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Fuel Starvation: Irreversible Degradation Mechanisms in PEM Fuel Cells

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Abstract

PEM fuel cell operates under very aggressive conditions in both anode and cathode. Failure modes and mechanism in PEM fuel cells include those related to thermal, chemical or mechanical issues that may constrain stability, power and lifetime. In this work, the case of fuel starvation is examined. The anode potential may rise to levels compatible with the oxidization of water. If water is not available, oxidation of the carbon support will accelerate catalyst sintering. Diagnostics methods used for in-situ and ex-situ analysis of PEM fuel cells are selected in order to better categorize irreversible changes of the cell. 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. Furthermore, it indicates that water electrolysis might happen at the anode. Cross sections of the membrane catalyst and gas diffusion layers examined by scanning electron microscopy indicate electrode thickness reduction as a result of reactions taking place during hydrogen starvation. Catalyst particles are found to migrate outwards and located on carbon backings. Membrane degradation in fuel cell environment is analyzed in terms of the mechanism for fluoride release which is considered an early predictor of membrane degradation.

1 Introduction

The mechanisms of fuel cell degradation are characterised by irreversible changes in the kinetic and transport properties of the cell and presently are not well understood [1-5]. PEM fuel cell operates under very aggressive conditions in both anode and cathode, typically at $\text{pH} < 1$ and with significant levels of water in vapour and liquid phase at temperatures between 60 and 80 °C. Anode catalysts are exposed to a strong reducing H_2 atmosphere whilst the cathode is under strongly oxidizing conditions (high O_2 concentrations and potentials $> 0.6 \text{ V vs. SHE}$). Corrosion of both Pt/C catalysts components (catalytic metal and support material) becomes an issue in PEM fuel cells.

Fuel starvation, inadequate fuel supply at the anode, affects the MEA in an irreversible way. Hydrogen is no longer available in sufficient amounts so that the demanded current can be maintained, in this way the anode potential will increase to levels where water electrolysis is possible at the anode ($E_{25^\circ\text{C}}^0 = + 1.23 \text{ V vs. SHE}$).



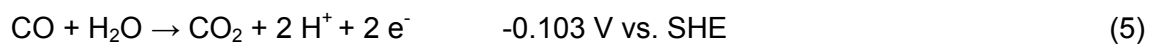
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For even higher potentials, the carbon in the anode catalyst (Pt/C) will be oxidized in the presence of platinum. Electrochemical oxidation of the carbon is thermodynamically possible above 0.2 V vs. SHE according to reaction (3) providing a supply of protons to support current demand [6].



Oxidation of carbon to carbon monoxide (4) is thermodynamically not favoured according to reaction (5):



The reaction affects not only the carbon present in the catalyst but also other carbon components such as the backing layers and eventually the flow field plates [7], leading to a reduction of the carbon content in the catalyst layer with time. As carbon is corroded away, noble metal nanoparticles will be lost from the catalyst layer and migrate to the polymer electrolyte interface or aggregated into larger particles.

In this work, failure modes and mechanism of the membrane-electrode-assembly (MEA) in low power PEM fuel cells are studied stressing the issues that may constrain stability, power and lifetime. Diagnostics methods and tools used include in-situ and ex-situ analysis in order to better categorize irreversible changes in the kinetic and/or transport properties of the cell after fuel cell ageing in extreme testing conditions will be 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 PEM 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 (a low power consumption air fan in the edge of the cathode manifolds was used providing an excess air stoichiometry condition). Hydrogen was supplied at a pressure of 0.2 bar. Electrochemical impedance spectra were ran using H₂/O₂ (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.

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.

Tests were conducted on 8, 16 and 25 cell stacks. The stack uses an open cathode and own-designed bipolar graphite plates. A low-power consumption air fan in the edge of the cathode manifolds was used, for combined high stoichiometric oxidant supply and stack cooling purposes. After fuel cell ageing in extreme testing conditions by applying a series of pre-defined load cycles, the stack was dismantled and MEAs were analysed. Load duty cycles included open circuit, constant current and full polarization curves in a step by step fashion.

3 Results

8 cell PEM stack

Polarization curves of the fuel cell before and after 1500 h of operation revealed that the maximum power that may be demanded from the fuel cell was reduced in 34%. The polarization curve obtained after cell activation exhibited maximum current densities over 1000 mAcm⁻². Data were obtained at 500 mbar H₂ relative pressure, room temperature with the air flow rate of 7.56 Lmin⁻¹ in a range of currents which varied from nearly zero (near the open circuit potential) to 3 A. The degradation in performance after 1500 h of operation was evident in the activation, ohmic and mass transfer regions of the polarization curve.

