h of operational life [5,6], but higher performance degradation rates have been measured when HTPEM fuel cells operate under variable load conditions [7–11].

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List of acronyms

CHP	Combined Heat and Power
CV	Cyclic Voltammetry
DOE	Department of Energy
ECSA	Electrochemical Surface Area
EIS	Electrochemical Impedance Spectroscopy
HTPEM	High Temperature Polymer Electrolyte Membrane
JRC	Joint Research Centre
LPG	Liquefied Petroleum Gas
LTPEM	Low Temperature Polymer Electrolyte Membrane
MEA	Membrane Electrolyte Assembly
NG	Natural Gas
OCV	Open Circuit Voltage
PBI	Polybenzimidazole
PC	Polarization Curve

Operating conditions strongly affect durability and hence, optimization of operation strategies is essential in mitigation of fuel cell degradation and many studies are aimed to analyze working parameters affecting MEAs durability.

Performance degradation of a HTPEM based on phosphoric acid-doped polybenzimidazole (PBI) membranes, such as the one considered in this work, is mainly due to undesired reactions and corrosive environment that can be also related to load cycling between low and high cell voltages, operation at low humidity and high temperature, and fluctuations in temperature and humidity [12–22]. The main problems reported in the literature [2] are the loss in the catalyst active area due to catalyst agglomeration, and phosphoric acid leaching out from the cell [13]. In the attempt to separate the effect of operating conditions on performance degradation, in this paper, the study area is limited mainly to high potentials and load cycling.

High potentials are an important cause of the degradation of the catalyst and its support [23]. Open Circuit Voltage (OCV) increases the Pt particle agglomeration because both Pt oxidation and carbon corrosion are favored at high electrode potential. The Pt oxidation starts the dissolution and the Ostwald ripening process, while the carbon corrosion triggers the agglomeration by coalescence [24,25]. Wu et al. [15] carried out a 1200 h test with a six-cell PEMFC stack operating

close to OCV. The cell degradation increased after 800 h: in the first period, the degradation of fuel cell performance was mainly attributed to catalyst degradation, while the subsequent dramatic decay has been supposed to be caused by membrane failure. Qi and Buelte [26] investigated the impact of OCV on the performance of HT-PEMFCs and measured a fast OCV increase in the first few minutes followed by a slower increase and a peak after 35 min. Electrochemical Impedance Spectroscopy (EIS) indicated loss of catalyst activity and XRD showed an increase of the cathode Pt crystallites size of 430% after 244.5 h of OCV exposure. A similar result has been reported by Zhang et al. [27] during a 250 h ageing test under OCV condition.

Since, at present, the main potential application for HTPEM FC is distributed micro co-generation, literature on HTPEM durability and performance degradation is mainly focused on steady-state operation [4,28,29] and its comparison with dynamic start/stop operation [8,30,31,33]. In these operation modes, many degradation mechanisms of different fuel cell components take place simultaneously and it is difficult to allocate malfunctions and effects. In order to focus on one single ageing phenomenon, it is necessary to develop specific testing procedures that allow forecasting and isolating a specific degradation mechanism. Some researches on HTPEM FCs have been focused on the effect of temperature cycling [34,35] on fuel cell performance and electrocatalyst degradation, but a limited number of publications deal with catalyst degradation induced by load cycling [31,36]. Specific tests to characterize the electrocatalyst degradation based on load cycling operation are common in low temperature PEMFCs research [37] as dynamic load operation is widely investigated because of its importance for automotive applications. Indeed, carrying out ageing tests based on load cycling on high temperature PEM fuel cells is not intended to study their behavior in real applications, but it could be of great interest in order to isolate the effects of electrocatalyst degradation from other mechanisms that can be favored during other operation modes. Load cycling has been proved to be a significant stressor for catalyst degradation [24,25,38,39,40] and it is possible to perform this operation keeping constant other parameters such as temperature and reactants flow.

