

The effect of chloride as catalyst layer contaminant on the degradation of PEMFCs

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Abstract

In this work, the effect of chloride as a catalyst contaminant was studied on the performance and durability of a low power open-cathode fuel cell, intended for passive management of water. In an ex-situ study, cyclic voltammetry was used to assess the redox behaviour of platinum in chloride contaminated solutions at room temperature. The cell was operated integrating a range of relative humidity (RH) from ~30 to 80% and temperatures from 5 to 55 °C. Results indicated that 60% RH is associated to maximum fuel cell performance over the studied temperature range. An examination of the fuel cell components after 100 h of operation revealed that chloride contamination has produced cathode failure associated to catalyst migration 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.

Keywords: PEM fuel cell, chloride, degradation, platinum instability, agglomeration

1 Introduction

A great deal of attention has been given, in the last few years, to materials ageing mechanisms and degradation in proton exchange membrane fuel cells (PEMFC) and their impact on performance. This is mainly 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, are among other factors that lead to the reduction in electrochemical surface area [3-9].

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 contamination with chloride ions possibly coming from two different sources: the

cathode feed-stream of air in the fuel cell and from the high-surface area catalysts synthesized from halide-containing compounds.

2 Experimental

The effect of the concentration of chloride ions on the redox characteristics of a carbon supported platinum catalyst was examined by cyclic voltammetry (CV) in a 0.5 M H₂SO₄ solution. Other solutions were prepared with added chloride to concentrations of 0.001 M, 0.01 M, 0.1 M and 0.6 M NaCl.

A Pt catalyst ink was painted on a glassy carbon plate with ~ 0.5 x 2 cm, the catalyst occupying an area of 0.25 cm². Cyclic voltammograms (CV) were run in all solutions in a Greene electrochemical cell, using a Lugging-Harber capillary as a bridge to an external Ag/AgCl KCl saturated electrode. A platinum wire was used as a counter electrode. The CVs were conducted using an EG&G Potentiostat /Galvanostat, Model 273A.

A low power fuel cell, intended for passive management of water, was operated integrating a range of relative humidity (RH) from 30 up to 80% and temperatures from 5 to 55 °C. The stack used in this work was composed by 4 cells connected in series, operating with pure hydrogen and air with a cathode designed to contribute to easy 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) with carbon supported catalyst, con-

taining 0.3 mgcm^{-2} Pt. The geometrical active area was 3.8 cm^2 . Polarization curves were registered for a full stack characterization using a purpose-built test station which allows control over gas flow, pressure, temperature and relative humidity. The fuel cell was subjected to several experimental conditions, during approximately 100 h operation, including periods at the open circuit potential.

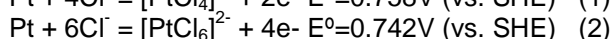
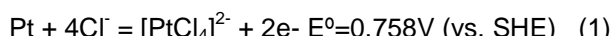
After fuel cell failure, a post mortem analysis of materials and components was undertaken. The fuel cell was dismantled and the MEAs embedded in a resin for cross section morphological and elemental analysis using a Phillips Scanning Electron Microscope, Model XL 30 FEG, coupled to an Energy Dispersive Spectrometer, EDS, which also allowed elemental mapping. Transmission electron microscopy (TEM) of 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.

3 Results and discussion

3.1 Electrochemical activity

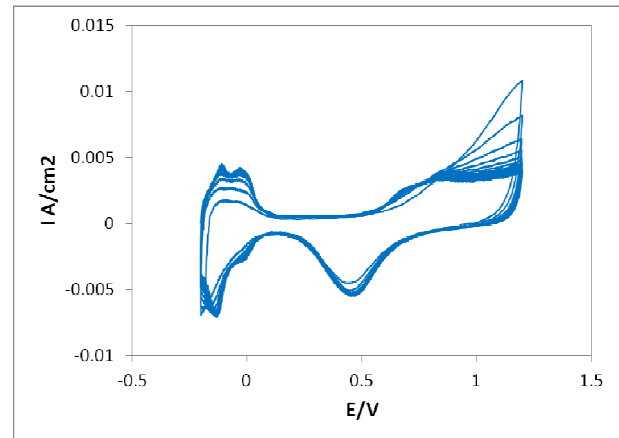
Fig.1a) shows typical cyclic voltammograms for Pt/C catalyst in acid medium. An increase in the electrochemical surface area (ECSA) with cycling was evident and associated to the increase in the charge in the hydrogen adsorption-desorption region showing the activating effect of cycling which is also evident in the Pt oxide formation region.

