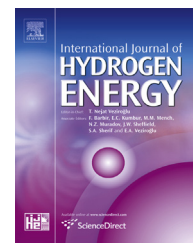


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Failure of PEM water electrolysis cells: Case study involving anode dissolution and membrane thinning

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ABSTRACT

Keywords:

Water electrolysis
Polymer electrolyte membrane
Membrane-electrode assembly
Catalytic layer
Degradation mechanism
Cell failure

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 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 accelerated degradation 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.

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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 (mainly brine 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 of attention. The technology now offers high efficiencies at high current densities and low operating temperatures ($<100^{\circ}\text{C}$). PEM water electrolysis (sometimes also called solid polymer electrolyte (SPE) water electrolysis) was first developed by General Electric in the 1960s for space applications [4]. It rapidly demonstrated significant advantages [5–7] over alkaline water electrolysis. Such advantages include (i) use of non-corrosive electrolyte, (ii) significantly higher hydrogen production capacity, (iii) higher hydrogen purity and (iv) higher efficiency at much higher current densities. 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 [7–11]. In contrast to that, publications on membrane-electrode assemblies (MEAs) were rather limited, although in the meanwhile, a large number of papers were reported on MEAs for the polymer electrolyte membrane fuel cell sister technology [12–15]. Low temperature PEM water electrolysis is somewhat very close to PEM fuel cell technology [16–18] (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 operating 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 [19]. Many techniques have been reported in the literature to

characterize the membrane degradation. Xiao-Zi Yuan et al. [20] 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 was the dramatic increase in hydrogen crossover, caused by significant membrane thinning 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 [21] 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 showed that membrane degradation is the most important factor with two severe consequences: the drop of protonic conductivity (and subsequent ohmic losses) and the destruction of the MEA. Mechanical degradations were considered to have the highest probability to occur, followed by thermal and chemical degradations.

The performance of MEA in water electrolysis can be affected by 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 (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 on platinum surfaces, e.g. Ni^{2+} , were observed at the cathode [6,22]. The deposit of alien metal monolayers cover the surface of the cathodic catalyst, thus hindering effective hydrogen evolution and causing increased electrochemical overpotential. Some other metallic cations, e.g. Ca^{2+} , have very negative Nernst potential and cannot be reduced at the cathode. But they can precipitate in the form of hydroxides [23] 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 purpose of this research work is to perform degradation test on PEM water electrolysis MEAs and to identify some 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.

Experimental setup

Cell description

Experiments were made using a thermostated single electrolysis cell of circular geometry (7 cm^2 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 [24]. 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 Nafion-115 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. Schematic diagram of the experimental set-up is shown on Fig. 1.

Accelerated degradation tests

Fig. 2 shows the load profiles applied to the water electrolysis cell to accelerate the degradation rate of the MEA. During the first 100 h 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.

Post-mortem analysis

Post-mortem analysis of the MEA was performed using energy-dispersive X-ray spectroscopy (EDX) and scanning

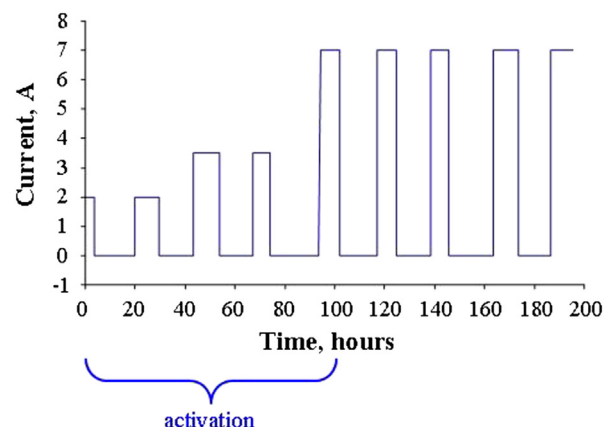


Fig. 2 – The current profiles of single cell operating in on/off cycles.

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 the membrane by TEM analysis, cross-sectional samples of the MEA were prepared by epoxy resin impregnation and ultramicrotome sectioning with a diamond knife. SEM observation of membrane surface was performed 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.

