CELL FAILURE MECHANISM IN PEM WATER ELECTROLYZERS

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ABSTRACT

PEM water electrolysis offers an efficient and flexible way to produce "green-hydrogen" from renewable (intermittent) energy sources. Most research papers published in the open literature on the subject are addressing performances issues and to date, very few information is available concerning the mechanisms of performance degradation and the associated consequences. Results reported in this communication have been used to analyze the failure mechanisms of PEM water electrolysis cells which can ultimately lead to the destruction of the electrolyzer. A two-step process involving firstly the local perforation of the solid polymer electrolyte followed secondly by the catalytic recombination of hydrogen and oxygen stored in the electrolysis compartments has been evidenced. The conditions leading to the onset of such mechanism are discussed and some preventive measures are proposed to avoid accidents.

1. INTRODUCTION

Hydrogen is currently produced from natural hydrocarbons (natural gas, oil and coal), using steam reforming or gasification processes. As a result, large amounts of carbon dioxide are emitted in the atmosphere (0.3–0.4 m^3CO_2/m^3H_2) [1] and CO_2 is considered as responsible for the increasing greenhouse effects and associated climate changes. In this context, hydrogen from water offers a CO_2-free alternative path and a lot of R&D is carried out on the subject in view of the so-called "hydrogen economy".

The water splitting reaction (dissociation of water molecules into molecular hydrogen and oxygen) is a non-spontaneous and endo-energetic process : at standard conditions (298.15 K, 101.3 kPa), the standard Gibbs free-energy change $\Delta G° = + 237.19$ $kJ.mol^{-1}$ [2]. ΔG is also a function of both operating temperature and pressure. ΔG becomes negative (*i.e.* the dissociation of water molecules becomes a spontaneous process) at very high temperature (≈ 2500 K), opening the way to the direct thermal dissociation of water into hydrogen and oxygen. However, the development of technologies operating in this elevated temperature range remains very challenging, both in terms of materials and reactor design and the reaction is not feasible (at least using conventional materials and technology) even from concentrated solar energy sources. This is why, solar chemistry focuses on thermochemical cycles which proceed in several steps and enables hydrogen generation at moderate temperatures which are manageable by using more conventional engineering materials [3].

Besides thermal processes, electricity can also be used to decompose water. Water electrolysis offers a convenient and flexible way to produce hydrogen. The total amount of energy bound in one mole of water is given by the enthalpy of formation of water (in standard conditions, $\Delta H° = +285$ $kJ.mol^{-1}$). To dissociate water molecules, part of ΔH can be supplied as thermal energy, with a maximum of $\Delta Q = T.\Delta S$ (where ΔS is the entropy change associated with the water splitting reaction), and the remaining part (ΔG) as electricity. Thus, the total energy can be supplied by a combination of electricity and heat and the amount of electricity can be reduced by increasing the operating temperature. This is an advantage in some cases, in particular when high-temperature heat is available as a by-product [4]. From a practical viewpoint, different water electrolysis technologies are available for operation at different temperatures. At low temperature (room – 100°C), alkaline and polymer-electrolyte membrane (PEM) technologies can be used. They differ mainly by the pH and the nature of the electrolyte. In the higher temperature range (800-1000°C), the less-mature solid oxide water electrolysis (the reverse of solid oxide fuel cell) can be used. Results reported in this communication pertain to the low-temperature PEM water electrolysis process [5], which is a sister-technology of PEM fuel cell technology [6-8] (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). Although the large scale production of hydrogen by PEM water electrolysis has been considered from both technical and financial viewpoints in the early eighties [9], the aim of most R&D programs since that time was to develop and optimize small (up to several Nm^3 H_2/hour) electrolysis units for the generation of molecular oxygen for breathing purpose in anaerobic environments. Civilian applications appeared in the late XXth century when the world energy situation urged for the development of a non-fossil fuel economy. It turned out that PEM technology was well-suited for operation using intermittent and fluctuating electricity sources and was therefore called to play a major role in the management of renewable energy sources. However, domestic and industrial applications both require cheap and reliable technologies. To reduce investments costs and meet market requirements, the possibility of increasing operating current density up to several $A.cm^{-2}$ has been investigated. In state-of-art technology, a PEM water electrolyzer can now operate at 1 $A.cm^{-2}$ with a high heating value efficiency close to 75-80% and the multiple $A.cm^{-2}$ range is now accessible. In addition, the possibility of delivering pressurized hydrogen up to several hundred bars without additional energy cost to facilitate hydrogen storage in pressurized containers was demonstrated [10,11]. On the less positive side, there are increasing operational risks (explosion of H_2/O_2 gas mixtures) associated with such severe operating conditions. Although highly desirable, higher operating current density, temperature and pressure must not lead to a less reliable technology and for practical applications (both stationary and intermittent), enhanced electrochemical performances should remain very stable and the lifetime of PEM water electrolyzers should be in the upper range of the 10^4-10^5 hours time interval.

