

FAILURE OF PEM WATER ELECTROLYSIS CELLS: CASE STUDY INVOLVING ANODE DISSOLUTION AND MEMBRANE THINNING

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ABSTRACT

Polymer electrolyte membrane (PEM) water electrolysis is an efficient and environmental friendly method that can be used for the production of molecular hydrogen of electrolytic grade using zero-carbon power sources such as renewable and nuclear. However, market applications are asking for cost reduction and performances improvement. This can be achieved by increasing operating current density and lifetime of operation. Concerning performance, safety, reliability and durability issues, the membrane–electrode assembly (MEA) is probably the weakest cell component. Most performance losses and most accidents occurring during PEM water electrolysis are usually due to the MEA. The purpose of this communication is to report on some specific degradation mechanisms that have been identified as a potential source of performance loss and membrane failure. An ageing test has been performed on a MEA by applying galvanostatic pulses. Platinum has been used as electrocatalyst at both anode and cathode in order to accelerate degradation rate by maintaining higher cell voltage and higher anodic potential that otherwise would have occurred if conventional Ir/IrO_x catalysts had been used. Experimental evidence of degradation mechanisms have been obtained by post-mortem analysis of the MEA using microscopy and chemical analysis. Details of these degradation processes are presented and discussed.

1. INTRODUCTION

Hydrogen is an important reactant and energy carrier, especially in view of the so-called “hydrogen economy”. Molecular hydrogen can be obtained from natural hydrocarbons (natural gas, oil and coal), using steam reforming or gasification processes, from water (electrolysis, thermolysis) or from biomass. Electrolysis (of brine or water) is a simple and mature way of producing hydrogen of electrolytic grade [1]. However, the world hydrogen production by electrolysis accounts to only approximately 4% of the total world production [2]. And water electrolysis, which is more specifically considered in this paper, to less than 1%. This is mainly due to the fact that the energy required to extract hydrogen from water is about four times larger than the energy required to extract hydrogen from methane. In spite of this handicap, water electrolysis may become a competitive source of hydrogen in the future [3], because of the decline of global fossil fuel reserves, the ever growing availability of electricity from other renewable energy resources and the technology improvement of water electrolysis itself. Over the last years, PEM water electrolysis has received a lot attention. The technology offers high efficiencies at high current densities and low operating temperatures (< 100°C). Compared with the alkaline electrolysis technology, PEM water electrolysis has several advantages, mainly in terms of safety and higher gas purity [4-7]. Decentralized hydrogen production processes by PEM water electrolysis find application in both stationary and transport sectors.

PEM water electrolysis (which used to be named as solid polymer electrolyte (SPE) water electrolysis) was first developed by General Electric in the 1960s for spacecraft applications [8]. It rapidly demonstrated significant advantages [9-11] over conventional alkaline water electrolysis. The advantages include (i) the use of significantly less corrosive electrolyte, (ii) a significantly higher hydrogen production capacity, (iii) higher hydrogen purity and (iv) higher efficiency at much higher current densities. Therefore, PEM water electrolysis is considered to be a very promising technique for hydrogen production, that could replace the alkaline process in the long-term. PEM water electrolysis