For load cycling test protocols there are many studies and propositions [19,41,15,42,43] and, in this work, it has been chosen to implement for the HTPEM FC a load cycle derived

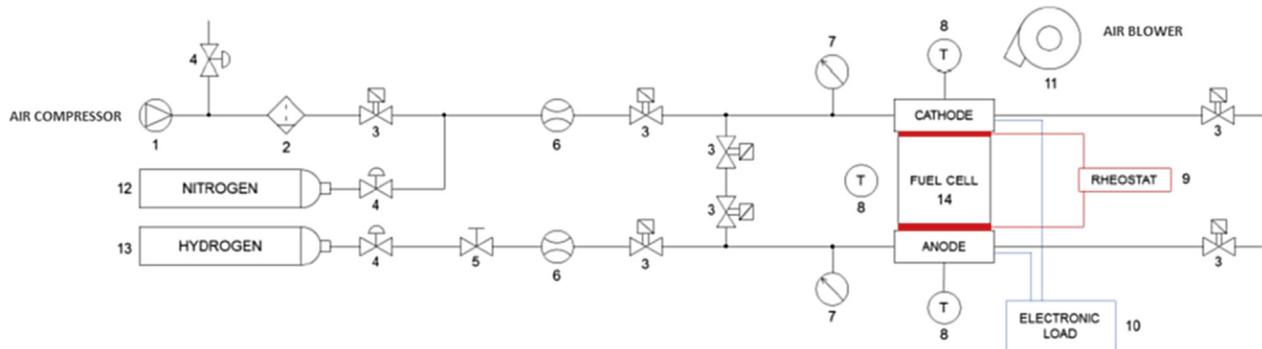


Fig. 1 – Simplified schematic of the test bench: (1) air compressor, (2) air filter, (3) solenoid valve (4) pressure regulator, (5) valve, (6) flow meter, (7) pressure transducer (8) thermocouples, (9) rheostat, (10) electronic load, (11) air blower (12) nitrogen cylinder, (13) fuel cylinder and (14) fuel cell.

from the accelerated stress test protocol developed in 2009 for electrocatalysts analysis in low temperature PEM fuel cells by U. S. DOE [44,45]. The modified protocol, described in Section [Methodology](#), has already been used a first time by the authors to study a set of HTPEM MEAs [6] and, one of the aims of this paper, is to assess if the protocol, applied a second time on the same type of MEAs, gives the same data in terms of performance degradation.

In the attempt to separate the load cycle effect from the constant load induced degradation, two MEAs have been subjected to constant load operation for an amount of hours equal to the length of the load cycle protocol.

Methodology

The tests have been performed on 45.16 cm² BASF Celtec-P1000 HTPEM MEAs operated with hydrogen and air. The test bench used for the aging tests is schematically presented in [Fig. 1](#). Two pressure transducers are used to measure the reactants inlet pressures. The cell temperature is measured using K-type thermocouples fitted on the anode and cathode endplates. Reactants flow rates are measured and controlled using two mass flow controllers: a Sierra SmartTrack M100 for the air circuit and a Bronkhorst El-Flow F201 for the hydrogen circuit.

Before starting the degradation tests, all MEAs have been operated for 100 h under reference conditions as suggested by the manufacturer ($T = 160\text{ }^{\circ}\text{C}$, $i = 0.22\text{ A/cm}^2$). Two aging profiles have been tested on three MEAs hereafter named MEA C and MEA D and MEA E and afterwards compared with results already obtained by the authors in a previous work [6] on MEAs named MEA A and MEA B.

In the previous work, MEA A had been subjected to 100 000 triangular sweep cycles between 0.01 A/cm² and 0.5 A/cm² ([Fig. 2](#)) corresponding to 440 h of operation.

MEA C (as previously done on MEA B) has then been subjected to 100 000 triangular sweep cycles between Open Circuit Voltage (OCV) and 0.5 A/cm² ([Fig. 3](#)) corresponding to 440 h of operation. MEA D and MEA E have been subjected to 440 h of constant load operation at 0.2 A/cm² ([Fig. 4](#)). This methodology has been considered in the attempt to separate the effect of load cycling from constant load operation.

During load cycling, MEAs temperature has been kept constant at 160 °C. Air flow has been kept constant at 2 sl/min

and no backpressure applied to the cathode outlet. Anode was maintained, only during test cycles, in dead end operation with a purge every 3 min.

In order to measure cell performance degradation, fuel cell potential variation with time, Polarization Curves (PC), Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) have been recorded.