In this context, it is important to learn more about degradation processes and to have a better understanding of the mechanisms which can ultimately lead to the destruction of a PEM cell/stack. Most research papers published in the literature on PEM water electrolyzers are addressing performances issues. Indeed, the improvement of cell efficiency at increasing operating current density values remains a critical challenge. Concerning safety issues, some information is also available, in particular those associated to high pressure operation [12], but results are mostly related to risk analysis and prevention issues. The failure mechanism of PEM cells, a topic of major interest, is seldom treated in the open literature. The purpose of this paper is to provide an insight on such mechanism and to show that in some cases, it can lead to stack destruction. Some recommendations are provided to monitor operational risks and improve the durability of the equipment.

2. EXPERIMENTAL SECTION

2.1. Membrane-electrodes assemblies

Results presented in this communication were obtained using a PEM stack operating at a maximum pressure of a few bars and delivering a maximum of 100 Nliter H_2 / hour. 75 cm^2 membrane – electrode assemblies (MEAs) were prepared using conventional (commercially available) materials. Perfluorosulfonic acid polymer (Nafion® 117, Ion-Power Inc.) was used as solid polymer electrolyte. Platinum-group metals (PGM) were used as electrocatalysts. Carbon (Vulcan®, Cabot Co.)-supported metallic platinum (with a loading of approximately 0.4 $mg.cm^{-2}$ of Pt) was used at the cathode for the hydrogen evolution reaction (HER) and a loading of approximately 2.0 $mg.cm^{-2}$ of metallic iridium was used at the anode for the promotion of the oxygen evolution reaction (OER) [13]. The MEAs were prepared as follows. Suspensions of PGM catalyst particles in isopropanol were mixed with a 5 wt.% alcoholic solution of Nafion® (Sigma-Aldrich Co.) and sonicated at 60°C. The catalytic inks thus obtained were repeatedly sprayed over the membrane in order to obtain a homogeneous coverage of the active surface.

2.2. PEM cell

Main components of PEM water electrolysis cells are (Fig. 1) : (1) the proton exchange membrane onto which are platted (2a, 2b) two electrocatalytic layers; (3a, 3b) the porous current collectors (1.2 mm thick plates of sintered titanium powder are commonly used with an optimum open porosity of 40% [14]); (4a, 4b) a 2 mm thick cell spacer (rectangular grooves, machine-made in the thickness of bipolar plates, or titanium grids used as spacers) used to manage a void were liquid water is circulated, and (4a, 4b) 2 mm thick titanium bipolar plates used to separate individual electrolysis cells in the stack. Carbon-based gaskets (not represented) are used as cell sealants. They usually can sustain an operating pressure of a few bars. In a PEM cell, electric current flows from one bipolar plate (4a) to the next one (4c). Liquid water molecules are transferred from the anodic bipolar plate (4a) across the anodic current collector (3a) up to the anode (2a) where they are oxidized into oxygen, electrons and protons. Gaseous oxygen is then transferred back to the anodic bipolar plate across the anodic current collector. Solvated protons are driven across the membrane (1) down to the cathode (2c) where they are reduced into hydrogen which is then transported across the cathodic current collector (3c) up to the cathodic bipolar plate (4c). Water solvent molecules are released at the cathode (so-called electro-osmotic flow of water). Current collectors of large porosity will facilitate gas removal from the interfaces but will also increase the ohmic resistance of the plates and introduce additional parasite ohmic losses at contact points between current collector and catalytic layers (front sides) and between current collectors and channels (backsides). Therefore, an optimization of the geometry of the pore structure is required in terms of overall porosity and pore size distribution. As discussed in Ref. [14], an open porosity of 40% is an adequate value.

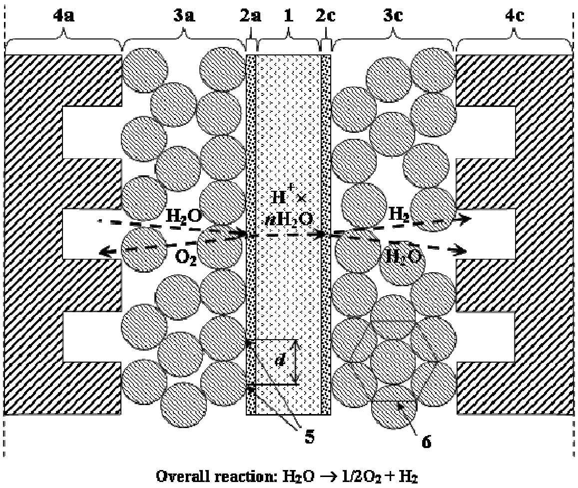

Figure 1. Schematic cross-section of a PEM water electrolysis cell.
1 – solid polymer electrolyte; 2 – electrocatalytic layers; 3 – porous current collectors;
4 – bipolar plates; 5 – contacts points between current collectors and electrocatalytic layers
(d – average distance between contact points between current collector and catalytic layers);
6 – current collectors with closely packed hexagonal powder particles. (a – anodic, c – cathodic)

2.3. PEM electrolyzer

The electrolyzer is made of seven individual (75 cm^2 active area each) cells stacked in series in a filter press configuration (Fig. 2).