Results and discussion

Results of degradation test

After approximately 5500 h of operation, a cell short-circuit was detected and the experiment was stopped. During the degradation 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 degradation experiment is provided in Fig. 3.

As can be seen from Fig. 3, the cell voltage at 1 A/cm² is rather high (2.3 V). This is because platinum is used at the anode for the oxygen evolution reaction. 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 4000 h or so. Then, an inflexion point is observed and the voltage increases much faster between 4000 and 5000 h up to 3.48 V (about 0.008 V increase every 100 h). After that, the cell shows a quick degradation rate (0.04 V increase every 100 h) that ends suddenly by the short-circuit of the cell after ca. 5500 h of continuous operation.

Metallization of the membrane

At the end of the experiment, a post-mortem analysis of the MEA was performed using SEM, TEM and EDX analysis in order

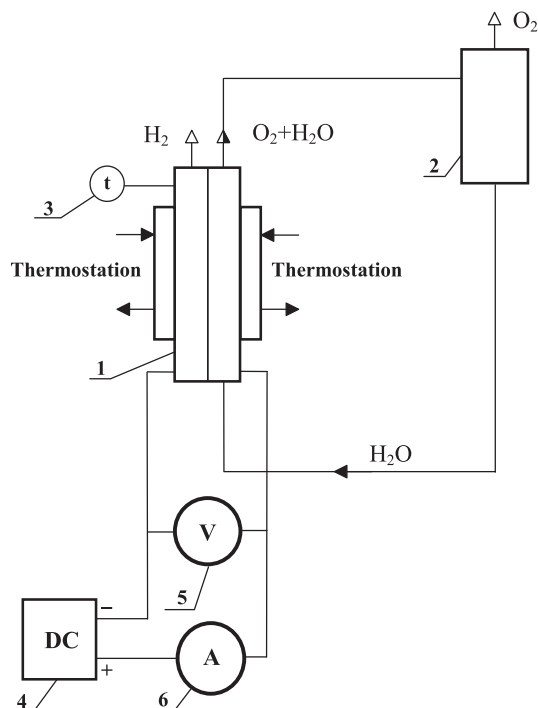


Fig. 1 – Schematic diagram of the experimental set-up including: (1) PEM electrolysis cell; ancillary equipment: (2) liquid–gas separator; (3) temperature detector; (4) DC power supply; (5) voltmeter; (6) amperemeter.

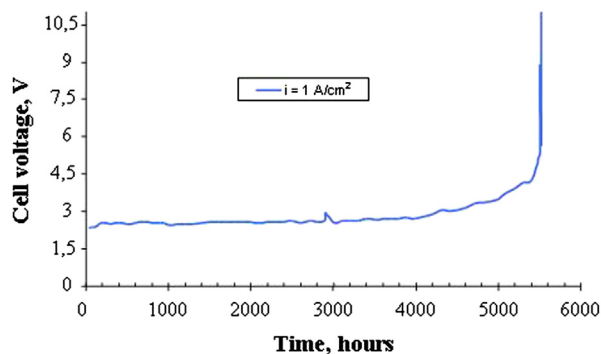


Fig. 3 – Cell voltage of the water electrolysis cell as a function of time during the degradation test.

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 [25–27]. We made similar observations on our MEA after 5500 h of electrolysis operation. Cross-sectional TEM pictures of the anodic area are shown in Fig. 4. 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 degradation test.

A 5 μm thick platinum layer is observed on Fig. 4(a). Platinum particles clearly appear on the different micrographs obtained at different magnifications (Fig. 4((b) and (c))). 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. 5 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 [25–28], 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.

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.