has been the subject of extensive R&D developments in recent years. Most of such research focused on the quest for novel cathode or anode catalysts [11-15]. In contrast to that, publications on membrane electrode assemblies (MEAs) are rather limited, although a large number of papers on the very similar MEAs for polymer electrolyte membrane fuel cells have been reported [16–19]. Low temperature PEM water electrolysis can be considered as a sister-technology of PEM fuel cell technology [20-22] (H_2/O_2 PEM fuel cells were initially developed at the dawn of the US space program, in view of electricity production in zero gravity environments). Proton-conducting polymer electrolyte membranes are the main component of PEM electrolyzers. They act as cell electrolyte and cell separator to prevent the direct mixing of hydrogen and oxygen. Typical membrane degradation in a fuel cell results from mechanical, thermal, and chemical mechanisms occurring over time or under harsh conditions. Mechanical damage includes membrane cracks, tears, punctures, and pinholes as a result of uneven stress or other mechanical factors, and is often the main cause of early failures, especially for very thin membranes. According to numerous experimental results, membrane degradation is strongly dependent on operating conditions such as temperature, humidity, freeze-thaw cycling, transient operation, and start-up/shut-down. All these working conditions can be employed as accelerated stressors in membrane accelerated stress tests (ASTs) [23]. Many techniques have been reported in the literature to characterize the membrane degradation. Xiao-Zi Yuan et al. [24] carried out accelerated stress test of a four-cell stack with Nafion membranes of different thicknesses. The results indicated that under these conditions, membrane degradation is the major source of the overall cell performance degradation. The predominant reason for the drastic performance decay that occurred after 800 h for thinner membranes was the dramatic increase in hydrogen crossover, caused by significant membrane thickness loss and pinhole formation. Although the performance of thin membranes degraded much faster than that of thick membranes, the thickness loss for the former was lower (thin membranes have less material to degrade). The mechanism of membrane thinning can be understood through the simulation of Nafion weight loss via main chain unzipping. L. Placca and R. Kouta [25] used a Fault Tree membrane degradation modeling to quantify specific degradations, and their effects on the global degradation of the cell. The results obtained in that work show that membrane degradation is the most important factor with two severe consequences : the drop of protonic conductivity and the destruction of the MEA. Mechanical degradations were considered to be the highest probability to occur, followed by thermal and chemical degradations. After 1,000 simulations of 100 h operation in cycling conditions, the probability was 7×10^{-5} for mechanical degradations, 2.8×10^{-6} for thermal degradations and 2.8×10^{-8} for chemical degradations. It resulted to a probability of 7.3×10^{-5} for the membrane degradation. Haolin Tang et al. [26] studied the degradation behavior of Nafion NR111 membrane under various mechanical, chemical and polarization conditions. The Nafion membranes were stable in separate H_2 and O_2 atmospheres at various conditions of atmospheric humidity, saturated humidity and acidic solution. The decomposed fragments were found to contain H_2O_2 in the presence of Fe, Cr and Ni ions. Both FTIR and NMR analysis indicate that the decomposition of the Nafion polymer started from the ends of the main chain, resulting in the loss of the repeat units. The voids and pinholes appeared in the proton exchange membrane with the increase in the repeat unit loss and caused increasing hazards of reactant gas crossover and mixing. M.R. Ashraf Khorasani et al. [27] proposed a diagnosis method for identifying defected cell with a defected membrane. A diagnosis method was introduced in detail and was used in determining and localizing the failed cell of a 5-cells short stack. In this method, the short stack was test in OCV condition and the voltage vs. time curves were analyzed. Analyzing of voltage-time curves and backpressure variation can show a gas-to-gas leakage and, therefore, the membrane rupture. Some impurities may not be in its original form but have been chemically converted. Presumably, the microbes in the feed water, detected as total organic carbon (TOC), were electrolyzed at the anode in the work of Guoqiang Wei et al. [28]. Their sulfur and nitrogen containing organics can also be oxidized to sulfate and nitrate and carbon oxidized to CO_2 [29], which then escape from water. This would explain the large decrease of TOC and the appearance of SO_4^- and NO_3^- in the feed water when the test finished. The performance of MEA in water electrolysis can be affected by the impurities in a number of ways. Metallic cations from feed water can contaminate MEA by exchanging with protons in the Nafion polymer electrolyte of the MEA. The contaminants in the polymer electrolyte will result in higher resistance, or ohmic drop, to the ionic conduction in the MEA, since a metal cation migrates much slower than a proton does. Driven by the cell voltage, the exchanged metallic cations will travel across the Nafion membrane to the cathode side. Underpotential deposition of some of these metal cations, *e.g.* Ni^{2+} , could occur at the cathode [10, 30]. The deposit of metal monolayer will cover the surface of the cathodic catalyst, thus hindering effective hydrogen evolution and causing increased electrochemical overpotential. Some other metal cations, *e.g.* Ca^{2+} , have very negative Nernst potential and cannot be reduced at the cathode. But they could precipitate as hydroxides [31] at the interface between the membrane and the cathode and block the active sites of the Pt catalyst. The hydroxide precipitates, having very poor electrical conductivity, will also increase ohmic drop. The contaminants

can be removed. The simple treatment of the MEA was tried in [28] after the 208 h stability test. The MEA was boiled in 1 mol/dm³ sulfuric acid solution for 1 h followed by rinsing copiously with deionized water. The renewed MEA turned out to perform nearly as good as the original, in term of V–I polarization curve. The cell current at 1.8 V recovered from the lowest 420 mA/cm² to 635 mA/cm², a 98% restoration relative to the initial 645 mA/cm² of the MEA. The purpose of this research work is to perform ageing tests on PEM water electrolysis MEAs and to identify degradation mechanisms. The stability of the MEA was investigated by not only monitoring the performance decline of water electrolysis with the operation time, but also tracing any changes in the MEA components by using different characterization methods.

