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Platinum instability in PEM fuel cells MEA's subjected to chloride contamination

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Abstract

In this work a low power fuel cell, intended for passive management of water, was operated integrating a range of relative humidity (RH) from ~30 to 80% and temperatures from 5 to 55 ºC.

The stack was fed with pure hydrogen. An open air cathode was designed for easy water removal and stack cooling. The stack uses own design flow field drawn on graphite plates from Schunk and a commercial MEA with carbon supported catalyst containing 0.3 mgcm^{-2} Pt.

Polarization curves were registered for a full stack characterization using a purpose-built test station and a climatic chamber with temperature and RH control. Results indicated that 60% RH is associated to maximum fuel cell performance over the studied temperature range. While water management is done in a passive fashion, heat management is done on the basis of the injection of air at the cathode with the fuel cell showing good performances at relatively low currents where back diffusion towards the anode is favored.

The loss of performance with temperature increase was related to an increase in the membrane resistance which may correspond to loss of water on the anode side. Performances at temperatures lower that room temperature showed only slight decrease in power.

An examination of the fuel cell components after 100 h of operation revealed that chloride contamination has produced cathode failure associated to catalyst migration anomalies favored by operation conditions that allowed platinum particles to break free from their carbon backing and migrate toward the polymer electrolyte. Migration resulted in precipitation with larger mean particle size distribution within the solid electrolyte when compared to the original catalyst layer, rendering a very significant loss of thickness in the cathode material. Coarsening of platinum particles occurs at nano and micro-scale. The mechanism for the lost of catalyst by dissolution and growth is discussed on the basis of a joint electrochemical and SEM/TEM study.

Keywords: PEM Fuel Cells, Electrode degradation, Catalyst agglomeration, Platinum dissolution, Chloride

1   Introduction

Materials ageing mechanisms and degradation in proton exchange membrane fuel cells (PEMFC) and their performance on impact have received a great deal of attention in the last few years. This is due to the maturity reached by the technology, demonstrated in the various viable options for applications, and the advent of the first markets.

Membrane-electrode assembly (MEA) ageing and degradation mechanisms are not well understood, being affected by the unavoidable degradation of materials in the context of load cycling and/or the influence of operating conditions such as temperature and humidity. Common degradation mechanisms concerning the membrane include conductivity loss and chemical attack due to poor water management or by internally generated species as a result of the redox reactions and also due to thermal or mechanical stress[1-2].

The catalytic layer durability is a key issue in view of meeting requirements for long-term performance. Fuel cell voltage at any given current depends largely on the available catalyst surface area. Chemical deactivation or poisoning, sintering of the catalyst nanoparticles, carbon corrosion, among other factors lead to the reduction in electrochemical surface area [3-7].

In this work, platinum agglomeration and particle growth, Pt loss and migration occurring in normal operating conditions in a low power 4-cell PEM fuel cells is induced by external contamination with chloride ions coming from the feed-stream of air that feeds the cathode fuel cell.

2 Experimental

The fuel cell used in this work is a PEM technology low power FC, developed by SRE.

Stack polarization curves were registered for a full characterization using a purpose-built test station which allows control over gas flow, pressure, temperature and relative humidity. In a first approach, tests at temperatures between 5 and 55ºC were undertaken, integrating a range of variation for relative humidity from ~30 to 80%. Tests were conducted in a climatic chamber BINDER, at the various temperature and relative humidity's.

The stack used in this work was composed by 4 cells connected in series operating with pure hydrogen, and an air cathode which was 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 stack uses own design flow field drawn on graphite plates from Schunk.

The MEA is a catalyst coated membrane from 3M and a gas diffusion layer (GDL/GDE) from Johnson Matthey with carbon supported catalyst, containing 0.3 mgcm^{-2} Pt. The geometrical active area was 3.8 cm^2.

The stack was activated before use. The fuel cell was subjected to experimental conditions schematically shown in Fig 1, during approximately 100 hours operation, including periods at the open circuit potential (~650 h life time).

