

## MEA Degradation and Failure Modes in PEM Fuel Cells

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### Abstract

*The mechanisms of fuel cell degradation are not well understood. Even though the numbers of installed units around the world continue to increase and dominate the pre-markets, the present lifetime requirements for fuel cells cannot be guaranteed, creating the need for a more comprehensive knowledge of material's ageing mechanism.*

*In this work, failure modes and mechanism of the membrane-electrode assembly (MEA) in PEM fuel cells are studied stressing the issues that may constrain stability, power and lifetime.*

*Diagnostics methods and tools used for in-situ and ex-situ analysis of PEM fuel cells were used in order to better categorize irreversible changes in the kinetic and/or transport properties of the cell.*

*Data for MEA degradation obtained during and after fuel cell ageing in extreme testing conditions will be discussed. Electrochemical Impedance Spectroscopy (EIS) is found instrumental in the identification of fuel cell flooding conditions and membrane dehydration associated to mass transport limitations / reactant starvation and protonic conductivity decrease, respectively. Cross sections of the membrane catalyst and gas diffusion layers examined by scanning electron microscopy indicate electrode thickness reduction as a result of ageing. Catalyst particles are found to migrate outwards and located on carbon backings. Nafion degradation in fuel cell environment is analysed in terms of the mechanism for fluoride release which is considered an early predictor of membrane degradation. The application of a full range of diagnostic techniques and modelling is felt necessary in order to aid design and operating strategies in PEM fuel cells.*

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**Keywords:** PEM fuel cells, durability, reliability, ageing mechanism.

### 1 Introduction

PEM fuel cells are considered as promising power sources, due to their high power density, low operating temperature and high power-to-weight ratio.

As the technology matures and the timescale for commercialization continues to decrease, durability, reliability and cost are amongst the most critical issues, creating the need for a more comprehensive knowledge of material's ageing mechanism.

The present lifetime requirements for fuel cells cannot be guaranteed. The mechanisms of fuel cell degradation are not well understood being affected by irreversible changes in the kinetic and/or transport properties of the cell [1-4].

In this work *in-situ* and *ex-situ* evaluations of MEA degradation were conducted after fuel cell ageing in defined testing conditions. MEA degradation modes and mechanisms are discussed.

### 2 Experimental

Electrochemical techniques were used in combination with structural and chemical analysis to correlate the performance of the cell with the material properties of the various components and their ageing. Polarization curves were conducted, using a purpose built PEM test station, on a low power fuel cell that uses own designed flow field plates integrated in a series configuration, and a cathode that allows feeding with air, cooling and water removal. Electrochemical impedance spectra were run using H<sub>2</sub>/O<sub>2</sub> (air) gas feeding. A Frequency Response Analyser (model 1250, Solartron) connected to an Electrochemical Interface (model 1286, Solartron) was used to obtain impedance spectra covering a suitable range of frequencies for fuel cell processes.

An ion selective fluoride electrode from SENTEC was used to estimate membrane degradation as a function of fluoride release at anode outlet. Calibrations were made using NaF as electrolyte.

Post mortem analysis of materials and components degradation, required to enhance understanding of these processes, was undertaken. After cell

dismantling, cross sections of MEA samples were observed for morphological and elemental analysis using a Phillips Scanning Electron Microscope, Model XL 30 FEG, coupled to EDS allowing elemental mapping. Cross sections of the membrane, catalyst and gas diffusion layers were cut into squares of 0.5x0.5 cm mounted in resin and gold coated. Afterwards, samples were examined using the aforementioned microscope.

Test were conducted for a 5 cell stack and also for 25 cell stack. Figure 1 shows the largest stack used. An open-air cathode type stack is provided with a conventional configuration that comprises two end plates, 25 bipolar plates, 24 MEAs and gaskets, see figure 1. The stack uses a low-power consumption air fan in the edge of the cathode manifolds, for combined high stoichiometric oxidant supply and stack cooling purposes, avoiding the use of costly, large, heavy and power-consuming air pumps and external cooling systems. After fuel cell ageing in extreme testing conditions, the stack was dismantled and some MEAs were analysed. Figure 2 shows typical aspect of MEAs after dismantling.