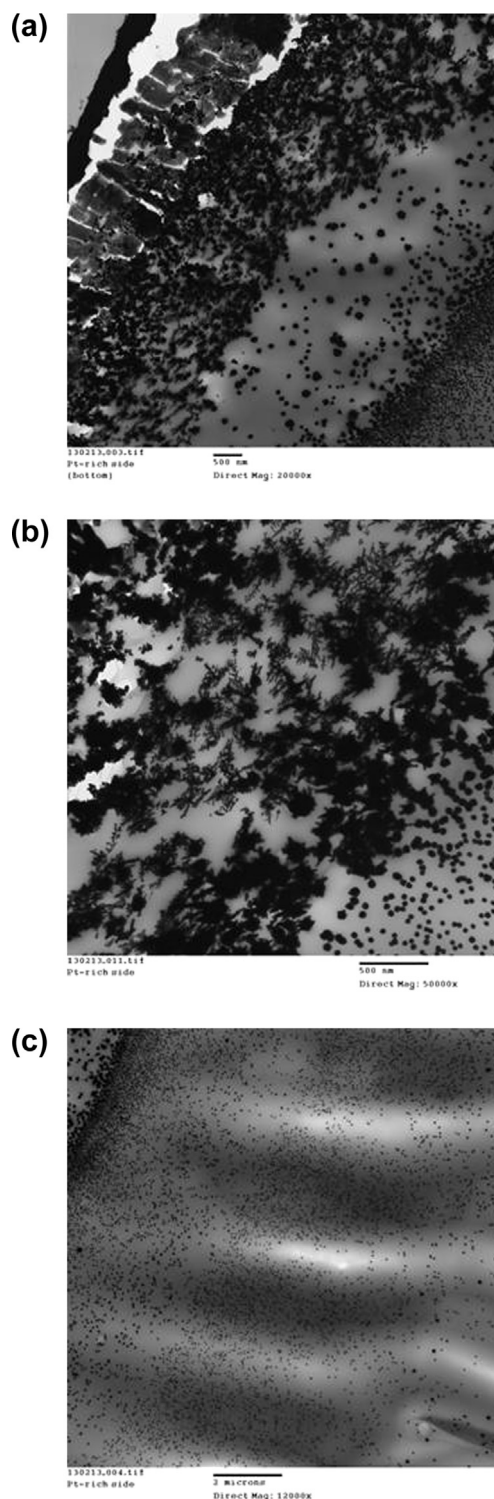


Fig. 4 – Cross-section TEM micrographs of the MEA at the end of the experiment. Magnification of the anodic area where a layer of metallic platinum is visible.