2 Experimental

2.1. Cell description

Experiments were made using a thermostated single cell of circular geometry (7 cm² active area). This geometry was chosen in place of rectangular shape to avoid the risk of formation of gaseous atmospheres in the upper part of the cell, close to the cell outlet, as described elsewhere [32]. Two porous titanium plates (0.58 mm thick at the anode and 0.95 mm thick at the cathode) were used as current collectors, one on each side of the membrane. The MEA was fabricated using Nafion115 as polymer electrolyte membrane. Pt was used as electrocatalyst on both sides in order to accelerate the degradation rate by maintaining higher cell voltage that otherwise would not have occurred if Ir/IrO_x catalysts were used. At the cathode, Vulcan[®]-supported platinum (Pt loads of 2.5 mg/cm²) was deposited at the surface of the cathodic current collector. At the anode, an unsupported Pt powder (2.5 mg/cm²) was deposited at the surface of the anodic current collector. During the experiments, the electrolysis cell was thermostated at a constant temperature of 90°C.

2.2. Post-mortem analysis

Post-mortem analysis of the MEA was performed using energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscope (SEM), transmission electron microscopy (TEM). Cross-sectional morphology between electrode and membrane interface and thickness changes in the MEA as well as Pt band formation in the membrane was carried out by TEM (JEOL JEM 1200 EX TEMSCAN with Tracor-Northern detector). To confirm the migration of Pt particles into membrane the cross-sectional samples of the MEA were prepared by epoxy resin impregnation and ultramicrotome sectioning with a diamond knife for TEM analysis. SEM observation of membrane surface was done using Tescan Vega II LSU system with IMAX detector (Oxford Instruments). EDX was used to perform elemental analysis of the membrane after degradation. Elemental analysis of metallic deposits was carried out using Oxford Instruments Inca EDS (Energy Dispersive X-ray Spectroscopy) system.

3 Results and discussion

3.1 Experimental operating conditions

Fig. 1 shows the load profiles applied to the cell to accelerate the degradation rate of the MEA. During the first 100 hours the cell was gradually activated by applying constant voltage steps of 2.1–2.2 V until the current density reached the nominal value of 1 A/cm². Then, a succession of on/off galvanostatic cycles (ranging between 0 and 1 A/cm²) have been applied over approximately 5,500 hours of operation, until the cell failed. After 5,500 hours of operation, a cell short-circuit was detected and the experiment was stopped.

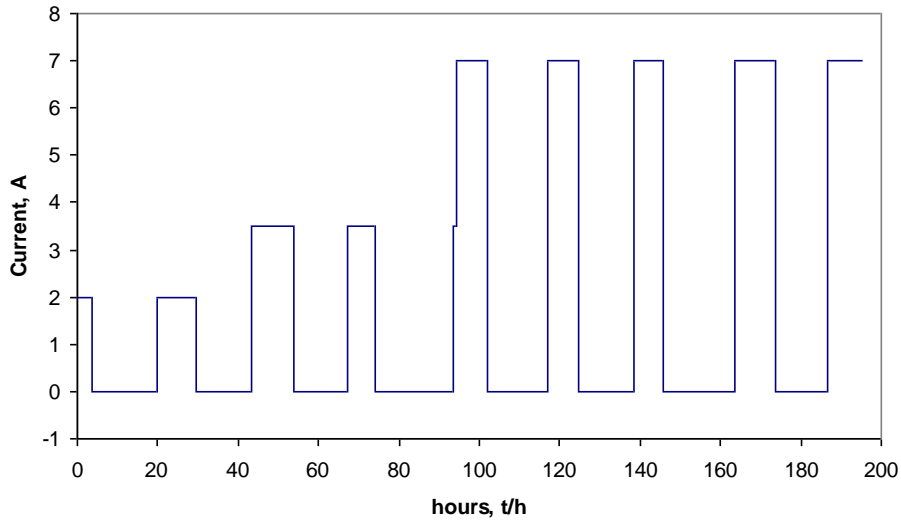


Figure 1. The current profiles of single cell operating in on/off cycles.