Polarization curves have been carried out following a specific procedure based on JRC recommendations [46,47]. In particular, as suggested in Ref. [46], for single cell testing, reactants flows have been kept constant over the entire polarization curve; H₂ flow was set to 0.5 sl/min while air flow was set to 2 sl/min. For each point of the PC, a steady state condition was maintained for 2 min. The polarization curves have been measured in galvanostatic mode from 0 to 500 mA/cm² with steps of 22 mA/cm². The presented data are the average of two polarization curves measured at 4 h time interval.

EIS has been carried out according to the methodology described in Ref. [9] and discussed in Section [EIS](#). Cyclic Voltammetry has been carried out according to the methodology described in Ref. [6] and discussed in Section [Cyclic voltammetry](#).

Experimental results

Polarization curves

[Fig. 5](#) shows the MEA C PCs before and during the aging cycles.

The performance loss, in terms of potential reduction, between the beginning and the end of the 100 000 load cycling procedure, is less than 6% for all current densities. These results are comparable with the data obtained by authors in previous work [6] with the same membrane and load cycle profile. Degradation after 100 000 cycles at 200 mA/cm² has been found to be 19 mV (2.8%) while in the previous work on MEA B, for the same current level, it has been found a degradation of 20 mV which is in good accordance and confirms the repeatability of the test.

Regarding the constant load tests, [Fig. 6](#) shows the PCs recorded in different period of the test on MEA D.

In this case, degradation after 440 h at 220 mA/cm² has been found to be 13 mV (2.0%).

For MEA E ([Fig. 7](#)), subjected to the same constant load test, the performance loss, in terms of potential reduction,

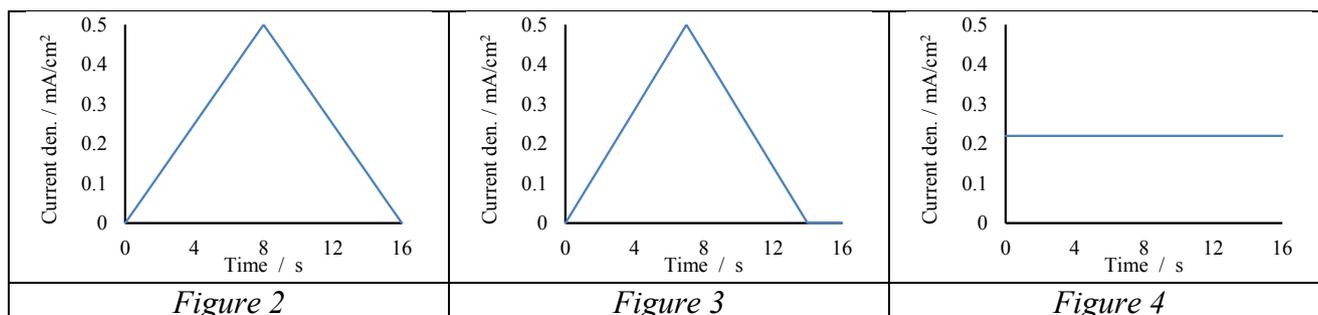


Fig. 2-4 – Figure 2: Load cycle profile MEA A. Figure 3: Load cycle profile MEA B and MEA C. Figure 4: Load cycle profile MEA D and MEA E.

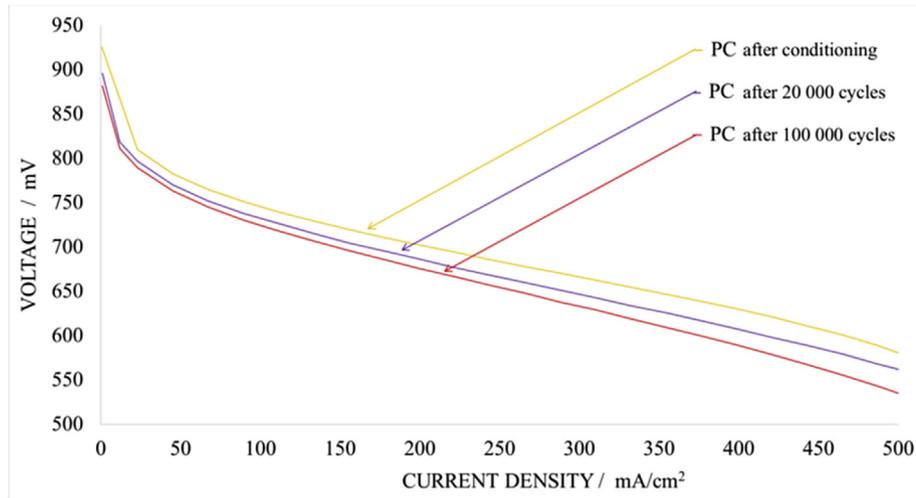


Fig. 5 – MEA C – Polarization curves during and after the ageing test.

between the beginning and the end of the 440 h of constant load operation is, as for MEA D, lower than 4.5% for all current densities. A loss of 24 mV (4.2%) has been found for a current density of 440 mA/cm², and a loss of 16 mV (2.4%) has been found at 220 mA/cm².