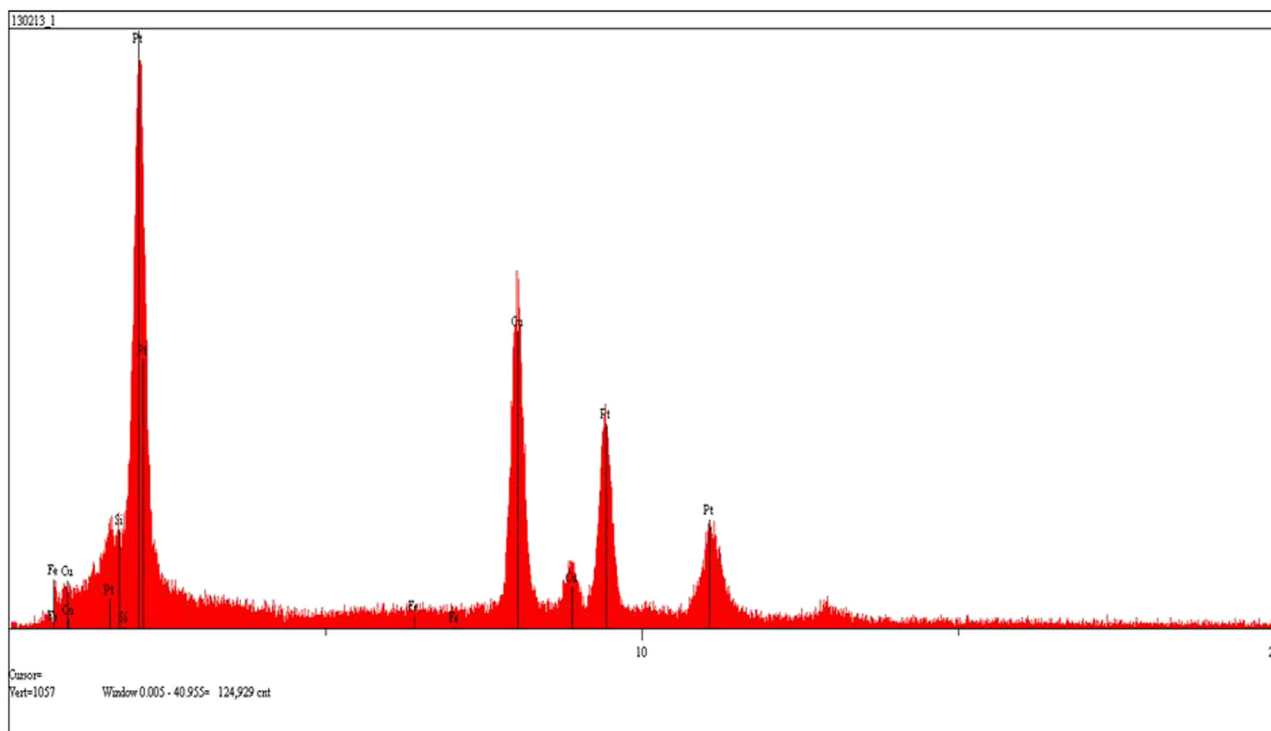


Fig. 5 – EDX spectra of the Pt particles in the membrane.

Membrane thinning

The loss of activity due to platinum dissolution does not account for the sudden end of the experiment after 5500 h of operation. Another problem that was found to dramatically affect the efficiency and durability of the electrolyser is known as “membrane thinning” [29]. The Nafion-115 membrane used in the degradation test was also analyzed after 5500 h Fig. 6 shows a low magnification TEM image of the entire cross-section of the MEA at the end of the degradation test. It was

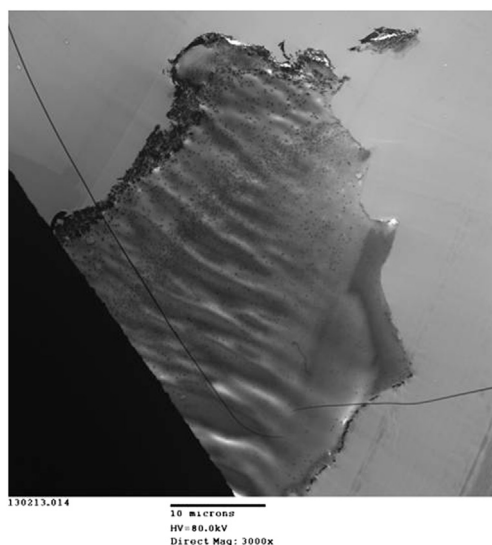


Fig. 6 – Low magnification TEM micrographs obtained from the cross-sectional MEA.

