HIGH PRESSURE PEM WATER ELECTROLYSIS AND CORRESPONDING SAFETY ISSUES

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ABSTRACT
In this communication, safety considerations related to the operation of proton-exchange membrane (PEM) water electrolysers (hydrogen production capacity up to 1 Nm^3/hour and operating pressure up to 130 bars) are presented. These results were obtained in the course of the GenHyPEM project, a research program on high pressure PEM water electrolysis supported by the European Commission. Experiments were made using a high-pressure electrolysis stack designed for operation in the 0-130 bars pressure range at temperatures up to 90°C. Besides hazards related to the pressure itself, hydrogen concentration in the oxygen gas production and vice-versa (resulting from membrane crossover permeation effects) have been identified as the most significant risks. Results show that the oxygen concentration in hydrogen at 130 bars can be as high as 2.7 vol. %. This is a value still outside the flammability limit for hydrogen-oxygen mixtures (3.9-95.8 vol. %), but safety measures are required to prevent explosion hazards. A simple model based on the diffusion of dissolved gases is proposed to account for gas cross-permeation effects. To reduce contamination levels, different solutions are proposed. First, thicker membranes can be used. Second, modified or composite membranes with lower gas permeabilities can be used. Third, as reported earlier, external catalytic gas recombiners can be used to promote H_2/O_2 recombination and reduce contamination levels in the gas production. Finally, other considerations related to cell and stack design are also discussed to further reduce operation risks.

1. INTRODUCTION
General principles of PEM technology (Grubb cell) were described in the early fifties, at the dawn of the US space program [1]. H_2/O_2 fuel cells were used for the production of electricity in zero-gravity environments. In PEM cells, conventional liquid electrolytes are replaced by thin (50-250 μm thick) proton-conducting membranes used as solid polymer electrolyte (SPE). In the late sixties, the introduction on the market of chemically stable sulfonated tetrafluoroethylene based fluoropolymer-copolymer (W. Grot, E.I. DuPont Co., Nafion® products) opened the way to water electrolysis applications. Nafion® was the first of a class of synthetic polymers called ionomers with ionic properties. These materials are obtained by copolymerization of a perfluorinated vinyl ether comonomer with tetrafluoroethylene (TFE). They offer good ionic conductivity and low gas permeability [2,3]. Nowadays, other polymer materials are also available. PEM technology has been mostly used to produce oxygen in anaerobic environments (for example for space and underwater applications) but has also been considered in the early eighties for the large scale production of hydrogen (peak shaving of electricity production from nuclear reactors) from both technical and economic viewpoints [4]. A renewed interest for PEM water electrolysis started at the beginning of the XXIst century when the world energy situation urged for the development of hydrogen as an energy carrier. With conversion efficiencies above 70 % at high current densities (> 1 A.cm^{-2}), PEM water electrolysis has been identified in the European Hydrogen and Fuel Cell programme as a key process for transforming zero-carbon electricity sources into the supply of zero-carbon hydrogen and oxygen for miscellaneous end-uses [5] and the European Commission is actively supporting R&D

activities in this field [6]. The characteristics of PEM electrolysers are such that they are well-suited for water splitting using intermittent power sources, especially when hydrogen is produced at pressures up to a few bars since cross-permeation phenomena are then less significant. High pressure operation is potentially interesting for the direct storage of hydrogen in pressurized vessels. Some applications, for example in the automotive industry, require storage pressures up several hundred bars. At higher operating pressure (in the 10-150 bars pressure range), gas cross-permeation effects and related safety issues must be considered [6,7]. The solubility and mobility of gases (H_2 and O_2) in hydrated perfluorinated SPEs are such that the concentration of hydrogen in oxygen produced at the anode and the concentration of oxygen in hydrogen produced at the cathode both increase with temperature and pressure [8], especially at low current densities [7], leading to potentially significant hazards. It is therefore necessary to choose the proper SPE as a function of operating conditions, and to optimize the geometry of PEM cells and stack to avoid gas accumulation, as discussed in this communication.