These results on PBI membranes are confirmed in literature [28,30].

In Ref. [28] a degradation rate of 150 μV/h was found for a similar PBI MEA operated at constant load of 640 mA/cm². This value could be compared to the value of 140 μV/h measured by the authors at 450 mA/cm² for MEA D.

The results presented in Ref. [30] can be interesting for comparison at lower current densities: in this research a PBI MEA has been subjected to a constant load of 0.2 A/cm² and a degradation rate of 25 μV/h over a period of 780 h. This value can be comparable with the results obtained on MEA D (30 μV/h) and MEA E (29 μV/h).

Table 1 shows the degradation rate for all the MEAs tested by the authors. It can be inferred, as expected, that load cycles stress more the MEAs and that OCV operation is detrimental [31].

The increased degradation observed in MEA C and MEA B with respect to other MEAs is complex to analyze as it could be attributed to a higher degree of Pt particles agglomeration, favored by permanence at OCV or, as it can be inferred by the voltage shift at OCV conditions in the polarization curves of MEA C, other mechanisms, such as reactants crossover and internal short circuit, could play a role [27].

Another variable that could affect the degradation during the stress tests is the total energy produced by the cell during the entire test. Since one typical application of HTPEM is cogeneration, it can be interesting to compare the degradation at constant total energy production, in order to analyze which operating conditions are more favorable. Hence, to allow comparison between cycles, energy yields have been calculated:

- Triangular [0.01–0.5]V: 11.8 MJ
- Triangular [0–0.5]V – 2s OCV: 10.0 MJ
- Constant load 0.22 A/cm²: 10.0 MJ

One of the information that can be inferred from these values is that the total energy produced with MEA A (11.8 MJ) is

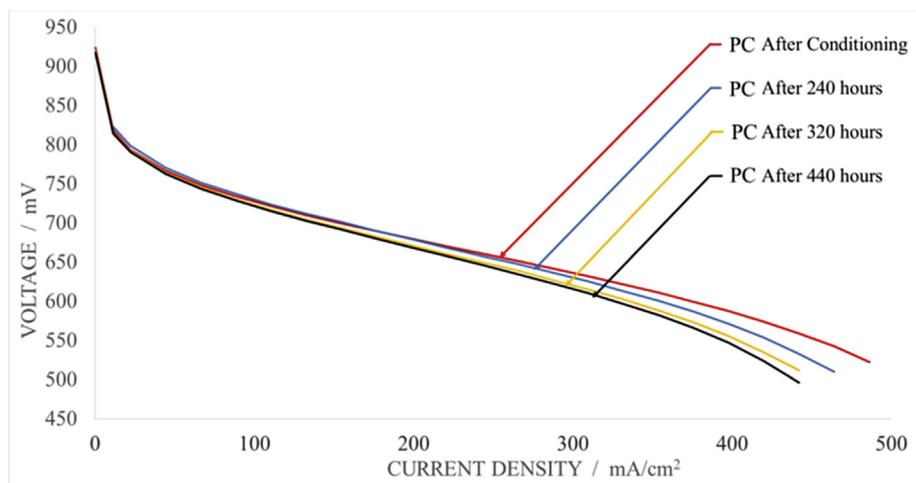


Fig. 6 – MEA D – Polarization curves before, during and after the constant load test.