Figure 1. PEMFC fuel cell stack, used in this work.

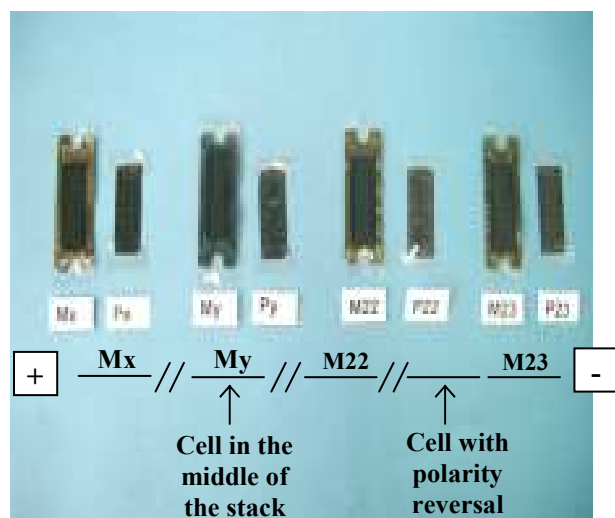


Figure 2 Membrane electrodes assemblies, gas diffusion layers and carbon paper selected to be analyzed. Schematic representation of the stack and the cells selected to be analyzed.

### 3 Results

#### 3.1 In-situ degradation analysis (5 cell stack)

Polarization curves provided information about the performance of single cells or stack as a whole. Several load cycles at different current values were undertaken with polarization curves being carried out afterwards, at currents of 1 and 3 A, corresponding to 50 and 100% of maximum power, see figure 3.

Polarization curves were also carried out for individual cells. The first and the last cell in the stack reflected voltage losses due to cathodic overvoltage and mass transfer effects respectively, see figure 4.

Predominance of back diffusion of water from the cathode to the anode according to measurements of the relative humidity of the hydrogen at anode outlet [2].

EIS diagrams for PEM fuel cell under study, using a  $H_2$  (humidified)/ $O_2$  (air) gas feeding, are shown in figure 5. Typical results show two arcs, accounting for charge and mass transfer processes at high and low frequencies respectively. Results were fitted with an equivalent circuit representative of a Randles circuit where the conventional double layer is substituted by a constant phase element, CPE.

Obtained cell resistance values were found to agree with values taken from the slope of polarization curves at the relevant potentials. EIS impedance response of the cell was found to be very useful in the identification of cases of increase in resistance due to poor water management at high current values (2,5-3A). Impedance data suggested that there is an advantage in the used of non-humidified hydrogen for the present fuel cell when working at high currents.

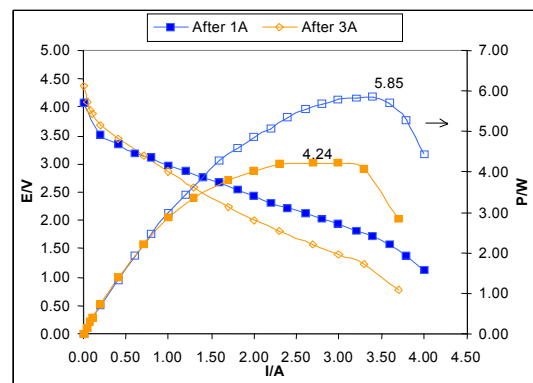


Figure 3 Polarization curves for air breathing fuel cell stack showing voltage and power vs. current profile after load cycles at fixed current of 1A and 3A.