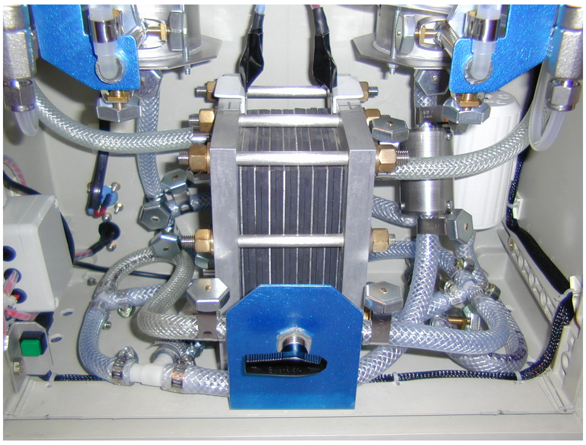

Figure 2. Photograph of the PEM water electrolyzer.

The stack itself is clamped between two thick (1.5 cm) aluminium end-plates. Individual water admission inlets are provided at the bottom of one end-plate for the cathodic and anodic cell compartments. Before operation, it was checked (using helium) that there is no gas leak between the different cells. Liquid water is mechanically pumped through both anodic and cathodic compartments. Liquid-gas mixtures are collected through outlets disposed on top of the end-plates. Biphasic liquid-gas mixtures (water - hydrogen on the cathodic loop and water – oxygen on the anodic loop) are then separated in gravity-separators and the water is re-cycled back to the electrolyzer. The pressure drop across the water outlet is such that liquid water pumped into the cell compartments is homogeneously distributed over the entire active area of the cell. This is a prerequisite to insure a homogeneous distribution of current lines along the stack and obtain a good overall efficiency.

2.4. Stack characteristics

2.4.1. Charge density

Distribution of current lines inside the stack is a critical issue. Heterogeneous current lines may be the initial step of a failure mechanism. Therefore, before operation, it is important to check that within the stack, each individual PEM cell experiences a similar electrical environment. As discussed elsewhere [15], cyclic voltammetry can be used for that purpose. By measuring the total coulombic charge associated with each cell (Fig. 3), it is possible to obtain information about the homogeneity of the electrical environment for each MEA and therefore about the distribution of current lines along the stack during operation. As can be seen from Fig. 3, the values obtained for the seven cells of the stack are bracketing the reference value measured on a 23 cm^2 MEA used as benchmark. There are differences from one cell to the other but the discrepancy of datapoints remains limited. This is an indication that the stack is homogeneously tightened and that current lines are homogeneously distributed.

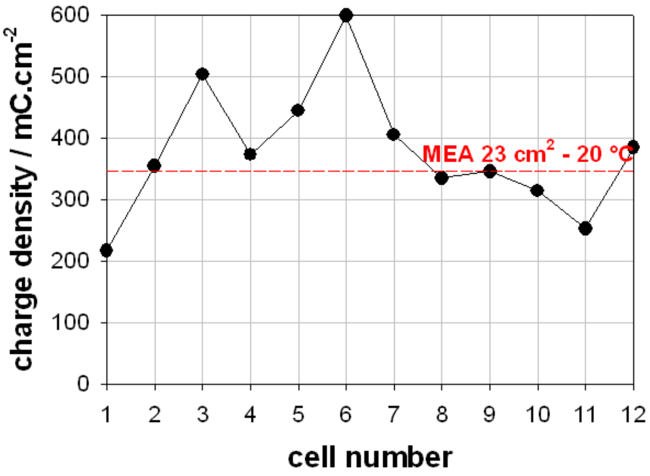

Figure 3. Charge densities measured on each cell of the PEM water electrolyzer [15].

2.4.2. Electrochemical performances

Before investigating degradation processes, it is necessary to record polarization curve of individual MEAs inside the stack in order to check that electrochemical performances are similar. As can be seen from Fig. 4-a (where individual cell voltages are plotted as a function of current density), an inflexion point is sometimes observed when the current density increases (at *ca.* 400 mA.cm^{-2} in this case). The situation is generally encountered when the stack is insufficiently tightened. As a result, a screening effect (formation of an insulating film of gas between the catalytic layer 2a or 2c and the porous current collector 3a or 3c) develops. From a practical viewpoint, this is of course a limiting current density beyond which it is not possible to operate. However, when the stack is appropriately tightened, this screening effect disappears and it is possible to increase the operating current density up to much larger values (several A.cm^{-2}). At an operating temperature of 80°C, a stack efficiency close to 80% (based on the high heating value of the reaction, i.e. on the energy required to split liquid water) was obtained at 1 A.cm^{-2} with the electrolyzer (Fig. 4-b). In such conditions, the electrolyzer is operating in a satisfactory way and there is no indication of potential dysfunction. In particular, it is assumed that current lines are homogeneously distributed between anode and cathode and that the mean temperature inside the stack is also homogeneous.