The stack degradation analysis comprises observation of catalytic surface layers and MEA cross sections. In the eight cell stack, cells were numbered from 1 to 8 starting from the cell located at hydrogen entry. Surface area seems to be lost with cycling; this was particularly evident for C8.

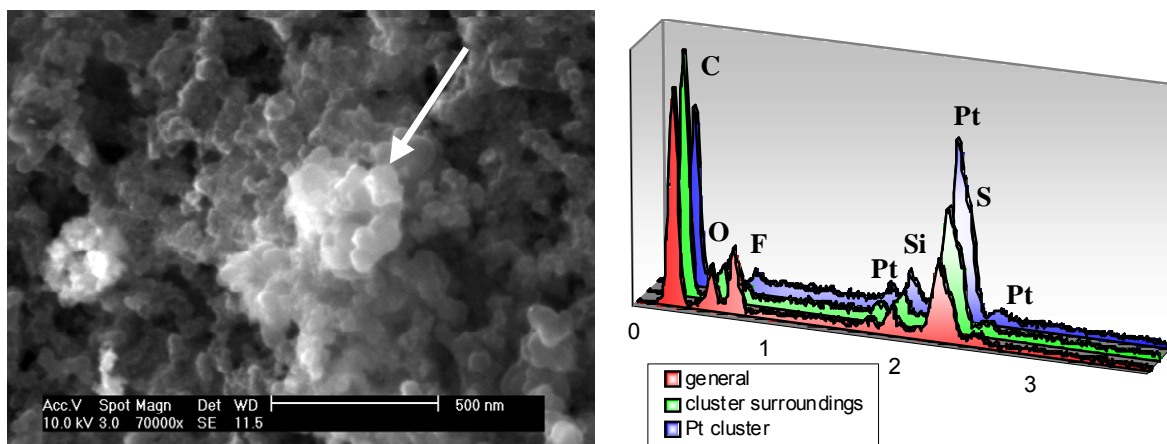


Figure 1: Typical Pt cluster on anodic catalytic layer of C8, as observed by SEM and respective.

Platinum clusterization, which is evident in Figure 1a), was also found. 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 1b). A spectra of an area where clusters were not observed is included for comparison. Other 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 (Si from piping and sealing gaskets) and debris GDL, electrode thickness variations, cracking and delamination, Pt and F migration; all of which contribute to gradual decrease of output voltage of the stack influencing performance and durability.

16 cell PEM stack

When increasing the number of cells in the stack by 2 regarding the previous situation, polarity reversal was observed in the last cell. While on fixed load, the cell potential values were individually measured showing a dependency on cell position in the stack. Lower values are reported for the farthest cells from hydrogen entry. The potentials values vary from 0.653 V down to 0.492 V, Figure 2a), with the lowest values associated to cells 15 and 16. With continuous operation using a reduced hydrogen flow, an inversion of polarity was observed in the 16th cell of the stack, evident in the potential vs. time plot in Figure 2b), as a result of insufficient hydrogen to reach the last cells. When the incursion into the negative potential values is not to accentuated the phenomenon is partially reversible. Once the phenomenon was made irreversible, the cell was dismantled in order to observe the degradation of the MEA under SEM. The cells images revealed the presence of morphological defects associated to fuel starvation.

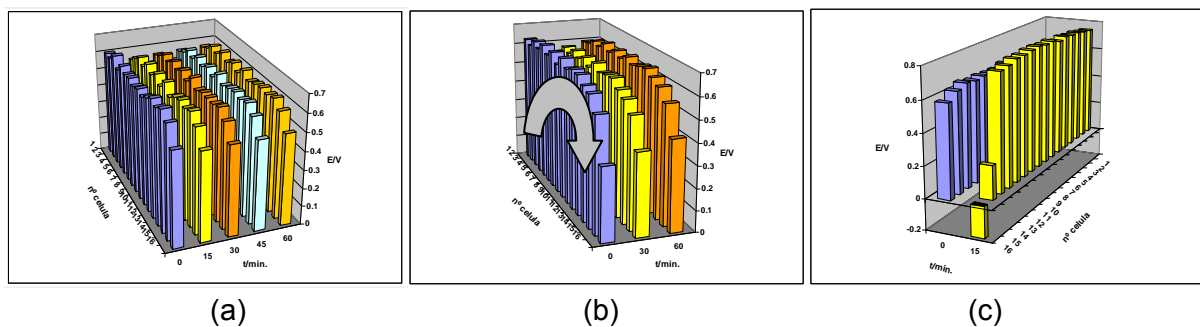


Figure 2: Cell potential *versus* time for a 15 W fuel cell stack of 16 cells. Data are referred to one hour operation, with measurements every 15 minutes (a); Cell polarity reversal in cell 16th was observed (b); Potential distribution after the full flux of hydrogen was replenished (c). The SEM observations of cross sections were accompanied by EDS mapping for Pt, S and F, corresponding to the 16th cell. The images show delamination at the anode and a striking difference of thickness when compared to the cathode catalyst layer (C), see Figure 3.