The voltammogram in $0.5 \text{ M H}_2\text{SO}_4$ can be divided into three regions: the region of hydrogen adsorption-desorption (from -0.2 to 0.1 V); the double layer region (from 0.1 to 0.5 V) and the surface oxidation of Pt region (from 0.5 to 1.25 V). The effect of the concentration of chloride ions on the Pt/C catalyst was also examined, see Fig. 1b). The effect of the chloride concentration is evidenced in the extension of the double layer charging region, more noticeable in the positive-going scan. This is thought to be caused by a strong retardation effect caused by adsorbed Cl^- , which suppressed oxide formation and is associated to the reduction in the charge of the Pt oxide reduction peak, noticeable in the negative-going scan (at 0.5 V). Some authors had attributed this to the dissolution of Pt [1-3] by the formation of the soluble chloride complexes as shown in Eqs. (1) and (2).

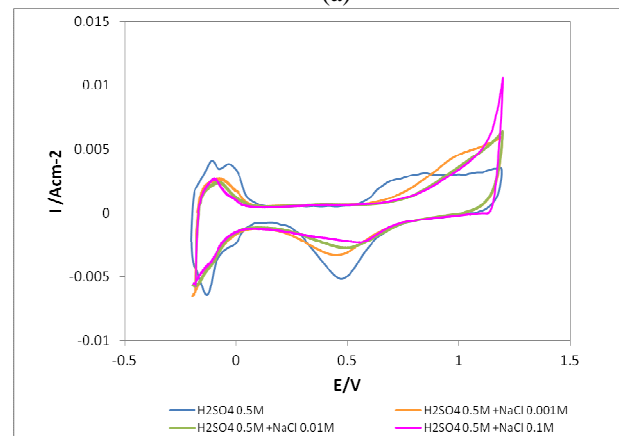


Moreover, the region of hydrogen adsorption-desorption is narrowed in the presence of Cl^- and also changes its shape apparently affecting Pt (100), probably due to strong adsorption of Cl^- . From the region of H_2 adsorption-desorption, ECSA has been determined. Results indicate reductions of 44%, 56%, 58% and 53% for the respective

chloride concentrations of 0.001M , 0.01M , 0.1M and 0.6M .



(a)



(b)

Fig. 1. Cyclic voltammograms of Pt catalyst ink deposited on glassy carbon at 50 mVs^{-1} in a $0.5 \text{ M H}_2\text{SO}_4$ solution (consecutive cycles in a number of 30 were conducted) (a), $0.5 \text{ M H}_2\text{SO}_4$ solution + added chloride ions (b).

3.2 Fuel cell testing

The stack was activated before use. The fuel cell was subjected to experimental conditions schematically shown in Fig. 2, including periods at the open circuit potential.

Results indicated that 60% relative humidity is associated to maximum performance on the fuel cell under study, see figure 3. A loss in performance is found with temperature increase, related to an increase in the membrane resistance which may correspond to loss of water on the anode side. Performances at temperatures lower than room temperature showed only slight decrease in power (not shown).

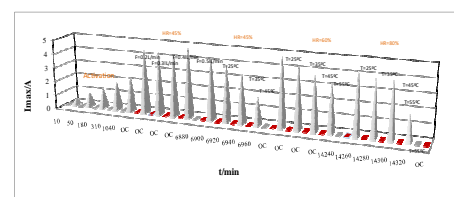


Fig. 2. Cycling of a low power 4 cell open cathode PEM stack vs time indicating polarization conditions and open circuit periods. OC: open circuit.