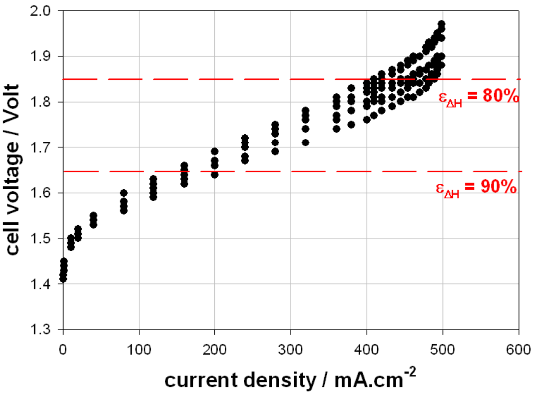

Figure 4a. Polarization curves recorded on individual PEM cells at 80°C.

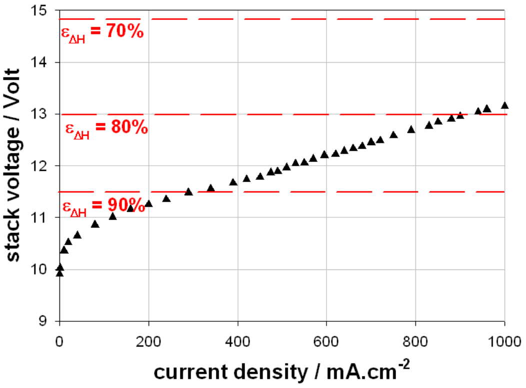

Figure 4b. Polarization curves recorded on the stack at 80°C.

3. RESULTS AND DISCUSSION

3.1. Experimental operating conditions

Experiments have been made to assess the ability of the electrolyzer to operate continuously at high (1.8-2.0 A.cm^{-2}) current density. Thermostated liquid water (80°C) was continuously pumped through each cell compartment to insure a constant supply of feed water to the anode and symmetrical operating conditions. The process was remotely monitored. Individual cell voltages were recorded on a regular time basis as well as temperature of input and output water flows and hydrogen content on the oxygen circuit. Before operation, several potential failure scenarios had been anticipated and the monitoring software was able to detect some specific dysfunctions during operation. In particular, faulty cells could be detected by comparing the value of their cell voltage to reference values. A reduce cell voltage is a sign for a possible short-circuit and a high value can be related to an increased cell resistivity and an insufficient supply of water to the anode. The hydrogen content in the anodic liquid-gas separator was also monitored. Would any criteria be satisfied for any cell, then the power supply was automatically shut-down within seconds. It is of course difficult, from an experimental viewpoint, to obtain valuable information on an irreversible degradation process. This is because there is in general no clear forerunning sign that can be used to detect an emerging dysfunction and because this is usually a slow process which suddenly diverges and can have dramatic consequences for the integrity of the electrolyzer. Nevertheless, in some situations, it has been possible to stop the electrolyzer before total destruction and to gain information on the failure mechanism. Results are presented and discussed in the following sections.

3.2. Step 1 of the failure mechanism : perforation of the MEA

3.2.1. Experimental result

A critical situation was met experimentally with the stack of Fig. 2 during a run at elevated (1.8 A.cm^{-2}) current density. The failure was detected automatically by the continuous monitoring of individual cell voltage. The voltage of one cell suddenly fell down below a threshold value of 1.5 V, suggesting the onset of an electrical short-circuit. A burst of hydrogen concentration in the oxygen production was also detected and the power supply was shut-down immediately to prevent the destruction of the stack. It was therefore possible to dismantle the stack and to get information about the failure mechanism at an early stage. It turned out that the membrane was perforated (Fig. 5). A hole was found in the upper area of the MEA, close to the exhaust pipe, and the membrane was significantly put out of shape. The chemical analysis of the white deposit observed in the vicinity of the hole revealed that it contained PTFE, suggesting a kind of local melting. Nafion® ionomer tolerates relatively high temperatures, with a melting point over 200°C. According to DuPont (the manufacturer of the ionomer) a maximum operating temperature of 190°C is possible when membranes are bonded to reinforcing materials (this is not the case here) or are used with liquids (this is the case here). A lower temperature of 150°C is quoted when the membrane is used in gas dryers with dry gases and is not reinforced. Thermal decomposition of Nafion® requires much higher temperatures. The presence of PTFE is the indication of a significant increase of local temperature which could be due to the spontaneous and exothermic recombination of H_2 and O_2. Therefore, it can be concluded that the run was stopped just after the perforation of the membrane and before the mixing of hydrogen and oxygen gases stored in the cell. It was also checked that bipolar plates were not perforated.

Figure 5. Photograph of the MEA after perforation.

3.2.2. Discussion

Potentially, there are different causes which may lead to the perforation of the membrane and to the subsequent mixing of hydrogen and oxygen gases.