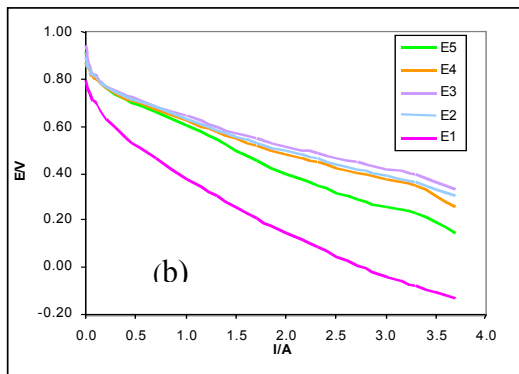
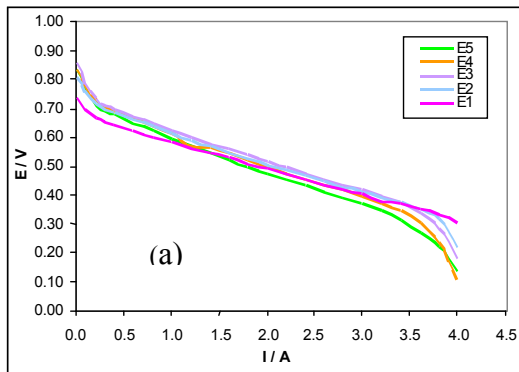


Figure 4 Polarization curves for individual cells of an air breathing fuel cell stack showing voltage and power vs. current profile after load cycles at fixed current of 1A (a) and 3A(b) .

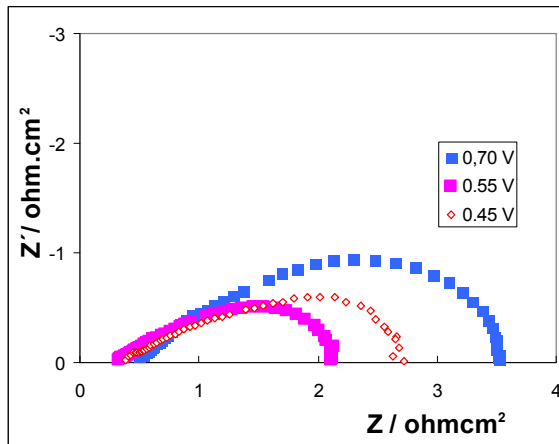


Figure 5 Electrochemical Impedance diagram for a low power PEM fuel cell used in this work using a  $H_2$  humidified/ $O_2$  (air) gas feeding at indicated potentials.

After 500 h cycling, maximum fuel cell power recorded was found to be reduced in 60%, being 3.7 W.

A study of fluoride leaching was conducted in a 5 cell stack, for the last 1000 hours of the stack life at the anode outlet, see figure 6. A striking drop in cell potential was associated to the noticeable increase in fluoride loss and end of MEA life. The membrane is subject to an oxidizing / reducing aggressive environment on the cathode/anode side. The decomposition of Nafion by peroxide radical attack is pointed out as a possibility. Some authors have identified  $H_2O_2$  in fuel cell product water. Moreover, when using Fenton as a source of hydroxyl ions, loss of fluoride from Nafion has been experimentally confirmed. Carboxylic end groups may be susceptible to attack by radical species generated by  $H_2O_2$  which is an intermediate of oxygen electrochemical reduction [6].

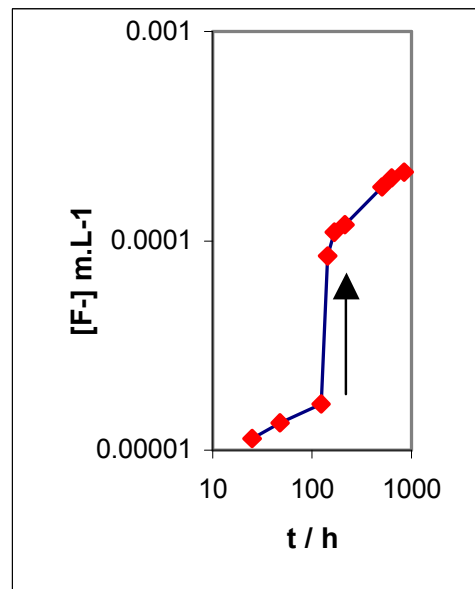
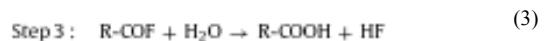
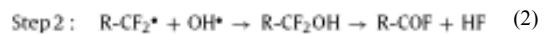
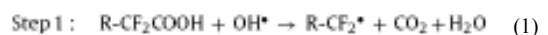


Figure 6 Fluoride leaching from the membrane for a 5 cell stack obtaining up to 1000 hours of cell functioning.