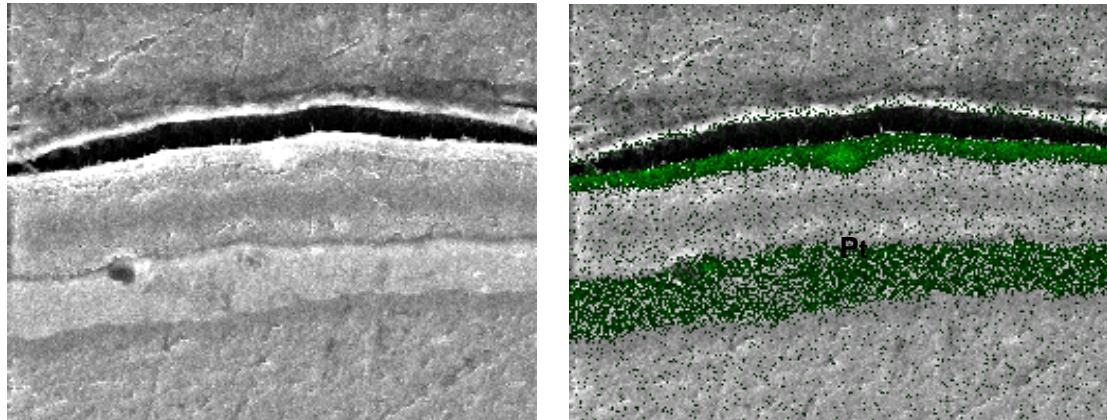


Figure 3: SEM image of cross section of the 16th MEA of the stack showing delamination and elemental mapping for Pt; A = anode, C = cathode and M = membrane (b).

Impedance data, not shown here, were instrumental in identifying membrane resistance increases and transport limitations in affected cells.

25 cell PEM stack

Figure 4 shows that the thickness of the anodic layer of a 25 cell stack is dramatically reduced due to polarity reversal, for the last cells of the stack while the cathode’s is maintained.

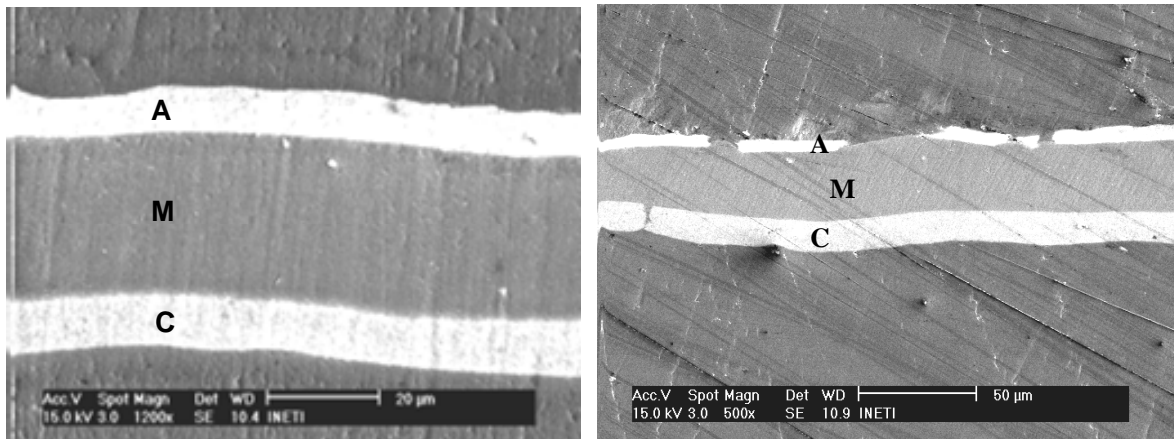


Figure 4: SEM cross section view of the 23rd MEA of a 25 cell stack. Reduction of thickness at anode.

4 Final Remarks

The reduced flow of hydrogen in the fuel stack caused the reversal of polarity of the cells with consequent deterioration of the properties of the stack. Last cells were always affected. Morphological aspects reveal deterioration of peripheral cells with emergence of delamination and varying the thickness of the catalyst layers anodic and cathodic. Furthermore, carbon corrosion and fluoride depletion in the membrane are suggested.

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