3.2 Observations

During the ageing test, the cell voltage was constantly measured. A plot of the cell voltage (for $i > 0$ A/cm²) measured over the entire duration of the ageing experiment is provided in Fig. 2.

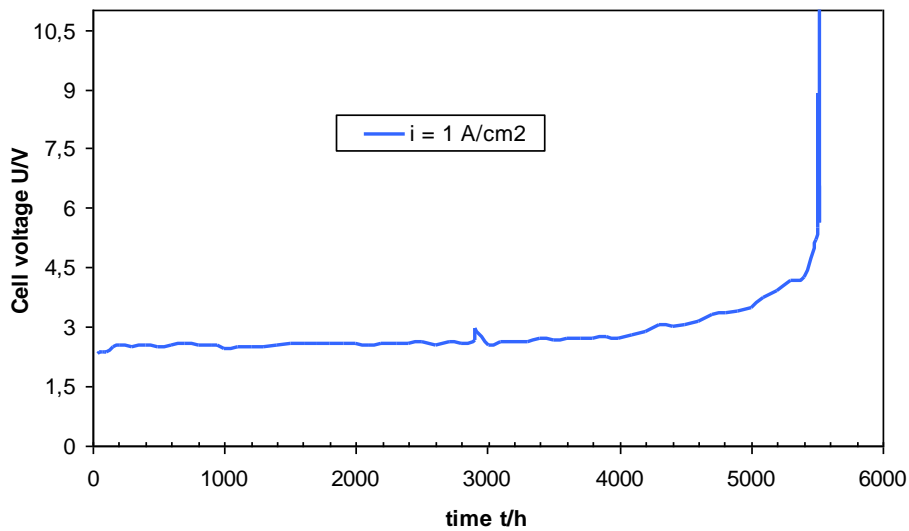


Figure 2. Cell voltage of the water electrolysis cell as a function of time during the ageing test.

As can be seen from Fig. 2, the cell voltage at 1 A.cm⁻² is rather high (2.3 V). This is because platinum is used at the anode for the oxygen evolution reaction (OER). During the experiment, the value of the cell voltage increases steadily and almost linearly from 2.34 V (beginning of test) to about 2.72 V over the first 4,000 hours or so. Then, an inflexion point is observed and the voltage increases much faster between 4,000 and 5,000 hours up to 3.48 V (about 0.008 V increase every 100 hours). After that, the cell shows a quick degradation rate (0.04 V increase every 100 hours) that ends suddenly by the short circuit of the cell after \approx 5,500 hours of continuous operation.

3.3 Post-mortem analysis of the membrane electrode assembly

At the end of the experiment, a post-mortem analysis of the MEA was performed using SEM, TEM and EDX analysis in order to analyze the observed loss of cell performance. As discussed in the introduction section, platinum dissolution at the cathode of PEM fuel cells followed by transport into the membrane and precipitation of platinum particles in the vicinity of the cathode is known as a significant degradation process for fuel cells [33-35]. We made similar observations on our MEA after 5,500 hours of electrolysis operation. Cross-sectional TEM pictures of the anodic area are shown in Fig. 3. The process was significantly amplified because the anode was made of platinum and was operating at a strongly anodic voltage of approximately 2.5 V during the ageing test.