A first hypothesis is that there might be some mechanical origins. However, it seems unlikely that the forced circulation of water in the anodic and cathodic compartments can lead to the perforation of the membrane by mechanical friction. As can be seen from Fig. 1, main water flows are circulating along the bipolar plates (4-a and 4-b) and not directly against the membrane surface. Also, the electro-osmotic drag of water from the anode to the cathode is not sufficient to cause mechanical friction. However, the soft membrane material is clamped between two hard metallic current collectors. If the stack is not homogeneously tightened, then there is a risk of perforation. Post-mortem analysis of MEAs commonly show the presence of some titanium particles deeply embedded inside the polymer. Surface prints and deformations which can ultimately lead to the short circuit of the cell are also observed. However, as discussed in section 2.4.1., this was not the case in the present set of experiments. Cyclic voltammetry measurements have shown that the cells were not short-circuited. Therefore, it can be concluded that the perforation occurred during electrolysis and the hole is not the result of a mechanical degradation process.

A second hypothesis is that the perforation was the result of so-called “hot spots” due to the uneven distribution of current lines over the active area. This assumption is supported by the fact that the failure occurred during operation at high current density. If, for any reason (for example non-homogeneous distribution of pressure forces at the surface of the cells), there is a surface-area where the current density is substantially larger than in others, then this is where the temperature will increase due to the Joule effect. Although it has been shown that heat dissipation in a PEM water electrolysis cell is not a limiting factor, even at current densities of several A.cm^{-2} [16], it is known that a Nafion® membrane soaked in water above 110°C loses all its mechanical strength and falls apart. Also, the increase in the degree of swelling of the membrane can lead to significant dimensional changes and generate some internal constraints which can reduce its mechanical strength. All these effects can contribute to the perforation of the membrane.

A third hypothesis is the local drying of the membrane due to insufficient amounts of water supplied to the anode. As can be seen from Fig. 1, two opposite flows are taking place at the same time across the anodic current collector (3a) : liquid water is supplied to the anode and gaseous oxygen is produced at the anode. The driving forces for these transfers are the gradients of concentrations across the current collector and capillary forces. Although the amount of liquid water required to fuel the reaction is of limited volume (e.g., at 1 A.cm^{-2}, liquid water is supplied to the anode at a rate of 0.1 mm^{3}.cm^{-2}.s^{-1}; at the same time, gaseous oxygen is produced from the anode at a rate of 58 Nmm^{3}.cm^{-2}.s^{-1}), it becomes more and more difficult to supply sufficient amounts of liquid water to the anode as the current density increases. As the result, the electrical resistance of the membrane in this area will increase and the temperature will increase by Joule effect. There is few information available in the literature about this phenomenon and it is difficult to know whether such heterogeneities exist at the micro- or macroscopic scale. However, as discussed in the experimental section, a direct consequence of local drying is the formation of a screening effect which can be detected by monitoring the cell voltage. Our experiments have been made at constant cell voltage. If a screening effect had occurred, then the total current would have decreased. This has not been observed.

A fourth hypothesis is the formation of a hydrogen-oxygen atmosphere in at least one cell compartment, before the perforation of the membrane. The biphasic liquid-gas mixtures in circulation in the PEM cells contain mainly liquid water and a dispersion of small gas bubbles (the mean bubble diameter is close to the diameter of the pores *i.e.* up to a few microns). Although the liquid-gas separation is organized outside the PEM stack in liquid-gas separators (gravitation is used as driving force), convection is such inside the PEM cells that liquid-gas separation can also take place (at least partly) inside the cells. As a result, a stationary gaseous cloud can form and remain trapped on top of the cell, close to the exhaust pipes where the hole shown in Fig. 5 formed (the formation of such gas clouds has been observed experimentally using transparent model electrolysis cells). The subsequent catalytic recombination of H_2 and O_2 (promoted by PGM catalysts at the surface at the membrane) can liberate sufficient heat to burn the membrane. It is therefore necessary to understand how such a H_2/O_2 atmosphere can form. The fact is that the polymer electrolyte is not fully gastight. This is not due to the existence of pinholes or microscopic pores (the quality and homogeneity of commercial membrane products is such nowadays that this is certainly not the main cause of gas transport across the membrane). In fact, this is due to gas cross-permeation phenomena which are known to take place. Under normal conditions of operation, hydrogen and oxygen produced at the cathode and the anode of the PEM cell are separated by the membrane which acts as a solid electrolyte (ionic conductor) and as a cell separator. However, H_2 and O_2 solubility in perfluoro-sulfonic polymers are such that gas permeability across the membrane is possible. As a result, trace amounts of hydrogen are measured in the oxygen stream and trace amounts of oxygen are measured in the hydrogen stream (the difference of concentration usually observed is due to the difference of H_2 and O_2 diffusion coefficients). The mechanism of gas permeability is the Fickian diffusion of dissolved gas across the membrane. Therefore, flows of permeating gases are proportional to gas mobility, membrane thickness and to the difference of pressure set across the membrane. Usually, impurity levels increase with operating pressure. A critical step is reached when the hydrogen concentration in the oxygen anodic production (or the concentration of oxygen in the cathodic hydrogen production) reaches a threshold value of 4 vol.%, corresponding to the lower explosion limit of the H_2/O_2 gas mixture. Such concentration levels can also be reached gradually inside the stationary gaseous clouds which may form in the cells. Such effects and associated contingency plans have been described and analyzed elsewhere [12,17].