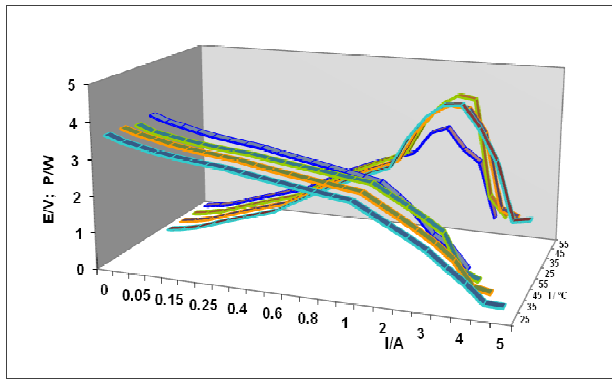


Fig. 3. Polarization and power curves for a 4 cell PEM stack. 60% RH and temperatures between 25 and 55 °C.

Open circuit potential values did not change significantly during the life span of the fuel cell as shown in fig 4. Even though a cell potential decay with time is measurable, it is found to be reversible when the system is purged indicating that potential decay is probably related to water accumulation.

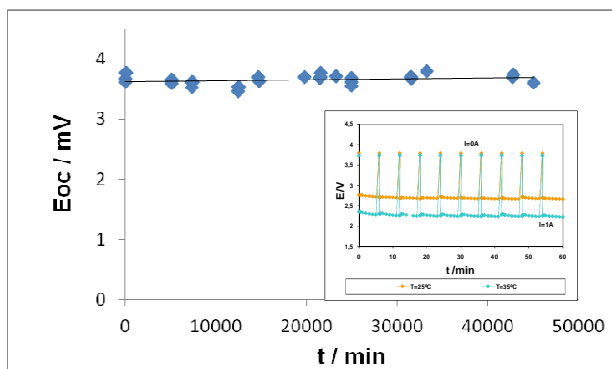


Fig. 4. Open circuit potential as a function of time for a 4 cell PEM stack. In the inset short term data show decay of the potential values at 1 A, reversible upon purging for 25 and 35°C.

3.3 Post mortem analysis

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 5). As a consequence of the loss of catalyst, the cathode thickness has been greatly reduced. Fig. 5b) 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. A common degradation among all of the analyzed MEAs was also the cracking of the catalyst layer, as can be observed in figure 5a). Delamination describes a MEA failure feature whereby the catalyst layer has been separated from the polymer membrane electrolyte. 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.

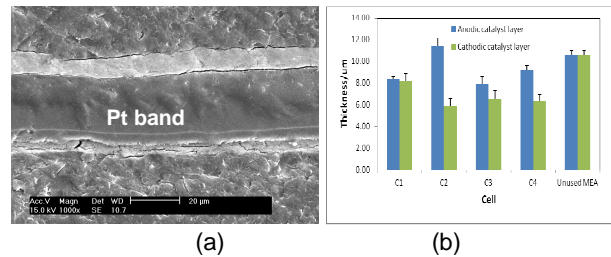


Fig. 5. SEM cross section of MEA showing Pt band near cathode interface, electrode delamination and thickness variation (a); thickness of catalyst layers showing marked reduction of the cathode, values obtained by SEM observations of 4 different cells of the PEM stack (b).

The Pt band was more clearly observed in the cross section TEM image. It is located at about 3 μm from the interface between the cathode catalyst layer and the membrane. 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. Nafion 111 type membrane was used.

Both SEM and TEM suggests that chloride contamination has produced cathode failure associated to catalyst migration anomalies favored by conditions that allowed platinum particles to break free from their carbon backing and migrate toward the polymer electrolyte membrane. It is suggested that the presence of chloride has induced Pt dissolution [1-3] producing Pt ions $[\text{PtCl}_4]^{2-}$ or $[\text{PtCl}_6]^{2-}$. Dissolution and migration of platinum 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, as demonstrated by TEM analysis.

TEM view of metallic Pt particles deposited within the membrane can be seen in figure 6.