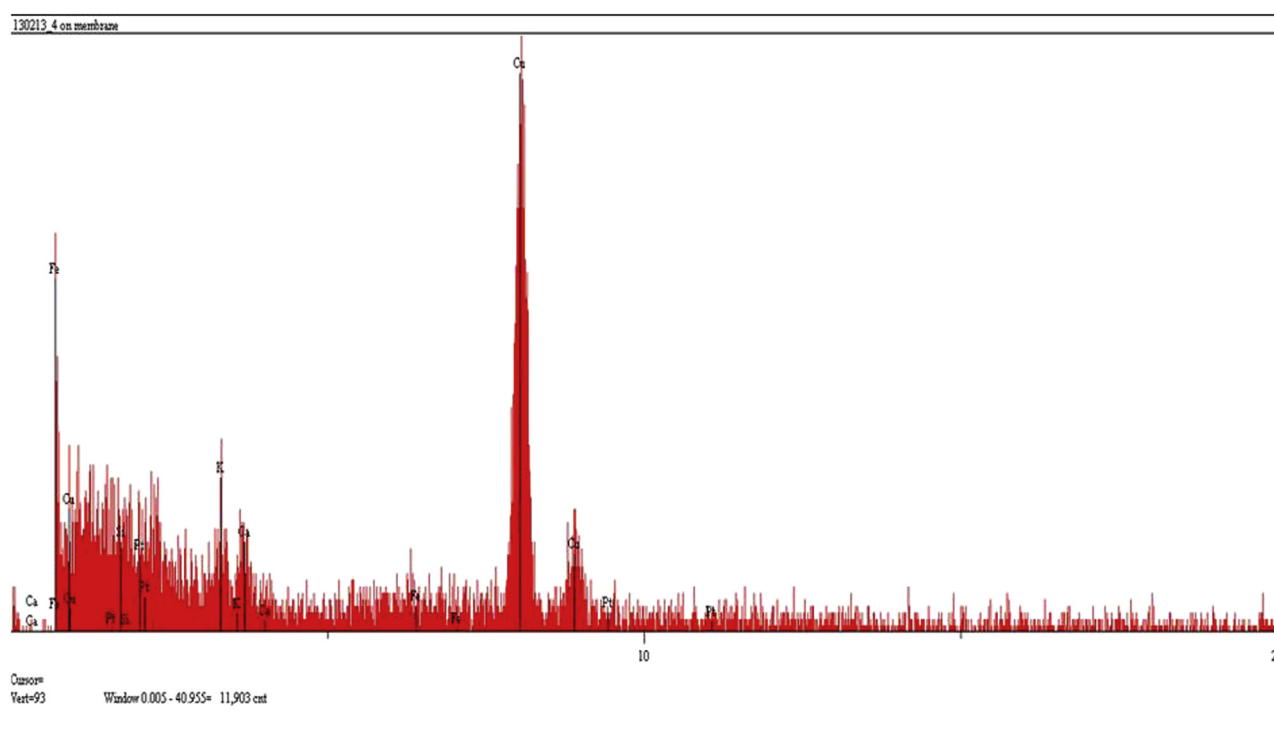
found on several samples that the membrane was significantly thinner after the degradation test than before.

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

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 $\text{M}\Omega\text{ cm}$) and left drying in filtered paper. At the end of the degradation 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 [30]. 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 type	Initial thickness, μm	After pre-treatment (washing), μm	Degraded after 5500 h, μm	Thickness loss, μm	Thickness decrease, %
Nafion-115	127	140	35	105	75

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 and leads to failure.



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test. Membrane thinning is therefore a second degradation mechanism that led to cell failure.