Carboxylic end groups of Nafion may be susceptible to attack by radical species generated as a result of reactions in the fuel cell.  $OH^\bullet$  are formed by decay of hydrogen peroxide which is an intermediate in the oxygen reduction:



### 3.2 Post mortem degradation analysis

#### 3.2.1 Stack (5 cells)

SEM analysis of cross sections of the MEA after end of life for the 5 cell stack was carried out. Cathode thickness reduction is striking as well as the reduction of fluoride density in the anode, confirming data obtained using the selective electrode, see figure 7.

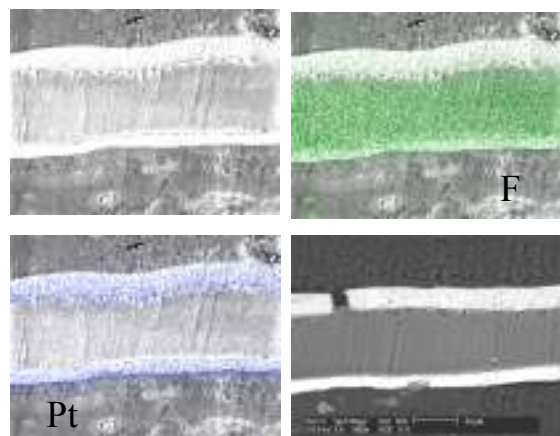


Figure 7 SEM cross section view of the MEA at the end of stack life, displaying results of elemental mapping analysis using EDAX coupled to SEM. 5 cell stack.

#### 3.2.2 Stack (25 cells)

A different situation was observed when analyzing the cross sections of the 25 cell stack.

The degradation of the MEA components (anodic layer – A; membrane – M and cathodic layer – C) of the various samples were analyzed by SEM.

As it can be seen, in figure 8, the thickness of the anodic layer is dramatically reduced for the last cells of the stack while the cathode's is maintained.

Table 1 shows average thickness values for the anode, cathode and membrane for MEAS located at the top (MX, MX) and bottom of the stack (M22, M23).

Table 1 Average thickness of the MEA components.

|          | Thickness ( $\mu\text{m}$ ) |                  |                  |                  |
|----------|-----------------------------|------------------|------------------|------------------|
|          | M X                         | M Y              | M 22             | M 23             |
| Anode    | 7.47 $\pm$ 1.79             | 7.10 $\pm$ 1.58  | 6.95 $\pm$ 3.06  | 5.95 $\pm$ 1.99  |
| Membrane | 28.93 $\pm$ 2.40            | 26.93 $\pm$ 2.75 | 28.55 $\pm$ 3.13 | 29.08 $\pm$ 1.48 |
| Cathode  | 11.52 $\pm$ 5.46            | 11.06 $\pm$ 2.26 | 13.12 $\pm$ 1.29 | 12.60 $\pm$ 0.84 |

For most cells, the anodic layer exhibits apart from a striking reduction in thickness cracks and

discontinuities. The cathodic layer also presented cracks and a more evident wavy patterned look.

M23 cell, which showed voltage reversal, has an heavily damaged anodic layer with thickness reduction and variation and layer rip-off (delamination), which we could not see in other cells.