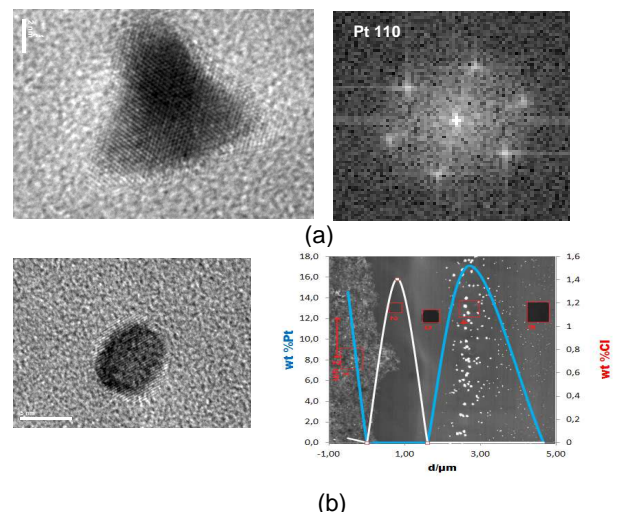


Fig. 6. TEM cross section image of the fuel cell membrane, showing platinum in the platinum band identified by X-Ray diffraction (a) and distribution of chloride in the neighbourhood of the platinum band (b).

Chloride ions concentrations up to 1.41 wt% were found between the cathode interface with the membrane and the platinum band. The amount of chloride in the catalyst layer diminished regarding the initial amount of chloride present. This was indicated by analysis of the fresh MEA. The amount of chloride that may come from the cathode feed-stream of air in the fuel cell could amount to 0.4 ppm according to measurements of chloride in the environmental chamber, where the cell was conditioned during testing. Loss of fluor is also indicated.

Figure 7 shows particle size analysis with a broad distribution for the cathode catalyst. Coarsening of particles is evident when compared to data obtained with a fresh MEA.

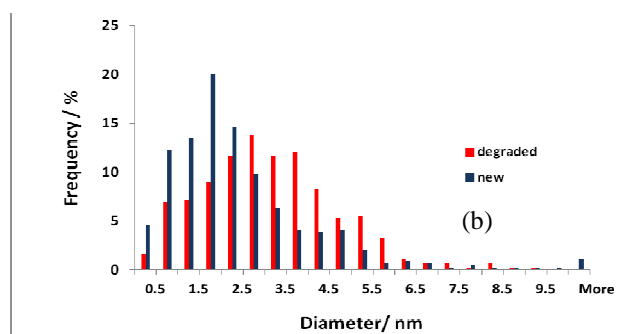


Fig. 7. Catalyst particle size distribution of new and degraded MEA (cathode).

4 Discussion

Traces of chloride ions can change the activity and stability of Pt as a catalyst when acting as a cathode in fuel cell environment. This is mainly due to the structure sensitive kinetics for the oxygen reduction reaction (ORR), which arises from a structure sensitive adsorption of anions. Single crystal studies show two main effects referred in the case of chloride adsorption on supported platinum: a blocking effect by Cl_{ads}^- of the adsorption of O_2 , reducing active sites, which has been suggested to be associated with (111) facets; an enhancement in peroxide production related to the adsorption of chloride ion on (100) facets and (110) corner/edge sites, which effect the breaking of the O-O bond. Moreover, based on HRTEM analysis the effect of Cl_{ads}^- can be explained by the single crystal results by the relationship between particle size and different surface sites in supported Pt [10].

Although these results were obtained in liquid media, they are expected to apply to electrodes in fuel cell environment and have implications regarding both blocking effects and stability of the Nafion membrane and ionomers present in the catalyst layer since results indicate loss of fluor. This will be further discussed.

5 Conclusions

Chloride presence in the catalyst layers has induced Pt dissolution. The effect was examined using cyclic voltammetry in aqueous media. ECSA losses of 44%, 56%, 58% and 53% in the presence

of 0.001M, 0.01M, 0.1M and 0.6M NaCl were attributed.

An examination of the fuel cell components after 100 h of operation revealed cathode failure associated to the presence of chloride up to 1.4 wt% allowing platinum dissolution as platinum chloride complexes and migration to the polymer electrolyte.

Precipitation of platinum, with larger mean particle size distribution, within the solid electrolyte rendered 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.

Acknowledgements

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6 References

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