After fuel cell failure, a post mortem analysis of materials and components, required for understanding of the degradation processes, was undertaken. The fuel cell was dismantled and the MEAs embedded into a resin for cross section morphological and elemental analysis using a Phillips Scanning Electron Microscope, Model XL 30 FEG, coupled to an Energy Dispersive Spectrometer, EDS, which also allowed elemental mapping.

TEM analysis of the individual cells of the stack was undertaken using a Tecnai F30 field emission gun instrument operated at an accelerating voltage of 300 kV. Cross sections were prepared by ultramicrotomy using a Leica Ultracut UCT apparatus. Elemental analysis was performed with an Energy Dispersive X-Ray spectroscopy system attached to the microscope.
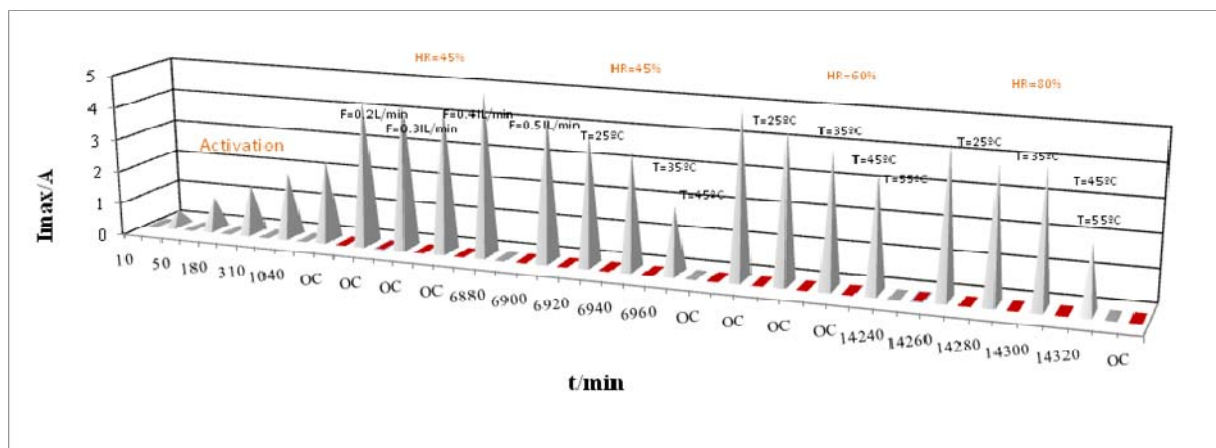

Fig 1. Schematic diagram of the experimental conditions at which the PEM fuel cell under study was submitted.

3 Results

Results indicated that 60% relative humidity is associated to maximum performance on the fuel cell under study, see figure 2.

Water management is done in a passive fashion. Heat management is done on the basis of the injection of air at the cathode with the fuel cell showing good performances at relatively low currents where back diffusion towards the anode is favored.

A loss in performance is found with temperature increase and it is related to an increase in the

membrane resistance which may correspond to loss of water on the anode side. Performances at temperatures lower that room temperature showed only slight decrease in power (not shown).
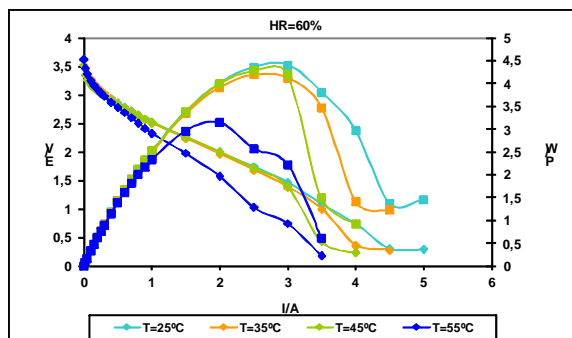

Fig.2 Voltage and power vs current curves for PEM low power stack fed with pure hydrogen at 0.25 bar, 0.5 Lmin⁻¹, for a relative humidity of 60%. The cathode is under excess air stoichiometry condition. Temperature varied from 25 to 55ºC.

