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PEM Fuel Cells: Materials Ageing and Degradation

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Abstract

As fuel cell technology matures and time scale to commercialization decreases, the need for a more comprehensive knowledge of materials ageing mechanisms is essential to attain specified lifetime requirements for applications. In this work, the membrane-electrode assembly (MEA) degradation of an eight cell PEM low power stack was evaluated, during and after fuel cell ageing in extreme testing conditions. The stack degradation analysis comprised observation of catalytic layer, morphology and composition. Cross sections examination of the MEAs revealed thickness variation of catalytic layer and membrane. Other modes of degradation such as cracking, delamination, carbon corrosion and catalyst migration were observed as well as membrane degradation.

Keywords: Fuel cells, durability, MEA ageing

1   Introduction

At present, lifetime requirements for PEM fuel cells applications can not be guaranteed. A more comprehensive knowledge about materials ageing and degradation mechanisms is needed.
The membrane-electrode assembly (MEA) is considered a key component in PEM fuel cells, with significant impact on cell performance [1]. MEA ageing mechanisms are not well understood, being affected by irreversible changes in the kinetic and/or transport properties of the cell [1-5].
In this work, *in-situ* evaluation of MEA degradation was conducted for an eight cell PEM low power stack in extreme testing conditions. *Ex-situ* failure analysis was performed after the end of life of the stack.

2   Experimental

The stack, uses own designed flow field graphite plates, integrated in a series configuration. The open cathode allows feeding with air, which is designed to contribute to water removal and stack cooling. An air fan located at the edge of the cathode manifolds was used to provide an excess air stoichiometry condition. The cells were fitted with a commercial MEA using Nafion 111.
The stack was activated by a series of potentiodynamic and potentiostatic cycles before

use [2]. The fuel cells analyzed in this work were the cells located at the beginning and at the end of the stack, assigned as C1 and C8, and also the cell present at the middle of the stack, identified as C5. C1 was the nearest cell to the anode gas inlet.
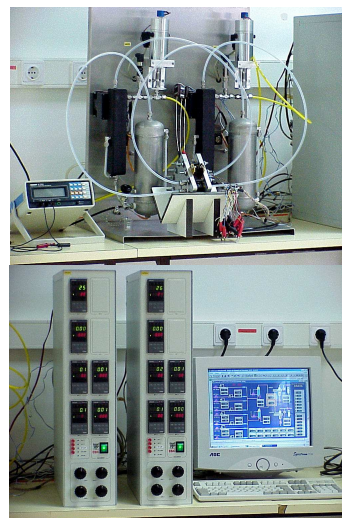

Fig. 1 Purpose-built test station for PEM fuels cells, used in this work.

To accelerate de MEAs degradation, in this study the fuel cell was subjected to extreme experimental conditions, during approximately 1500 hours.

Polarization curves were conducted, using a purpose built PEM test station. Operating conditions used were optimized in previous work [2].

Post mortem analysis of materials and components degradation, required to enhance understanding of these processes, was undertaken. The MEAs were previously embedded into a resin for the morphological and elemental analysis using a Phillips Scanning Electron Microscope, Model XL 30 FEG, coupled to an Energy Dispersive Spectrometer, EDS, allowing elemental mapping.

3   Results and Discussion

3.1. In-situ degradation analysis

Figure 1 shows the polarization curves of the fuel cell before and after 1500h of operation. The polarization curve obtained after cell activation exhibited maximum current densities over 1000 mAcm^{-2}. Load duty cycles included open circuit, constant current and full polarization curves in a step by step fashion. Data were obtained at 500 mbar H_2 relative pressure, room temperature with the air flow rate of 7.56 L.min^{-1} in a range of currents which varied from nearly zero (near the open circuit potential) to 3 A. The maximum power of the cell was found to be reduced in 34 % after operating for 1500h.

The degradation in performance after 1500h of operation is clearly evident in the activation, ohmic and mass transfer regions.
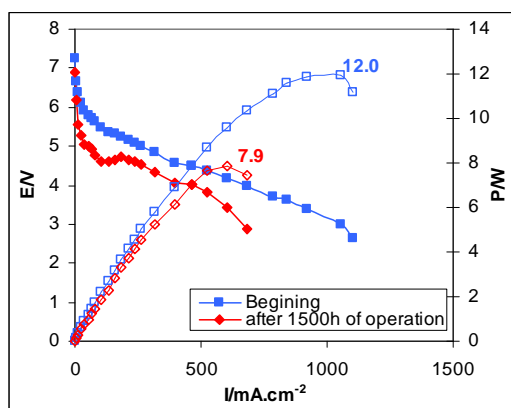

Fig. 1   Polarization curves for the 3.8 cm^2 stack operated at 0.4L.min^{-1} hydrogen flow rate under constant air flow rate of 7.56 L.min^{-1} at 500 mbar, at room temperature, after activation and after 1500h operation.