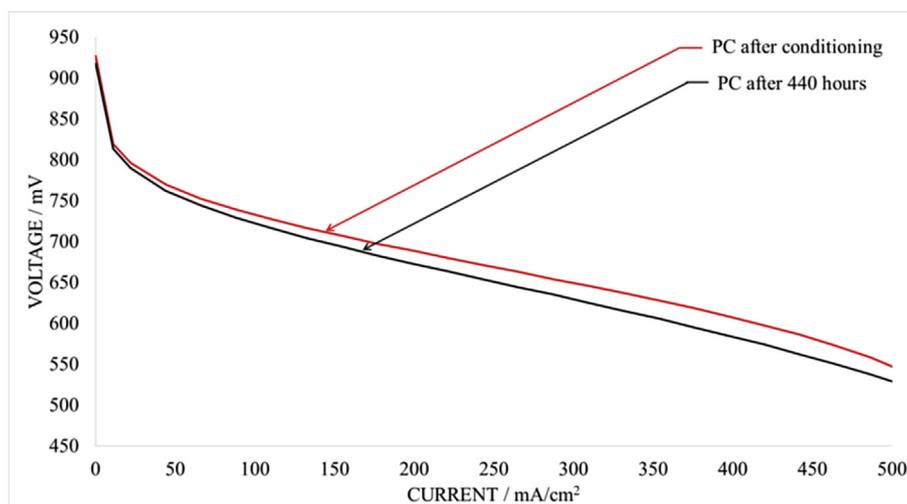


Fig. 7 – MEA E – Polarization curves before, during and after the constant load test.

Table 1 – MEAs degradation rates.

MEA label	Load profile	Current density	Degradation rate
MEA A – previous work [6]	Triangular [0.01–0.5]V	200 mA/cm ²	34 μV/h
MEA B – previous work [6]	Triangular [0–0.5]V – 2s OCV	200 mA/cm ²	45 μV/h
MEA C – this paper	Triangular [0–0.5]V – 2s OCV	220 mA/cm ²	44 μV/h
MEA D – this paper	Constant load 0.22 A/cm ²	220 mA/cm ²	30 μV/h
MEA E – this paper	Constant load 0.22 A/cm ²	220 mA/cm ²	29 μV/h

higher than that produced with MEA B and C (10.0 MJ) therefore, as expected, this is an additional confirmation that the operating cycle (in this case the permanence at OCV conditions) is affecting the degradation (higher in MEA B and C compared to MEA A).

EIS

Fig. 8A–C shows the Electrochemical Impedance Spectroscopy (EIS) of the MEA C respectively at 22 mA/cm², 220 mA/cm² and 330 mA/cm² before and after ageing test.

EIS is carried out in galvanostatic mode. The amplitude of the perturbation sinusoidal function has been chosen to be of 10% of the base current.

The EIS spectrum has been measured for 100 frequencies from 0.1 Hz to 1000 Hz.

Results in terms of the EIS spectrum and its evolution with ageing are in accordance with similar studies [1,9], on HTPEM.

EIS plots are related to the polarization processes occurring at the cathode and their shape is affected by the current regime selected for the test. In general, the polarization decreases as the current increases. Two main components at high (HF) and low frequency (LF) are present which are attributable to charge transfer and mass transfer processes respectively [9]. At low current the mass transfer phenomena are negligible and it is possible to distinguish only one arc related to activation losses. The dependence of this component on the current implies that charge transfer resistance represents the largest contribution to the MEA internal losses

[9]. However, with the increase of current, diffusion processes become also significant.

The effect of aging is similar for all the membranes: at low current no changes are observed, meaning, presumably, that the nature and morphology of the electrode/electrolyte interface remain the same; at higher currents the HF and LF components increase, which implies a decrease of catalytic active area within the electrode. The cause of this degradation is probably related to the agglomeration of platinum particles. Several studies [9,32] have confirmed that the acidic conditions encountered in this type of MEA favor the dissolution of platinum and its agglomeration over time, recognizing this as one of the main causes of cell deactivation.

Another possible mechanism of MEA degradation, which was observed when a cell operates at high potential, is carbon corrosion [23,32]. Oxidation of the support leads to the possible loss, isolation and agglomeration of the catalyst. Moreover, carbon corrosion can be responsible of a higher hydrophilicity of the cathode, causing a depletion of acid. A reduction of the acid may be responsible of lower conductivity of the electrode along with a reduction of three phase boundary zone. It is interesting to notice that while in spectrum of MEA C (Fig. 8) the ohmic resistance has increased from the beginning to the end of the ageing test, there is almost no variation of ohmic resistance in spectrum of MEA D (Fig. 9A–C) as well as in MEA E (Fig. 10A–C).