After 100 hour operation the dominant degradation mode found after examination by SEM was Pt precipitation as a Pt band on the membrane near to the cathode, which was found in every single cell (see figure 3).
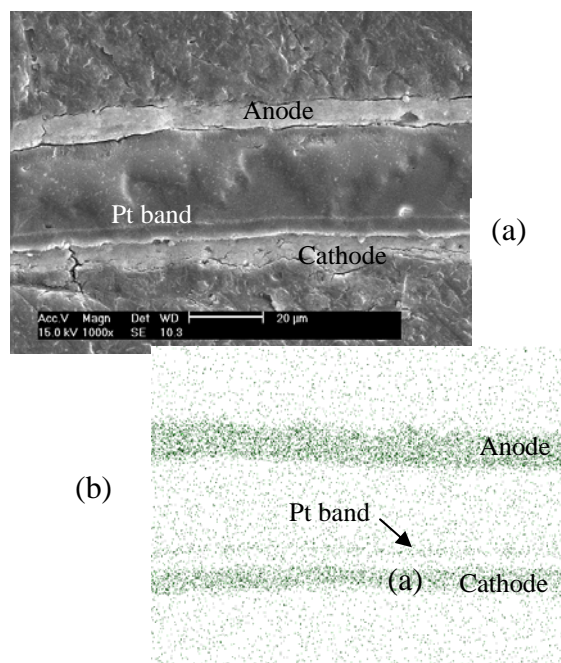

Fig. 3 Typical scanning electron micrograph of a cross section of a MEA of the fuel cell under study (a) and X-Ray Pt elemental mapping (b) showing Pt distribution in the catalyst layers, Pt band inside membrane and reduced cathode thickness.

The Pt band is more clearly observed in the cross section TEM image. It is located at about 4 micron from the interface between the cathode catalyst layer and the membrane. Five different zones localized between the interface and the platinum band (marked 1 to 5 on the TEM image in figure 4) were selected by EDS analysis. Results are presented in table 1.

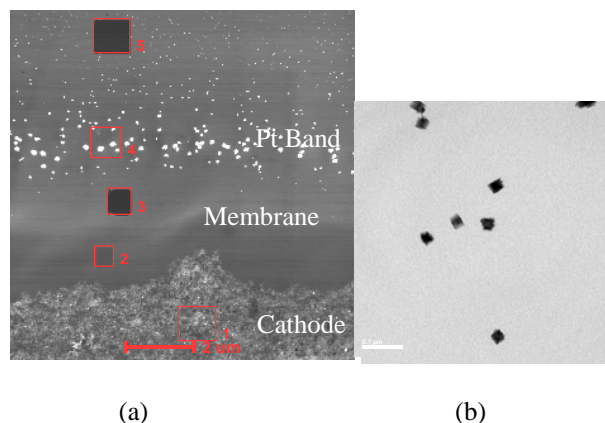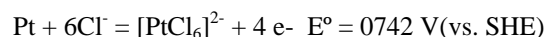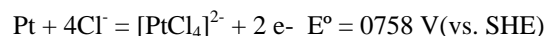(a)   (b)
Fig. 4 TEM image of Pt band inside of MEA (a); magnification of coarse faceted Pt particles located in the Pt band.

Table 1 EDS elemental analysis for areas 1-5 show in fig 5.

Elements wt %	Area 1	Area 2	Area 3	Area 4	Area 5
Cl	0.45	1.41	0	0	0
Pt	14.58	0	0	17.13	0

Chloride is found at concentrations between 0.45 and 1.41 wt% within the catalyst layer and in the cathode interface with the membrane, but not in the Pt band where all the Pt is in the metallic state, constituting an important loss of catalyst since the particles are not electrochemically active.

It is suggested that the presence of chloride has induced Pt dissolution producing Pt ions ($[PtCl_4]^{2-}$ or $[PtCl6]^{2-}$) according to the following reactions [3]:

$$Pt + 4Cl^- = [PtCl_4]^{2-} + 2 e- \quad E^o = 0758 \text{ V(vs. SHE)}$$

$$Pt + 6Cl^- = [PtCl_6]^{2-} + 4 e- \quad E^o = 0742 \text{ V(vs. SHE)}$$

Platinum is thought to be reduced by action of hydrogen supply via gas crossover from the anode. In this way the position of the band depends on the relative partial pressures of hydrogen and oxygen and their relative permeability through the membrane.