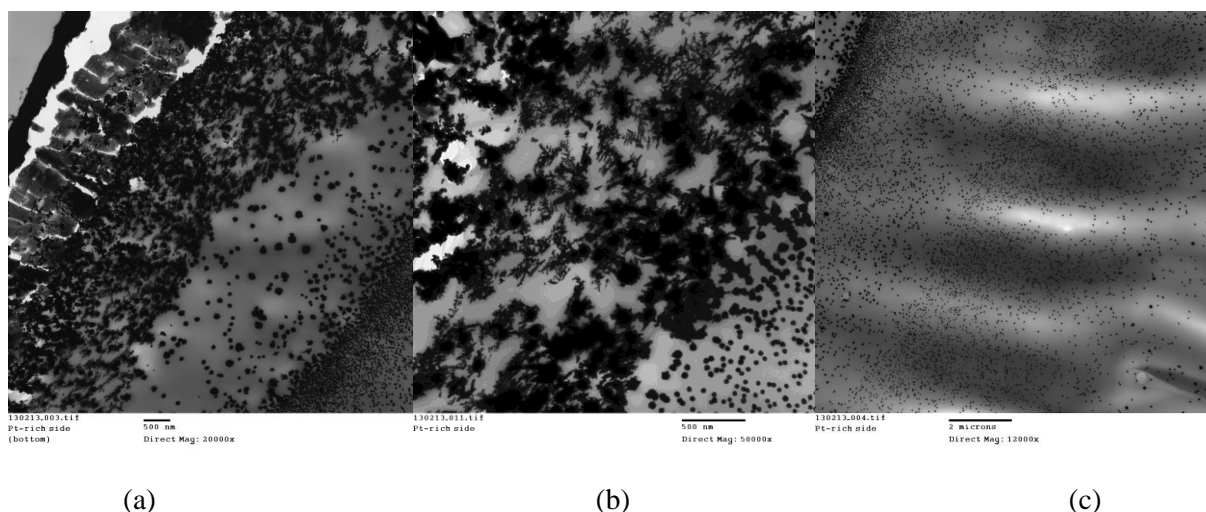


Figure 3. Cross-section TEM micrographs of the MEA at the end of the experiment. Magnification of the anodic area where a layer of metallic platinum is visible.

A 5 micrometers thick platinum layer is observed on figure (a). Platinum particles clearly appear on the different micrographs obtained at different magnifications. Most of these particles (3–125 nm thick) precipitated inside the membrane are not electrochemically active because they are not in electrical contact with the surface catalyst layer. Fig. 4 shows the result of the spot EDX analysis on one of the Pt particles found inside the membrane in the vicinity of the anode. It is seen that the particle is predominantly made of pure platinum. The Cu signal is from the TEM grid. From these observations, the following mechanism is proposed. First, metallic platinum particles located at the surface of the membrane in the active layer are oxidized during operation. They dissolve into the polymer electrolyte as cationic (Pt^{2+}) species which then migrate toward the cathode, because of the electric field. At some distance from the anode, they react with dissolved hydrogen that cross-permeates from the cathode and they are chemically reduced into platinum particles. Since this process involves 1 D transport of platinum in the direction normal to the membrane surface, a platinum layer is formed parallel to that surface. We assume that there is no significantly different mechanism steps compared to what occurs in PEM fuel cells [33-35], except that kinetics of platinum dissolution is much faster here because the potential of the anode in the PEM water electrolysis cell is much higher than the potential of the cathode in the PEM fuel cell.