2. GAS PERMEABILITY AND CROSS-PERMEATION PHENOMENA

2.1. Microstructure of SPE membranes

In PEM water electrolysis technology, perfluorinated membranes are used as SPE, the most commonly used being Nafion materials from E. I. DuPont Company. Nafion products are characterized by their equivalent weight (EW), the number of grams of dry Nafion per mole of sulfonic acid groups when the material is in the acid form. EW can be ascertained by acid-base titration. They gather a number of physical properties which are necessary for operation in PEM water electrolysis cells : (i) a high ionic conductivity (> 10 mS.cm^{-1}); (ii) a poor electronic conductivity; (iii); a good chemical and mechanical stability; (iv) a high thermal conductivity (> 0.1 J.s^{-1}.m^{-1}.K^{-1}) and (v) a limited permeability to hydrogen and oxygen. Proton conductivity, water management, relative affinity to water, hydration stability at high temperatures, electro-osmotic drag, and mechanical, thermal, and oxidative stability of these materials are directly determined by their chemical microstructure. From a historical perspective, the cluster-network model of Gierke et al. [9] has been used for many years for interpreting the properties of Nafion membranes (especially ion and water transport and ion permselectivity). In this model, it is assumed that there are ≈ 40 Å -in-diameter clusters of sulfonate-ended perfluoroalkyl ether groups that are organized as inverted micelles and arranged on a lattice. These micelles are connected by pores or channels that are $\approx$ 10 Å in size. These -SO$_3^-$-coated channels were invoked to account for intercluster transfer of cations and ion conductivity. Also, among the earliest concepts that were set forth regarding microstructure are those of Yeager and Steck [10] (figure 1). As compared with the model of Gierke et al., the clusters do not have a strict geometry and their geometrical distribution has a lower degree of order. Most importantly, intermediate interphase domains are found between hydrophobic and hydrophilic regions. For the development of PEM water electrolysis applications, Nafion can be considered as a homogeneous two-phase medium, a mixture of hydrophobic regions concentrating fluoro-carbon backbones and hydrophilic regions containing water, where proton conductivity takes place. Nafion is prone to significant dimensional changes in relation with water content, which is also directly affecting most of its physical properties.

2.2. The origin of gas cross-permeation

The reason why the hydrogen content in the oxygen produced at the anode of a PEM cell is not zero and conversely, the oxygen content in the hydrogen produced at the cathode is also not zero, comes from the fact that H_2 and O_2 solubility and mobility in perfluorinated membranes, although small, have finite values. The driving force to the transfer of dissolved gases from one side to the other of the cell is the gradient of chemical potential across the SPE during operation, resulting from the gradient of pressure (concentration). The mass transport mechanism is mostly diffusion-controlled (convection has also been reported but found less significant since the size of ionic clusters in the SPE is very small). The most striking point concerning cross-permeation phenomena in PEM cells is that dissolved gases can diffuse across the SPE membrane and the porous electrodes without being totally re-oxidized (hydrogen at the anode) or reduced (oxygen at the cathode). In fact, gases are partly consumed at the electrodes and this is

the reason why the faradaic yield at each interface is less than unity. But it should be kept in mind that theses gases are dissolved in liquid water, and the kinetics is much lower than in the gas phase. As a result, a significant amount of these gases can come through the electrodes and can be released in the opposite compartment of the PEM cell, such polluting the gaseous production.

2.3. Gas solubility in perflorinated SPEs

There are different reports available in the literature on gas (H_2 and O_2) solubility in Nafion materials [11-14]. The quantitative relationship between gas concentration in the polymer and partial pressure in the gas phase is given by Henry's Law :

$$P_i = H_i\,C_i \tag{1}$$

where P_i is the partial pressure of gas in the gas phase in Pa (the partial pressure of water vapour must be taken into account in the calculations); H_i is the solubility coefficient (Henry's constant) of species i in Pa.cm^3.mol^{-1}; C_i is the concentration of species i in mol.cm^{-3}.

Henry's Law constants for H_2 and O_2 are mainly function of equivalent weight (EW) of the polymer, water content, temperature and pressure. Nafion appears to behave water-like below *ca.* 50°C but not above, as also reported for ionic conductivity [15]. Gas solubility values in water can be taken, as a first approximation, for gas solubility in Nafion. For H_2, the following relations can be used in the 0-100°C temperature range and the 1-10 atm pressure range [16] :

$$\text{for } 0°C < T < 45°C : H_{H_2}^{H_2O} = 7.9x10^6 \exp(-545/T)\,x\,\left(1 + 0.000071\,P_{H_2}^3\right) \text{ in atm.mol}^{-1}.\text{cm}^3 \tag{2}$$
$$\text{for } 45°C < T < 100°C : H_{H_2}^{H_2O} = 8.3x10^5 \exp(-170/T)\,x\,\left(1 + 0.000071\,P_{H_2}^3\right) \text{ in atm.mol}^{-1}.\text{cm}^3 \tag{3}$$

For O_2, the following relations can be used in the 0-100°C temperature range, at 1 atm [16] :

$$\text{for } 0°C < T < 45°C : H_{O_2}^{H_2O} = 1.3x10^8 \exp(-1540/T) \text{ in atm.mol}^{-1}.\text{cm}^3 \tag{4}$$
$$\text{for } 45°C < T < 100°C : H_{O_2}^{H_2O} = 5.1x10^6 \exp(-500/T) \text{ in atm.mol}^{-1}.\text{cm}^3 \tag{5}$$

2.3. Gas permeability of perfluorinated SPEs

The most significant physical property of perfluorinated materials in view of high pressure PEM water electrolysis is the gas permeability P^m defined as :

$$P^m = \frac{v}{\Delta P}\frac{L}{A} \text{ in cm}^2.\text{Pa}^{-1}.\text{s}^{-1} \tag{6}$$

where v is the rate of gas permeation in Ncm^3.s^{-1}; ΔP is the difference of gas pressure across the membrane in Pa; L is the thickness of the membrane in cm; A is the section of the membrane in cm^2.