It is difficult at this stage to tell which mechanism among the above-mentioned phenomena is responsible for the perforation of the membrane. Additional experimental works is still required to obtain a better understanding. It can only be concluded that a critical step is reached once the membrane is perforated. What can happen next? In the case of Fig. 5, the perforation of the membrane led to a cell short-circuit which was easily detected. However, this is not because a hole is formed that the cathodic and anodic current collectors are immediately short-circuited. It is therefore expected that sometimes, it will be difficult to detect the accident. Even when the membrane is perforated, the remaining surface can still play its role of cell separator. The cell voltage is maintained and the gas production can proceed. This is probably why this degradation mechanism is quickly and irreversibly diverging, is difficult to detect and therefore difficult to stop. Once a hole is formed, the next step is the formation of a reactive gas mixture (gaseous hydrogen and oxygen) in the vicinity of the hole and the subsequent combustion of the two gases. Hydrogen and oxygen produced in stoichiometric proportions at the anode and the cathode can mix and the catalysts coated onto the membrane (at least platinum used at the cathode for the HER) can promote their direct chemical recombination. The process is spontaneous and exothermic. In turn, the energy is released to the surroundings. This is a divergent process. As discussed in the next section, this can lead to the total destruction of the electrolyzer.

3.3. Step 2 of the failure mechanism : hydrogen-oxygen combustion

3.3.1. Experimental result

There are other experimental situations for which any forerunning technical failure (such as the change in the cell voltage or a reduction of gas purity mentioned in the previous section) cannot be detected and for which the process can rapidly lead (within only a few seconds) to the total destruction of the stack. This is what happened in another run at high current density (1.8 A.cm^{-2}). When the automaton used to monitor the system detected a failure situation (sudden decrease of current) and shut down the power supply, it was already too late to avoid the destruction of the stack. As can be seen from Figs. 6 and 7, the combustion of non-metallic cell components (MEAs and sealants) was total, leading to the formation of carbon deposits over the titanium bipolar plates (combustion of MEAs and cell sealants). The electrolysis stack was destroyed by combustion within a few seconds.

Figure 6. Photograph of the MEA.

Figure 7. Photograph of the MEA.

Indirect information on the combustion process has been gained by examining the stainless steel tubes used to circulate water and liquid-gas biphasic mixtures in the circuitry. The effects of the combustion were not limited to the stack itself. As can be seen from Figs. 8 and 9, metallic elbow connectors located at a distance of *ca.* 20 cm away from the stack were neatly perforated during the combustion which originated in the stack. The section of the hole measured on these elements is equal to the internal section of the tube. Therefore, it can be concluded that a H_2/O_2 combustion flame formed inside the stack (at least in one cell) and then propagated along the tubing section up to the first elbows in the circuitry and acted as a H_2/O_2 torch flame. The flame temperature of a stoechiometric H_2/O_2 gas mixture is known to be close to 3200°C [18]. Even if the H_2/O_2 gas mixture is saturated with water vapor, the temperature of the flame is still expected to be sufficiently high to perforate the metallic components. An explosion would have produced mechanical distortions inside the circuitry which were not observed.

Figure 8. Photograph of a stainless steel fitting drilled by a H_2/O_2 flame formed inside the PEM stack.

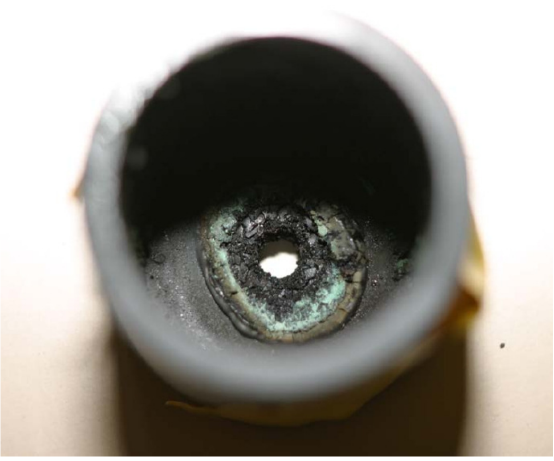

Figure 9. Photograph of a stainless steel nut drilled by a H_2/O_2 flame formed inside the PEM stack.

3.3.2. Discussion

Once the solid polymer electrolyte is perforated, the second step of the failure mechanism should logically be the mixing of gaseous hydrogen and oxygen in the vicinity of the hole and the subsequent combustion of hydrogen in oxygen. The combustion reaction is a spontaneous process over a large range of operating temperature. The combustion is not favored by the negative entropy change of the reaction (due to the reduction of mole numbers) but the reaction is largely exothermic (the enthalpy change is almost constant over the entire temperature range) and hence, ΔG is continuously negative. Although the operating temperature is low (< 100°C) and although hydrogen and oxygen are saturated with water vapor, the presence of finely divided platinum catalytic particles on each side of the polymer electrolyte can promote the recombination. Therefore, the main risk for the electrolyzer is the catalytic recombination of hydrogen and oxygen stored inside the PEM cells and even in the whole electrolysis unit. It should be noted here that in stationary conditions (constant current density), there is the same amount of hydrogen and oxygen in each cell compartment because the volume of each cell compartment is the same. Thus, the gas composition in the PEM cell is sub-stoechiometric in hydrogen fuel, the combustion of which is the limiting factor. Therefore, to evaluate the risk, it is necessary to determine the hydrogen amount inside the cell as a function of operating current density and pressure. This is not a trivial task because this is a biphasic liquid – gas mixture which is present in each compartment. A limiting case corresponding to a maximum energy value is obtained when there is no liquid inside the cathodic compartment. The total amount of gas stored in the cells is proportional to the size of the cells, to the internal geometry and to operating pressure. It is therefore possible to calculate the amount of energy stored in each cell as a function of operating conditions (in particular as a function of current density).