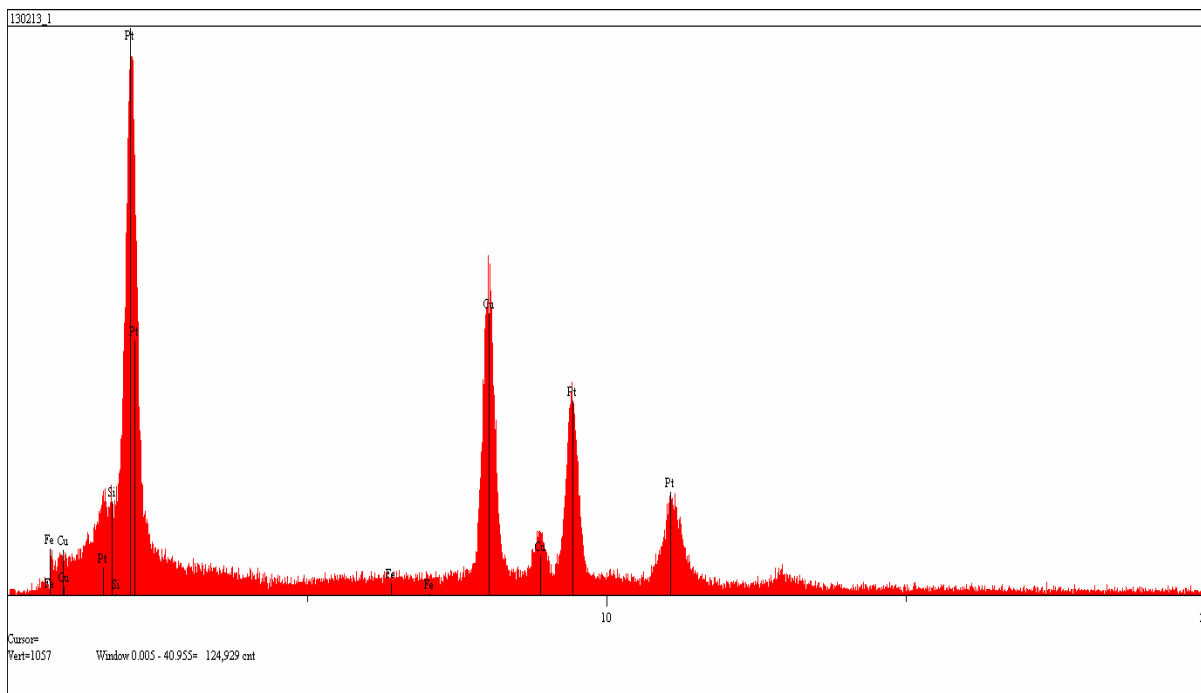


Figure 4. EDX spectra of the Pt particles in the membrane.

It can be concluded from these observations that, like in PEM fuel cells, the dissolution/precipitation of anode catalyst particles inside the membrane is a significant contributor to the overall degradation of the cell performances. As a result, the cell voltage at constant current density tends to increase because of the loss of activity of the anode.

3.3 Membrane thinning

The loss of activity due to platinum dissolution does not account for the sudden end of the experiment. Another problem that was found to dramatically affect the efficiency and durability of the electrolyser is known as “membrane thinning” [36]. The Nafion 115 membrane used in the ageing test was also analyzed after 5,500 hours. Fig. 5 shows a low magnification TEM image of the entire cross-section of the MEA at the end of the degradation test. It was found on several samples that the membrane was significantly thinner after the ageing test than before.

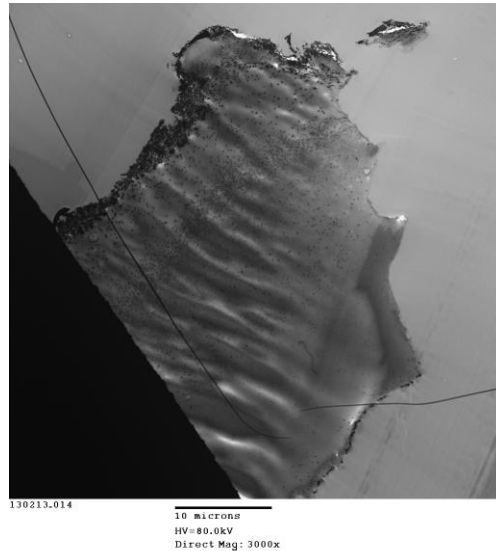


Figure 5. Low magnification TEM micrographs obtained from the cross-sectional MEA.

Mean thickness values measured at different stages of the ageing test are compiled in Table 1.

Table 1. Membrane thickness change before and after the ageing test.

	Fresh, μm	After preparation (washing), μm	Degraded after 5,500 hours, μm	Thickness loss, μm	Thickness decrease, %
Nafion 115	127	140	35	105	75

As indicated in Table 1, membrane water swelling led to a 13 μm increase of the thickness. Preparation was used to clean the membrane surface and to remove ionic impurities. It was boiled in nitric acid, after that boiled several times in distilled water (18 $\text{M}\Omega\cdot\text{cm}$) and left drying in filtered paper. At the end of the ageing electrochemical test, the membrane had lost approximately 75% of its initial thickness. Because the MEA is firmly tight between the two porous current collectors during operation (a tightening pressure of 20-30 bars is usually used), it is assumed that the ohmic contact with the catalytic surface remains efficient. In the course of the experiment, the membrane is gradually corroded and fluoride ions are released and detected in the feed water. To explain this phenomenon, it should be recalled that hydrogen peroxide (H_2O_2) is known to be a very aggressive chemical agent in PEM fuel cells. It was not possible to detect the presence of H_2O_2 inside the membrane at the end of the test (in-situ detection is non-trivial and post-mortem detection usually unsuccessful because the lifetime is limited). What is also known is that, when the membrane is contaminated by metal ions or metallic particles, these species or sites can promote the chemical decomposition of H_2O_2 and generate radicals which in turn can chemically degrade the perfluorinated PFSA backbone [37]. Although chemically and electrochemically inactive, trace amounts of impurities inside the membrane can therefore significantly contribute to the chemical degradation of the PFSA membrane and the MEA. Some of these impurities can be already present inside the membrane that is commercially available but most surely, most of them incorporate the membrane during cell operation. Although this is an indirect attempt to detect hydrogen peroxide inside the membrane, we performed EDX analysis to put into evidence the presence of such impurities inside the membrane. Fig. 6 shows EDX spectra obtained using spot elemental analysis in the cross-section area of PEM membrane, away from surface catalytic layers and Pt particles layer.