3.2. Post mortem degradation analysis

The stack degradation analysis comprises observation of catalytic layer surface variations, such as morphology, GDL debris and catalysts clusters.

Another study was done in cross sections of the MEAs, where thickness variation of catalytic layer and membrane were observed, as well as cracking, delamination, carbon corrosion and catalyst migration, and membrane degradation.

3.2.1. Catalytic layer surface analysis

The surface morphology of the catalytic layers of cells (C1, C5 and C8) is markedly different from the unused sample, as we can observe in figure 2.

Surface area seems to be lost with cycling, this is particularly evident for C8. Images were taken at 50000 magnification.
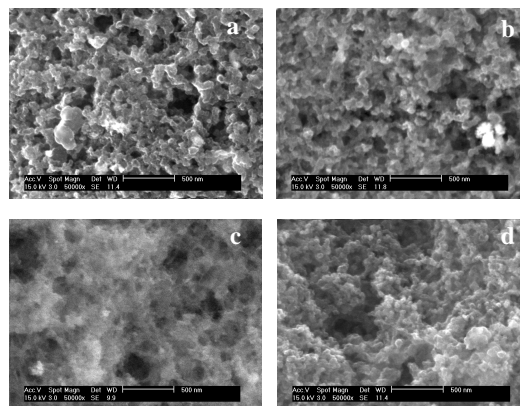

Fig. 2 SEM anode surface morphology for cells (a) C1; (b) C5, (c) C8 and (d) unused.

During the dismantling process, part of the GDL was peeled away and part of the GDL remained stuck on the catalyst layer. Figure 3 shows residues of GDL as light areas on the cathodic catalyst layer of C5. The residue actually shows that the compression force used in the assembly of the stack caused the bipolar plate to press the GDL into the catalyst layer. This compression will have an impact on the catalyst layer and GDL porosity underneath the ribs of the bipolar plate. It was observed, in all the cells, a GDL debris in both the anode and the cathode. In the case of C8, the anodic catalytic layer was totally covered with GDL; removal was accomplished after immersion in hot distilled water.
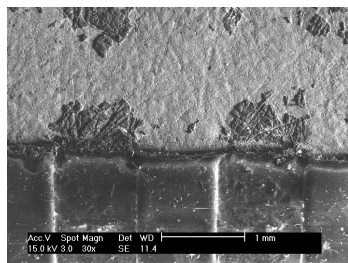
Fig.3 GDL debris on the cathodic catalyst layer surface of C5.

Another type of catalyst layer degradation found was **platinum clusterization,** which is evident in Figure 4.
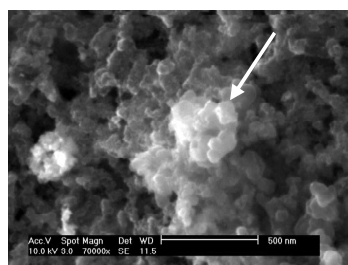

Fig. 4 Typical Pt cluster on anodic catalytic layer of C1, as observed by SEM.

EDS analysis was performed on clustered areas, which were shown to be platinum rich. The results obtained on the Pt cluster and its surroundings are presented in figure 5 exhibiting agglomerates of catalyst. A spectra of an area where clusters were not observed is included for comparison.
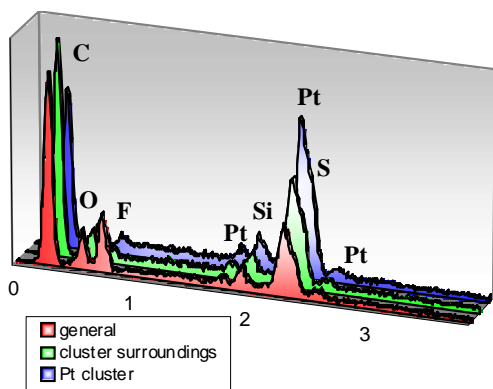

Fig. 5 EDS of a Pt cluster and surroundings surfaces.

The high concentration of platinum could result from catalyst detaching from the carbon supporting surface. The catalyst particles agglomerate to form a catalyst cluster. Pt clusters were also observed on the unused sample. The catalyst agglomeration leads to a gradual decrease in the electrochemically active surface area, increasing by this way the activation loss.

The presence Si has been identify in the EDS spectra in figure 5. The use of silicone piping and the sealing gasket are believed to have introduced silicon contamination in the MEA.

3.2.2. MEAs cross sections

MEA **thickness variations** may occur from the manufacture process or from the assembling pressure. Figure 6 shows from three MEA components (membrane, anodic and cathodic catalyst layer) a thickness decrease comparatively with the unused MEA. The decrease is more evident for the cell that suffered the highest degree of degradation and for which the assembling pressure have more drastic consequences (C8).