The higher potential degradation of MEA C found with the polarization curves analysis, could be related to the conditions selected for the aging. At OCV, high voltage strongly favors

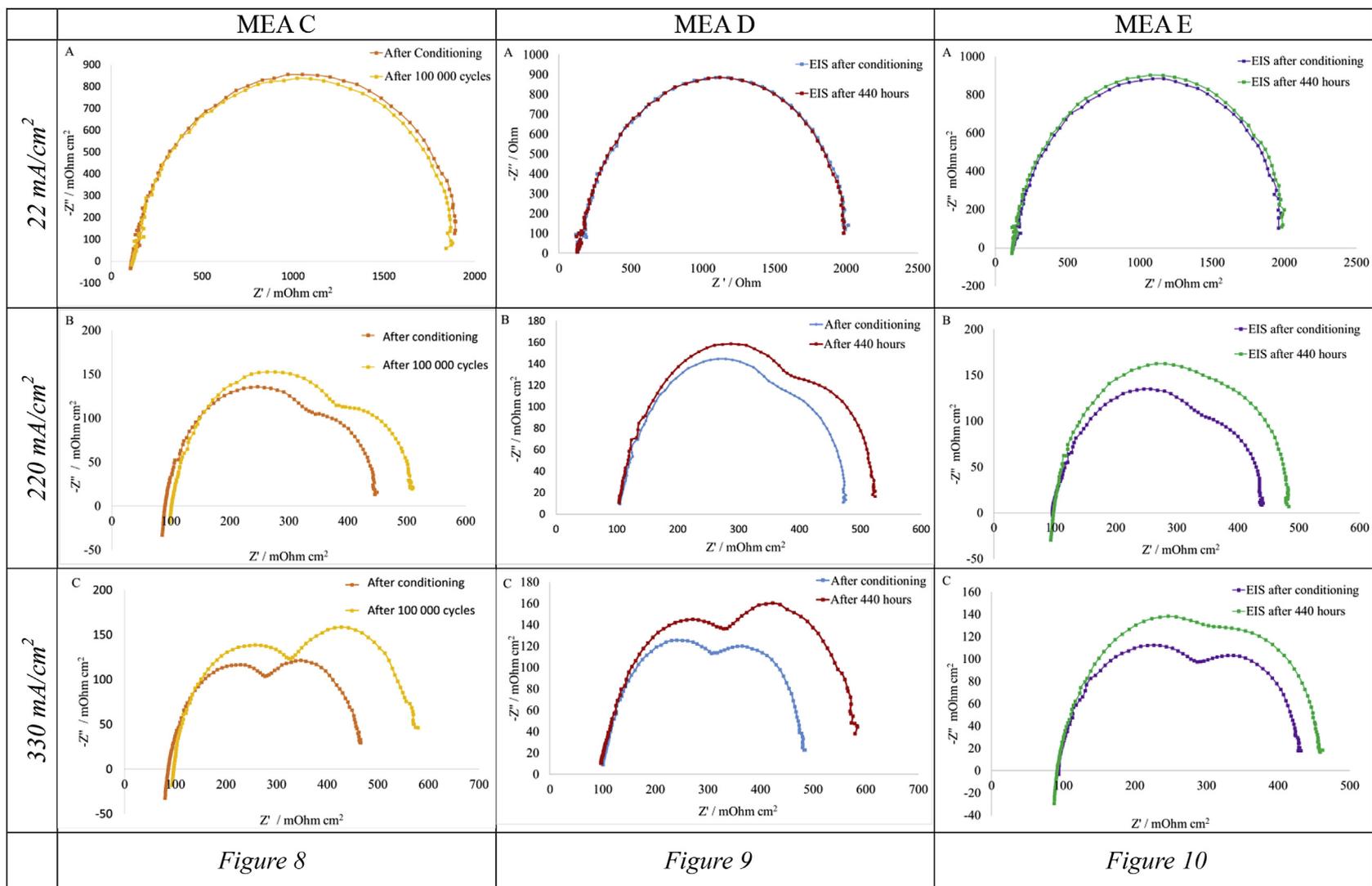


Fig. 8-10 – Figure 8: MEA C – (A) EIS before and after ageing test at 22 mA/cm². (B) EIS before and after ageing test at 220 mA/cm². (C) EIS before and after ageing test at 330 mA/cm². Figure 9: MEA D – (A) EIS before and after ageing test at 22 mA/cm². (B) EIS before and after ageing test at 220 mA/cm². (C) EIS before and after ageing test at 330 mA/cm². Figure 10: MEA E – (A) EIS before and after ageing test at 22 mA/cm². (B) EIS before and after ageing test at 220 mA/cm². (C) EIS before and after ageing test at 330 mA/cm².

oxidation processes which can accelerate the decay rate [24,25].