From geometrical considerations (Fig. 1), the internal volume V_{cell} of each electrolysis compartment expressed per cm^2 of active area is $V_{cell} \approx 0.22\ cm^3 / cm^2$. The maximum amount of hydrogen stored in the PEM cell is obtained when there is no liquid inside the cathodic compartment. This amount is a direct function of operating pressure. At atmospheric pressure (the pressure at which results reported in this communication were obtained), the maximum amount of hydrogen is 7.5×10^{-6} $mole.cm^{-2}$, corresponding to a maximum energy of 2.14 $J.cm^{-2}$ (HHV). If that amount of energy was released as heat, this would hardly be sufficient to raise the temperature of the membrane by *ca.* 25°C (the estimation is made by assuming that the medium is isotropic; no distinction is made between the fluoro-carbon backbone and the aqueous phase of the membrane). A temperature of 190°C would be reached for an operating pressure of 7.4 bar. Therefore, it is necessary to consider the total amount of gas stored in the stack to explain the combustion of the electrolyzer, not only the local concentration. The maximum amount of hydrogen stored in a 75 cm^2 PEM cell at atmospheric pressure is 16.5 Ncm^3. According to the literature, H_2-O_2 torches can produce high temperature (3200°C) flames by consuming few (2-5 cm^3) atmospheric hydrogen per second. Therefore, there is enough hydrogen in a 75 cm^2 PEM cell to fuel such a flame for 5 to 10 seconds and enough hydrogen in the seven cell stack to fuel such a flame for 30 seconds to one minute. Commercial H_2/O_2 torches are using a nozzle to slow down the combustion. In the PEM cell, the combustion is probably faster. Nevertheless, it can be concluded that there is enough energy in a PEM cell operating at atmospheric pressure to destroy the entire cell. Even if these calculations were made under the assumption that there was no liquid water inside the cells and even if the combustion of water-saturated hydrogen-oxygen gas mixtures provides less energy than the combustion of dried gases, the amount of energy stored inside the stack is sufficient to destroy the stack.

4. PREVENTION ISSUES AND RECOMMENDATIONS

The following technical measures are recommended to reduce operational risks in electrolysis stack.

4.1. Prevention measures for the electrolyzer

Some recommendations for high pressure water electrolysis are already available in the literature [19]. From the results presented here, there are different risk issues for a PEM water electrolyzer operating at high current density. Different recommendations can be made to prevent the onset of irreversible degradation processes. First, circular geometry should be preferred over rectangular geometry when designing a PEM water electrolysis stack to avoid the risk of formation of gaseous atmospheres in the upper part of the cell, close to the cell outlet. Second, it is necessary to measure the charge density for each cell before operation and to determine whether there are risks or not of uneven distribution of current lines. Third, the electrolyzer should operate at constant cell voltage and not constant current density. If for any reason the impedance of any cell increases, then the current dissipated in the stack will decrease. It is also highly desirable to monitor individual cell voltages : an increase in cell voltage can be related to inappropriate water distribution in the anodic compartment and a decrease in cell voltage can be due to a cell short-circuit and the formation of a hole in the MEA which in turn can lead to the formation of highly reactive H_2/O_2 gas mixtures. Of course, a continuous monitoring of the hydrogen content in oxygen and of the oxygen content in hydrogen is also recommended. If the electrolyzer is operating at high pressure, gas cross-permeation effects across the solid polymer membrane should be reduced as much as possible (for example by incorporating inorganic fillers in the polymer or by using thicker membranes), and the catalytic recombination of H_2 and O_2 should be actively promoted (for example by implementation of internal gas recombiners inside the PEM cells).

4.2. Prevention measures for the electrolysis unit

The discussion on operational risks can be extended to the entire electrolysis unit where larger amounts of gases are stored (in particular in the liquid-gas separators) and where explosion hazards are more severe. There are a number of safety requirements for the closed-premises in which hydrogen leaks can potentially occur. In particular, there is a need for a continuous ventilation on the production site in order to maintain the hydrogen concentration to values less than the 4 vol.% corresponding to the lower explosion limit of H_2/O_2 gas mixtures. Ventilation should be made with an inert gas to reduce the inflow of oxygen which could participate in the ignition or explosion of hydrogen.