As a consequence of the loss of catalyst, the cathode thickness has been greatly reduced. Figure 5 shows that the cathode catalyst layer thickness decreases comparatively with the unused MEA. The decrease is more evident for the cathode than the anode for all the cells, which is also represented in the figure together with the membrane thickness.
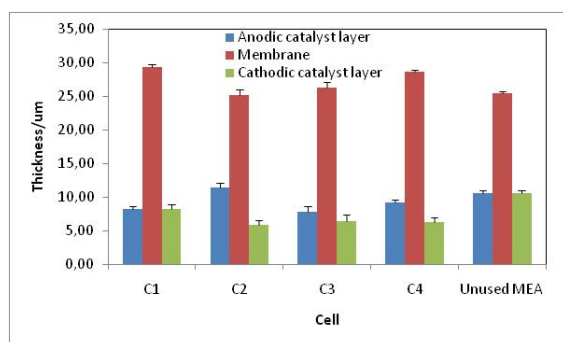

Fig. 5 Thickness variation of MEA components for all cells (C1, C2, C3 and C4) relatively to the unused MEA.

A common degradation among all of the analyzed MEAs was also the cracking of the catalyst layer, as can be observed in figure 3.

Delamination describes a MEA failure feature whereby the catalyst layer has been separated from the polymer membrane electrolyte (see also figure 3). This can be considered a defect which may result from MEA manufacturing procedure or from the dismantling of cell for posterior analysis, but it 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 prone to water accumulation they may degrade faster than other parts of the catalytic layers.

4 Final remarks

• An examination of the fuel cell components after 100 h of operation revealed cathode failure associated to catalyst migration anomalies favored by operation conditions that allowed platinum particles to break free from their carbon backing and migrate to the polymer electrolyte.

Migration resulted in precipitation with larger mean particle size distribution (analogous to the Ostwald ripening process) within the solid electrolyte when compared to the original catalyst layer, rendering a very significant loss of thickness in the cathode material. Coarsening of platinum particles occurs at nano and micro-scale.

• Chloride ions were detected in the catalyst layer and in the interface cathode/membrane and are suggested to promote Pt dissolution with significant cathode thickness reduction.

Work is in progress in order to quantify Pt instability and to suggest mitigation strategies taking into account the actual experimental conditions for low power PEM fuel cells.

5 References

[1] S. Kundu, M.W. Fowler, L. C. Simon, S. Grot. Morphological features (defects) in fuel cell membrane electrode assemblies. J. Power Sources 157 (2006) 650-656.

[2] Jinfeng Wu, Xiao Yuan, Jonathan J. Martin, Haijiang Wang, Jiujun Zhang, Jun Shen, Shaohong Wu, Walter Merida. A review of PEM fuel cell durability: Degradation mechanisms and mitigation strategies. J. Power Sources 184 (2008) 104-119.

[3] P.J.Ferreira, G.J LaO´, Y. Shao-Horn, D. Morgan, R. Makharia, S. Kocha, H. A. Gasteiger, Instability of Pt/C electrocatalyst in proton exchange membrane fuel cell, J. Electrochem. Soc.,152 (2005) A2256-2271.

[4] A. J. Steinback, C.V. Hamilton Jr., M.K. Debe, Impact of micromolar concentration of externally provided chloride and sulphide contaminantas on PEM reversible stability, ESC Transactions, 11 (2007), 889-902.

[5] Koji Matsuaka, Shigeru Sakamoto, Kunihiro Nakato, Akira Hamada, Yasuhiko Itoh. Degradation of polymer electrolyte fuell cells under the existence of anion species. J. Power Sources 179 (2008) 560-565.

[6] Jennifer Péron, Yanning Nedellec, Deborah J. Jones, Jacques Roziére. The effect of dissolution, migration and precipitation of platinum in Nafion-based membrane electrode assemblies during fuell cell operation at high potential. J. Power Sources 185 (2008) 1209-1217.

[7] Shensheng Zhang, Xiao-Zi Yuan, Jason Ng Cheng Hin, Haijiang Wang, K. Andreas Friedrich, Mathias Schulze. A review of platinum-based catalyt layer degradation in proton exchange membrane fuel cells. J. Power Sources 194 (2009) 588-600.