Cyclic voltammetry

On MEA C, MEA D and MEA E Cyclic Voltammetry has been carried out at the beginning and at the end of the ageing test.

The aim of the CV measurements was to evaluate the order of magnitude of ECSA changes with the aging treatment since, as reported in literature, for this kind of membrane the interaction with the adsorbed acid may hamper a precise quantification of ECSA [9].

The ECSA has been calculated from the H₂ desorption peak applying the methodology suggested by Ref. [48]:

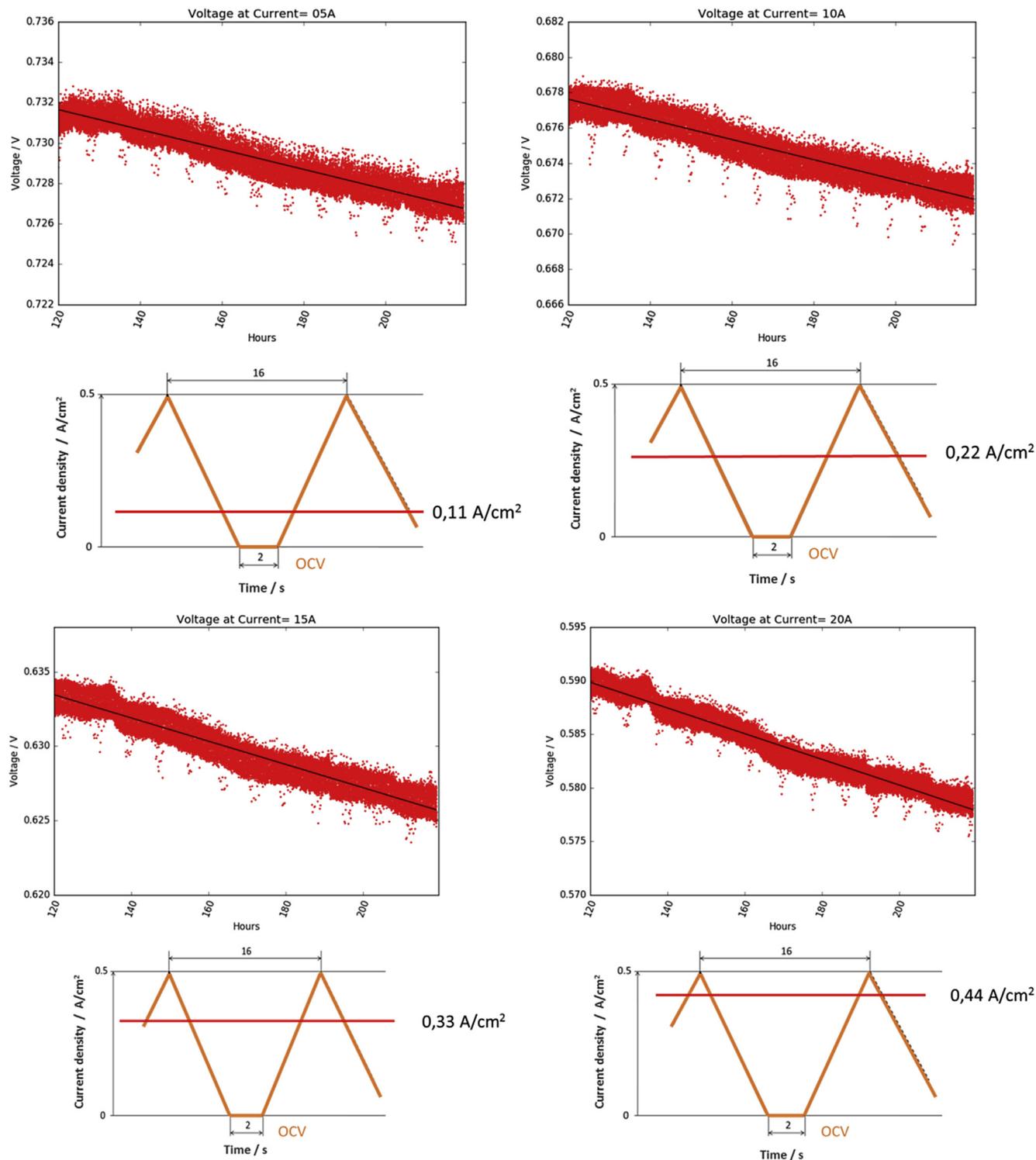


Fig. 11 – MEA C – Voltage degradation over time, during load cycling, at four current levels: 0.11 A/cm² (top-left), 0.22 A/cm² (top-right), 0.33 A/cm² (bottom-left) and 0.44 A/cm² (bottom-right).

Table 2 – MEA C – degradation rates.

Current density, A/cm ²	Degradation rate, μV/h
0.11	49
0.22	57
0.33	78
0.44	120

$$ECSA(cm_{Pt}^2/g_{Pt}) = \frac{q_{Pt}}{\Gamma \cdot L}$$

where q_{Pt} (C/cm² electrode) is the charge density obtained from the CV experiment, $\Gamma = 210 \mu\text{C}/\text{cm}_{Pt}^2$ is the charge required to reduce a monolayer of protons on Pt and $L(g_{Pt}/\text{cm}^2_{\text{electrode}})$ is the Pt content or loading in the electrode.

Cyclic Voltammetry has been carried out with a constant H₂ flow of 0.4 sl/min at the anode side and a constant N₂ flow of 0.5 sl/min at the cathode side. The minimum applied voltage was 0.03 V and the maximum voltage was 0.6 V, with a scan rate of 0.2 mV/s.

ECSA of MEA C (load cycle) underwent to approximately 50% reduction, while ECSA of MEA D and MEA E underwent to approximately 30% reduction. Values of degradation of ECSA are comparable with degradation found by other authors in similar works [9]. This difference on ECSA indicates, once again, the influence of load cycles on degradation of MEAs with respect to constant load operation [41].

Potential degradation over time

In addition to the evaluation of total degradation of MEA, before and after the ageing tests, the trend of degradation over time has been analyzed throughout the load cycling tests. The purpose was to evaluate degradation profile over time and effect of current density. Fig. 11 shows the potential trend for different current densities from 0.11 A/cm² to 0.44 A/cm².