5. CONCLUSION

PEM water electrolysis is considered as an efficient and flexible technology for the production of “green-hydrogen” from renewable (intermittent) energy sources. Whereas most research papers published on the subject are addressing performances issues, there is also a need to identify and analyze the mechanisms of performance degradation and the associated consequences. This is a topic seldom treated in the open literature. However, this is critical to assess the ability of the technology to operate safely on the long-term and to identify potential operational risks. Results reported in this communication have been used to analyze the failure mechanisms which can lead to the destruction of a PEM electrolyzer. Although it remains difficult to establish a clear relationship between operating conditions and degradation processes, there are some situations which can lead to the perforation of the membrane. It appears that the major risk is due to the possible catalytic recombination of hydrogen and oxygen stored inside the electrolysis compartments. According to our experience, internal H_2/O_2 combustion seems to prevail over explosion. However, additional insights are still required to clearly identify the causes of degradation processes because there is no clear forerunning sign that could be used to detect dysfunctions and because the failure of a PEM cell is usually a slow process which suddenly diverges over a very short period of time of only a few seconds. However, some preventive measures can be used to avoid accidents and some recommendations have been listed.

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REFERENCES

1. Muradov, N., Hydrogen via methane decomposition: an application for decarbonization of fossil fuels. *International Journal of Hydrogen Energy*, **26**, 2001, pp. 1165–75.
2. Mortimer, C.E., Chemistry, 1986, fourth Edition, Belmont.
3. Roeb, M., Neises, M., Säck, J-P., Rietbrock, P., Monnerie, N., Dersch, J., Schmitz, M. and Sattler C., Operational strategy of a two-step thermochemical process for solar hydrogen production, *International Journal of Hydrogen Energy*, **34**, 2009, pp. 4537–4545.
4. Kroschwitz, J.I. and Howe-Grand, M., editors, Kirk-Othmer Encyclopedia of Chemical Technology, 1995, Vol. 13, fourth edition, Wiley VCH, New-York.
5. Grubb Jr, WT., US Patent No. 2,913,511, 17 November 1959.
6. Barbir, F., PEM Fuel Cells, Theory and Practice, 2005, Elsevier Academic Press.

7. Grubb Jr, W.T., Batteries with Solid Ion-Exchange Electrolytes, *Journal of the Electrochemical Society*, **106**, 1959, pp. 275-279.
8. Millet, P., Andolfatto, F. and Durand, R., Design and Performances of a Solid Polymer Electrolyte Water Electrolyzer, *International Journal of Hydrogen Energy*, **21**, 1996, pp. 87-93.
9. Solid Polymer Electrolyte water electrolysis technology development for large scale hydrogen production, General Electric Company, DOE Report DOE/ET/26 202-1, 1981.
10. Millet, P., Ngameni, R., Grigoriev, S.A., Mbemba, N. Brisset, F., Ranjbari, A. and Etiévant, C., PEM water electrolyzers : from electrocatalysis to stack development, *International Journal of Hydrogen Energy*, **35**, 2010, pp. 5043–5052.
11. Millet, P., Ngameni, R., Grigoriev, S.A. and Fateev, V.N., Scientific and engineering issues related to PEM technology: Water electrolyzers, fuel cells and unitized regenerative systems, *International Journal of Hydrogen Energy*, **36**, 2011, pp. 4156-4163.
12. Grigoriev, S.A., Millet, P., Korobtsev, S.V., Porembskiy, V.I., Pepic, M., Etievant, C., Puyenchet, C. and Fateev, V.N., Hydrogen safety aspects related to high-pressure polymer electrolyte membrane water electrolysis, *International Journal of Hydrogen Energy*, **34**, 2009, pp. 5986-5991.
13. Grigoriev, S.A., Millet, P. and Fateev, V. N., Evaluation of carbon-supported Pt and Pd nanoparticles for the hydrogen evolution reaction in PEM water electrolyzers, *Journal of Power Sources*, **177**, 2008, pp. 281-285.
14. Grigoriev, S.A, Millet, P., Volobuev, S.A. and Fateev, V.N., Optimization of porous current collectors for PEM water electrolyzers, *International Journal of Hydrogen Energy*, **34**, n°11, 2009, pp. 4968-4973.
15. Millet, P., Mbemba, N., Grigoriev, S.A., Fateev, V.N., Aukauloo, A. and Etievant C., Electrochemical performances of PEM water electrolysis cells and perspectives, *International Journal of Hydrogen Energy*, **36**, 2011, pp. 4134-4142.
16. Millet P., Water electrolysis using EME technology : temperature profile inside a Nafion® membrane during electrolysis, *Electrochimica Acta*, **36**, N°2, 1991, pp. 263-267.
17. Grigoriev, S.A., Porembskiy, V., Korobtsev, S., Fateev, V.N., Aupretre, F. and Millet, P., High pressure PEM water electrolysis and corresponding safety issues, *International Journal of Hydrogen Energy*, **36**, 2011, pp. 2721-2728.
18. North American Combustion Handbook, 1983, North American Mfg. Co.
19. Marangio, F., Santarelli, M. and Calı, M., Theoretical model and experimental analysis of a high pressure PEM water electrolyser for hydrogen production, *International Journal of Hydrogen Energy*, **34**, 2009, pp. 1143 – 1158.