The thickness variations have an effect on the resistance through the MEAs and on the susceptibility to the degradation. The thinner areas of the catalyst layer will have a lower electronic resistance, while the thinner electrolyte areas lower ionic resistance.
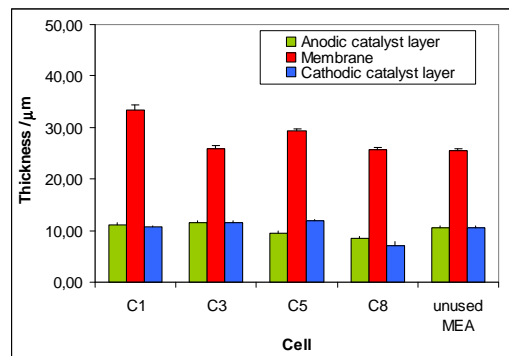

Fig. 6 Thickness variation of MEA components for cells C1, C5 and C8, relatively to the unused MEA.

A very common feature among all of the analyzed MEAs is the **cracking** of the catalyst layer. As shown in figure 7 it involves the cracking of the catalyst layer, but leaves the Nafion™ membrane mechanically undamaged. Thus, the fuel cell can still operate, but performance and durability may be reduced.
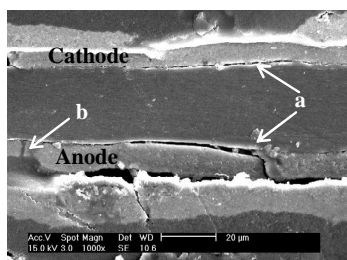
Fig. 7 Cross section SEM view of the MEA for C8 cell showing delamination (a) and cracking (b).

The cracks will increase the total resistance of the catalyst layer and if it leaves parts of the membrane exposed, the contact resistance between the catalyst layer and the membrane will also increased. On the other hand, the cracks will provide areas where the water could accumulate preventing reactant gases to reach the catalytic sites and consequently, reduces the reaction rate.

Another important consequence is the catalyst erosion due to the exposure of the catalyst surfaces to agents such a water and gas flux.

Delamination describes a MEA failure feature whereby the catalyst layer has been separated from the polymer membrane electrolyte as shown in figure 7.

This type of defect may result from MEA manufacturing procedure but can also be induced by the degradation of the catalytic layer. It forces the current to flow away from delaminated zones, through neighboring regions in which heat is locally produced. As these neighboring zones are also prone to water accumulation, they may degrade faster than other parts of the catalytic layers.

Catalyst migration anomalies can occur during operation conditions that may allow platinum particles to break free from their carbon backing and migrate to the polymer electrolyte phase.

This is associated to **carbon corrosion,** where carbon black particles become oxidized to form carbon dioxide, or when Pt becomes soluble. Both of these phenomena may take place under cell reversal conditions.

Tables 1 and 2 illustrate this phenomenon. Results are presented from elemental mapping analysis of fluoride and platinum, carried out using EDS of C8 cell.

The membrane degradation is indicated from the results present on table 1.

Fluoride migration with the H_2 stream occurs from C1 to C8. The results show a fluoride accumulation through the stack.

Table 1. Fluoride weight percentage on membrane of the fuel cells of the stack.

Fluoride Wt / %	C1	C5	C8	Unused
Membrane	21.25	34.03	46.84	39.36

Relatively to catalyst degradation, table 2 shows the weight percentage in all analyzed cells larger than the unused sample, increasing in the direction of hydrogen flow. This observation is consistent with the catalyst clustering encountered in the surface analysis by SEM.

Table 2. Platinum weight percentage on catalytic layers of the fuel cells of the stack.

Pt Wt / %	C1	C5	C8	Unused
Anode	29.54	36.26	34.94	20.92
Cathode	26.73	32.27	50.94	25.77

Standard deviation of Fluoride membrane content and of Platinum in the catalyst layer presented in Tables 1 and 2 were estimated with values up to 6.1 %.

4   Final remarks

Different degradation features were found upon analysis of the low power PEM fuel cell stack examined in this work after 1500 h of operation:

- chemical contamination and debris GDL,
- thickness variations,
- cracking,
- delamination,
- catalyst clusters,
- Pt and F migration.

all of which contribute to gradual decrease of output voltage of the stack influencing performance and durability.

A summary of the degradation features observed in this study and the consequence on the stack operation is presented in table 3.

Table 3. Summary of PEMFC degradation causes and failure modes observed in this study

Component	Degradation	Consequences on stack performance
Membrane	Thickness variation	Thin electrolyte segments will give decreased ionic resistance; Mechanical weakness
	Delamination	Development of flooded areas; Increased resistance in the MEA; Loss of apparent catalytic activity; Development of areas susceptible to erosion
	Membrane degradation	Increased point activity with consequent melt of surrounding electrolyte and pinhole formation
Catalyst Layer	Catalyst cluster	Reduced activity over the entire active area
	Thickness variation	Thicker areas will have higher electronic resistance
	Cracking	Increased resistance in the catalyst layer; Cracks provide flooding areas
	Carbon corrosion	Conductivity loss
	Catalyst migration	Loss of active catalyst; Change in catalyst layer porosity; Pt contamination in the membrane

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