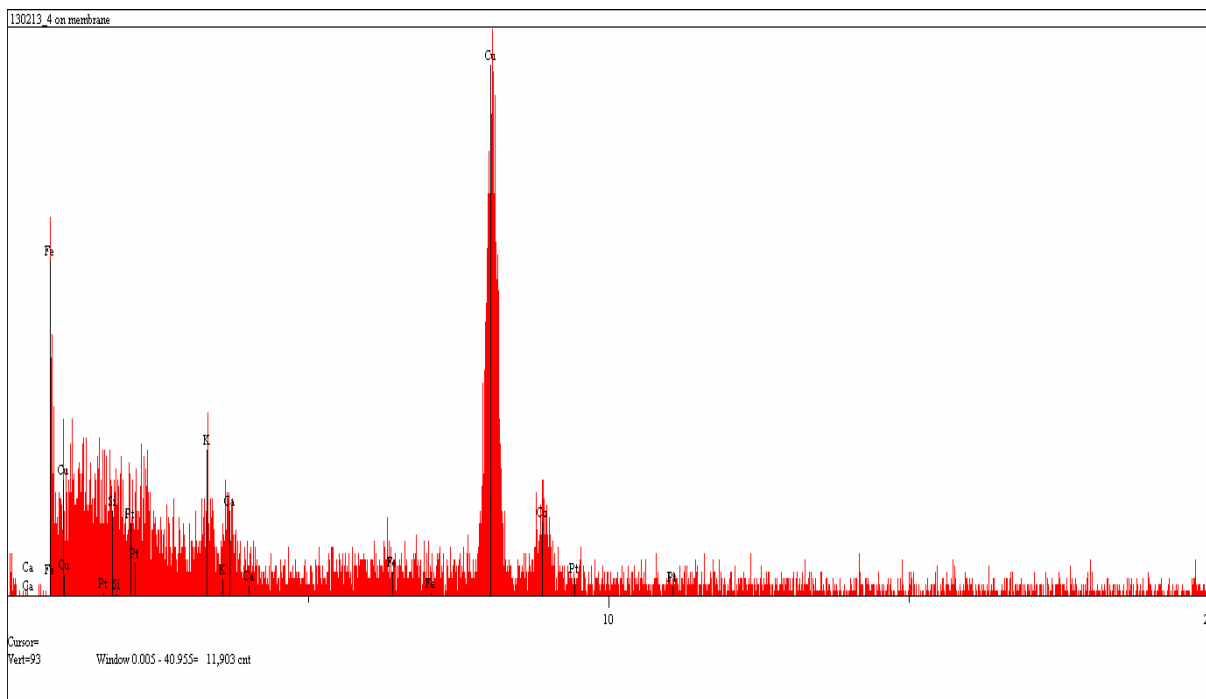


Figure 6. EDX spectra of PEM membrane away from Pt particles.

The chemical analysis revealed that the membrane contains many contaminants, predominantly cationic species of Si, K, Ca and less concentrated others (the Cu signal comes from the TEM grid). The origin of these impurities is the feed water used in the electrochemical process. In particular, the presence of Si can be explained by the use of silicon-containing glassware as water tank during the experiment. It should also be mentioned that all other parts of the electrolyser setup is made of glass (feed water tank). It is therefore assumed that Si leaking and incorporation into the membrane is due to the setup only. Once formed, cationic species can incorporate the proton-conducting membrane simply by ion-exchanging with protons. When necessary, the process can be indirectly followed by measuring the pH of the feed water. It should be noted that stainless steel elements (mainly Fe, Co, Ni and Cr) and titanium that may come from tubing sections of the experimental setup and from cell components were not detected in large concentration, probably because the duration of the experiment is rather limited.

Fig. 7 and Fig. 8 show a post-mortem SEM image of the Nafion 115 and the corresponding EDX analysis. The map surface mapping was determined for Si, Pt, and Ca species.