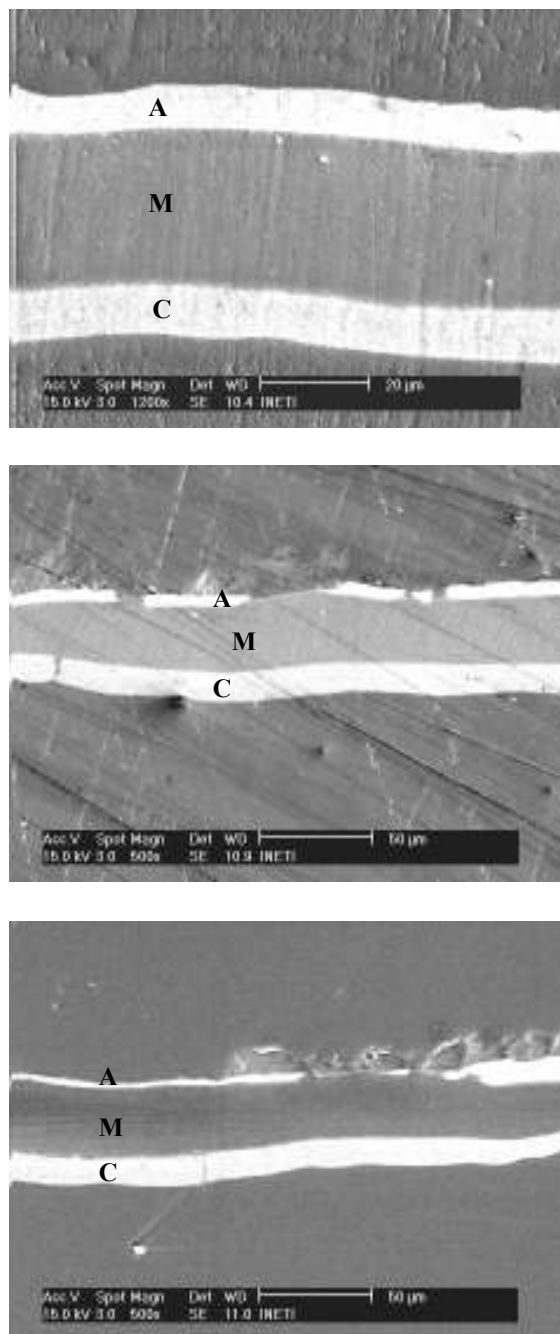


Figure 8 SEM cross section view of the MEA at the end of stack life (MX, M22, M23 samples).

The damage exhibited by both cathode and anode so far as thickness reduction is thought to be due to carbon corrosion as a result of gas feed starvation.

Reiser [7] showed that introducing hydrogen into either air or nitrogen on the fuel electrode of a fuel cell when air is present on the air electrode leads to high overpotentials at the air electrode. These high overpotentials lead to oxygen evolution, platinum oxidation and dissolution, and carbon corrosion at the air electrode. The damage to the cathode catalyst layer causes severe irrecoverable performance decay.

When hydrogen is not available for oxidation, the anode potential raises to values high enough for water oxidation or in its absence carbon oxidation. Oxygen crossover could cause reverse potential phenomena. Localized fuel depletion could result from water droplet accumulation in the anode gas diffusion layer or flow field channels, or from flow bypassing portions of the fuel electrode. Star-stop procedures can in itself produce local starvation conditions in which the anode is exposed to hydrogen and oxygen.

Degradation modes found in the post mortem analysis are summarized in Table 2.

Table 2 Main degradation modes and possible causes suffered by PEM stacks.

| Component      | Failure Mode   | Possible Causes   |
|----------------|--|---|
| Membrane       | Chemical attack  | Non-uniform distribution of reactants<br>Membrane drying, loss of fluoride<br>Thermal/mechanical stress<br>Uneven "pinch" |
|                | Conductivity loss  |   |
|                | Delamination   |   |
| Active layer   | Activation loss  | Ageing and sintering; Corrosion<br><br>Fuel starvation<br><br>Mechanical stress   |
|                | Decrease in mass transport rate and water management control |   |
|                | Thickness reduction  |   |
| GDL            | Decrease in mass transport rate reactants                    | Degradation of backing material<br>mechanical stress<br><br>Corrosion<br><br>Change in hydrophobicity of materials        |
|                | Conductivity loss  |   |
|                | Decrease in water management control                         |   |
| Bipolar plates | Fracture/ Deformation  | Mechanical stress   |
| Gaskets        | Mechanical Failure   | Corrosion, Mechanical Stress  |

## 4 Conclusions

Membrane failure is a major lifetime constraint of the examined low power fuel cell, leading to fluoride leaching.

Other degradation modes are reduction of electrodes thickness, sintering of the electrocatalyst, flooding of reaction sites, which contribute to gradual decrease of output voltage of the stack influencing performance and durability.

Cells which showed polarity reversal, exhibited a heavily damaged anodic or cathodic layer (thickness reduction) and layer rip-off (delamination), which we not observed in other cells.

Damage to the anode was found to be associated to the largest stack used and particularly to the last cells. Research is in progress in order to better understand the mechanisms for cell potential reversal.

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