Due to data acquisition problems, the only meaningful portion of the potential degradation over time is the one reported in Fig. 11 that takes in accounts 100 h of operation after the conditioning. For the considered period, the degradation of MEA C seems to be linear and degradation rate increases with current density. Thanks to this analysis, degradation rates can be straightly deduced from the slope of the linear tendency curves of experimental data shown in Fig. 11; the obtained values are reported in Table 2. These results are not in perfect agreement with the ones obtained through the polarization curves analysis and reported in Table 1. This is understandable since, in this later analysis, just a portion of data have been analyzed and degradation rate has been calculated interpolating load cycles data where working conditions (especially reactants pressure) could differ from the ones selected for the polarization curves. This type of data analysis needs confirmation through further experiments on other MEAs that will be done by the authors in future works.

Conclusion

In this paper an accelerated ageing test protocol has been used to assess the performance degradation rate on HTPEM MEAs.

In the attempt to differentiate the degradation due to constant load operation from that due to load cycling, additional test have been carried out at constant load operation for the same duration of the load cycling protocols.

Results seem to confirm the data already obtained on the same type of MEA in a previous research. This allows to infer that the protocol, derived from one used for LTPEM, seems to be useful for HTPEM as well. Moreover, as expected, data show that load cycling is more stressing than constant load operation and that OCV is detrimental in terms of performance degradation. Considering all the tests carried out so far by the authors, it has been found a degradation rate of 34 μV/h for the load cycle profile without reaching OCV conditions, 44–45 μV/h for the load cycle profile that reaches OCV conditions and 29–30 μV/h for constant load operation.

EIS and CV measurements suggest that the degradation processes is related to the stability of the catalysts in the conditions of testing.

Despite further nanomorphology analysis will be necessary to verify the inferred hypothesis, these preliminary results can be useful to identifying stack control strategies.

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