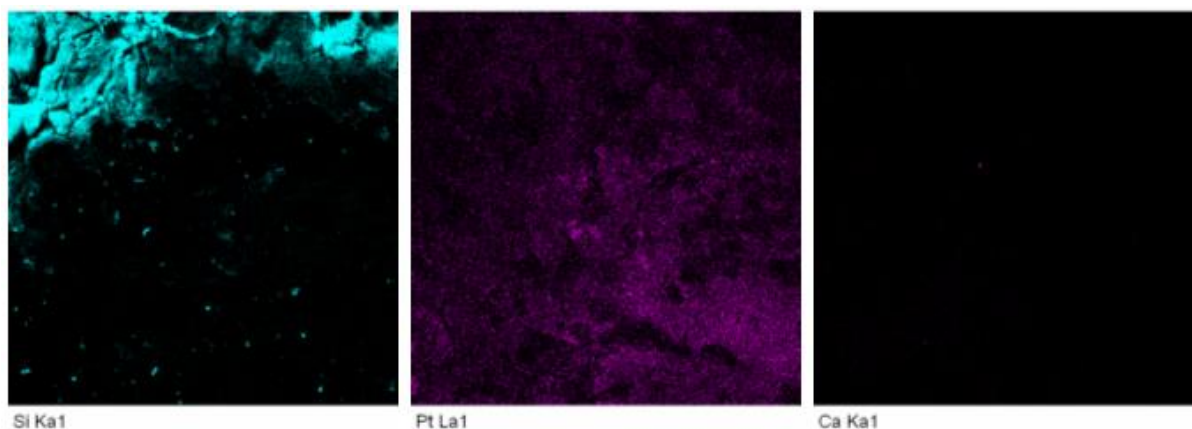


Figure 7. Typical EDX analysis of the membrane surface at the end of the ageing test.

Fig. 8 shows a Pt mapping of the membrane surface. Voids reveal local membrane damage.

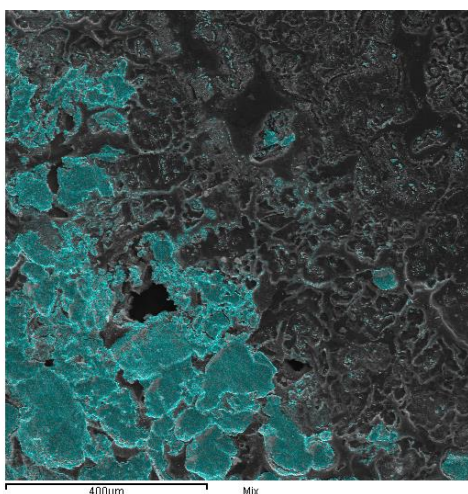


Figure 8. Typical SEM/EDX analysis of the membrane surface at the end of the ageing test. Pt appears in “greenish” color.

As a result of membrane thinning, hot spots can form and gas cross-permeation effects can increase. Although this was not measured during our experiment, the hydrogen content in the oxygen gaseous production and the oxygen content in the gaseous hydrogen production both tend to increase with time. As a result of PFSA chemical degradation and membrane thinning, the probability of membrane perforation increases dramatically.

4 Conclusion and summary

An ageing test has been conducted to determine which mechanisms may cause the degradation of PEM water electrolysis cells. The test consisted of successive on/off galvanostatic cycles between 0 and 1 A.cm⁻² at 90°C. During the test, the cell voltage steadily increased. A corrosion process, similar to those already identified in PEM fuel cells, has been observed. Post-mortem analysis of the MEA revealed that this increasing cell voltage was due to a loss of anodic activity resulting from partial dissolution of the platinum active layer. In conventional PEM water electrolyzers, iridium-based catalytic layers are used at the anode for the oxygen evolution reaction. Iridium is less prone than platinum to dissolution but the difference is a matter of kinetics. After 5,500 hours of operation, a cell short-circuit was detected and the experiment was stopped. It was found that the membrane thickness has been reduced by approximately 75% during the test. Membrane thinning is therefore a second degradation mechanism that led to cell failure. To explain this unexpected observation, we assume that partial (2 electrons) reduction of oxygen into hydrogen peroxide (caused by cross-permeating hydrogen issued from the cathode and catalyzed by either impurities or isolated platinum particles) may lead to the formation of chemically aggressive radicals that are known to chemically corrode PFSA materials.

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