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REFERENCES

- [1] Sang DH, Kee BP, Rana R, Singh KC. Developments of water electrolysis technology by solid polymer electrolyte. *Indian J Chem Sect A* 2002;41:245–53.
- [2] <http://www.hydrogenassociation.org/general/faqs.asp#howmuchproduced>.
- [3] Masson JP, Molina R, Roth E, Gaussens G, Lemaire F. Obtention and evaluation of polyethylene-based solid polymer electrolyte membrane for hydrogen production. *Int J Hydrogen Energy* 1982;7:167–71.
- [4] Grigoriev SA, Porembsky VI, Fateev VN. Pure hydrogen production by PEM electrolysis for hydrogen energy. *Int J Hydrogen Energy* 2006;31:171–5.
- [5] Nuttall LJ, Russell JH. Solid polymer electrolyte water electrolysis development status. *Int J Hydrogen Energy* 1980;5:75–84.
- [6] Millet P, Pineri M, Rurand R. New solid polymer electrolyte composites for water electrolysis. *J Appl Electrochem* 1989;19:162–6.
- [7] Blouin M, Guay D. Activation of ruthenium oxide, iridium oxide, and mixed $\text{Ru}_x\text{Ir}_{1-x}$ oxide electrodes during cathodic polarization and hydrogen evolution. *J Electrochem Soc* 1997;144:573–81.
- [8] Rasten E, Hagen G, Tunold R. Electrocatalysis in water electrolysis with solid polymer electrolyte. *Electrochim Acta* 2003;48:3945–52.
- [9] Marshall A, Borresen B, Hagen G, Tsympkin M, Tunold R. Preparation and characterization of nanocrystalline $\text{Ir}_x\text{Sn}_{1-x}\text{O}_2$ electrocatalytic powders. *Mater Chem Phys* 2005;94:226–32.
- [10] Ma HC, Liu CP, Liao JH, Su Y, Xue XZ, Wei X. Study of ruthenium oxide catalyst for electrocatalytic performance in oxygen evolution. *J Mol Catal A Chem* 2006;247:7–13.
- [11] Tavares AC, Trasatti S. Ni+RuO₂ co-deposited electrodes for hydrogen evolution. *Electrochim Acta* 2000;45:4195–202.
- [12] Wan CH, Lin MT, Zhuang QH, Lin CH. Preparation and performance of novel MEA with multi catalyst layer structure for PEFC by magnetron sputter deposition technique. *Surf Coat Technol* 2006;201:214–22.
- [13] Reshетенко TV, Kim HT, Krewer U, Kweon HJ. The effect of the anode loading and method of MEA fabrication on DMFC performance. *Fuel Cells* 2007;7:238–45.
- [14] Wee JH, Lee KY, Kim SH. Fabrication methods for low-Pt loading electrocatalysts in proton exchange membrane fuel cell systems. *J Power Sources* 2007;165:667–77.
- [15] Kim HS, Subramanian NP, Popov BN. Preparation of PEM fuel cell electrodes using pulse electrodeposition. *J Power Sources* 2004;138:14–24.
- [16] Barbir F. PEM fuel cells, theory and practice. New York: Elsevier Academic Press; 2005.
- [17] Grubb WT. Batteries with solid ion-exchange electrolytes. *J Electrochem Soc* 1959;106:275–9.
- [18] Millet P, Andolfatto F, Durand R. Design and performance of a solid polymer electrolyte water electrolyzer. *Int J Hydrogen Energy* 1996;21:87–93.
- [19] Zhang S, Yuan X, Wang H, Merida W, Zhu H, Shen J, et al. A review of accelerated stress tests of MEA durability in PEM fuel cells. *Int J Hydrogen Energy* 2009;34:388–404.
- [20] Yuan XZ, Zhang S, Ban S, Huang C, Wang H, Singara V, et al. Degradation of a PEM fuel cell stack with nafion® membranes of different thicknesses. Part II: ex situ diagnosis. *J Power Sources* 2012;205:324–34.
- [21] Placca L, Kouta R. Fault tree analysis for PEM fuel cell degradation process modeling. *Int J Hydrogen Energy* 2011;36:12393–405.
- [22] Kotz ER, Stucki S. Ruthenium dioxide as a hydrogen-evolving cathode. *J Appl Electrochem* 1987;17:1190–7.
- [23] Abdel-Aal HK, Husseina IA. Parametric study for saline water electrolysis: part III – precipitate formation and recovery of magnesium salts. *Int J Hydrogen Energy* 1993;18:553–6.
- [24] Millet P, Ranjbari A, de Guglielmo F, Grigoriev SA, Aupretre F. Cell failure mechanisms in PEM water electrolyzers. *Int J Hydrogen Energy* 2012;37:17478–87.
- [25] Lee S, Bessarabov D, Vohra R. Degradation of a cathode catalyst layer in PEM MEAs subjected to automotive specific test conditions. *Int J Green Energy* 2009;6:594–606.
- [26] Kundu S, Cimenti M, Lee S, Bessarabov D. Fingerprint of the automotive fuel cell cathode catalyst degradation: Pt band in the proton-exchange membranes. *Membr Technol* 2009;10:7–10.
- [27] Berejnov V, Martin Z, West M, Kundu S, Bessarabov D, Stumper J, et al. Probing platinum degradation in polymer electrolyte membrane fuel cells by synchrotron X-ray microscopy. *Phys Chem Chem Phys* 2012;14:4835–43.
- [28] Mamat MS, Grigoriev SA, Dzhus KA, Grant DM, Walker GS. The performance and degradation of Pt electrocatalysts on novel carbon carriers for PEMFC applications. *Int J Hydrogen Energy* 2010;35:7580–7.
- [29] Stucki S, Scherer GG, Schlagowski S, Fischer E. PEM water electrolyzers: evidence for membrane failure in 100 kW demonstration plants. *J Appl Electrochem* 1998;28:1041–9.
- [30] Liu H, Coms FD, Zhang J, Gasteiger HA, LaConti AB. Polymer electrolyte fuel cell durability. In: Buchi FN, Inaba M, Schmidt TJ, editors. New York: Springer Science+Business Media; 2009. p. 84.