As can be seen from figure 2, P^m varies markedly with both temperature and water content, bracketing values measured on poly(tetrafluoroethylene) (PTFE) and liquid water. From these data, it is interesting to notice that the transport of dissolved gases across Nafion takes place mainly through the ionic (hydrated) clusters. In a PEM water electrolyser, liquid water is electrolyzed and therefore, H_2 and O_2 permeabilities are maximal. To estimate permeation flows, it is necessary to determine the value of diffusion coefficients. Gas permeability of species i is related to the diffusion coefficient D_i in cm^2.s^{-1} through :

$$D_i = P_i^m\,R\,T\,C_i \tag{7}$$

where R is the constant of perfect gas : 82x10^5 Pa.cm^3.K^{-1}.mol^{-1}; T is the temperature in K; C_i is the concentration of species i in mol.cm^{-3}.
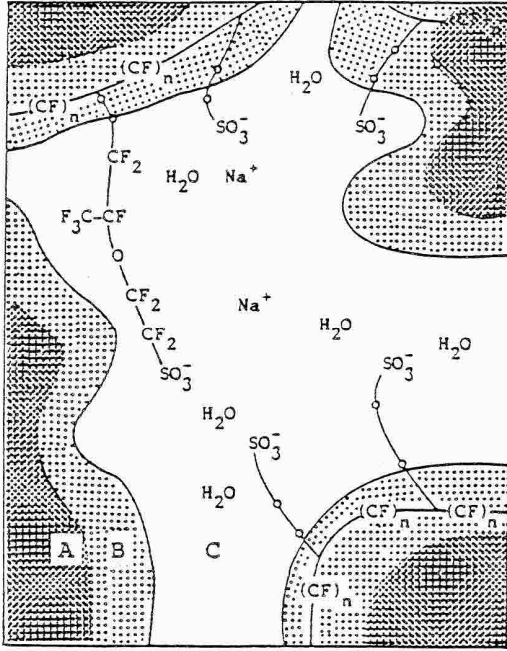
Figure 1. Three-phase model proposed by Yeager *et al.* [10] for the microstructure of Nafion materials.
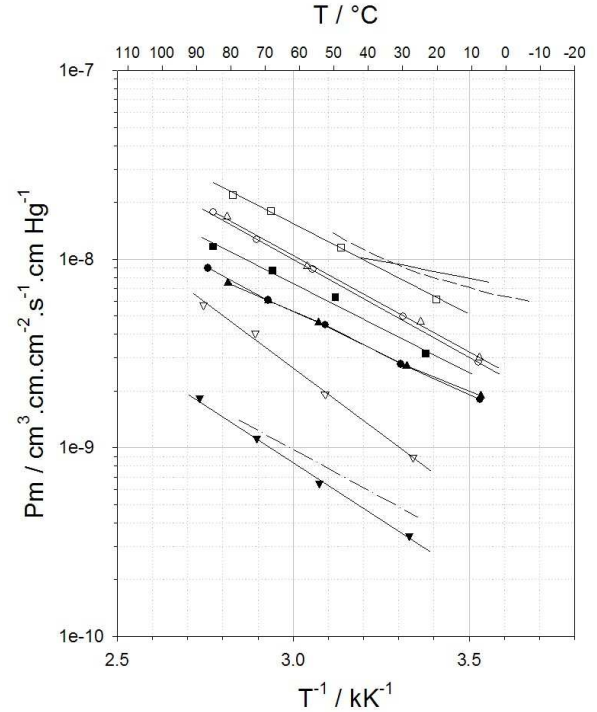
Figure 2. Hydrogen and oxygen permeability of Nafion 117 with temperature and water content [8].

Hydrogen and oxygen diffusion coefficients in Nafion 117 at different operating temperatures are compiled in table 1. D_{H2} is larger than D_{O2} by about a factor of two over the 0-100°C temperature range.

Table 1. H_2 and O_2 permeability and diffusion coefficient in fully hydrated Nafion 117 at different temperatures.

T / °C	10	20	40	60	85
P^m_{O2}/cm^2.Pa^{-1}.s^{-1}	2.1×10^{-12}	2.3×10^{-12}	3.7×10^{-12}	5.3×10^{-12}	8.4×10^{-11}
D_{O2} / cm^2.s^{-1}	2.1×10^{-7}	2.5×10^{-7}	4.2×10^{-7}	6.5×10^{-7}	1.1×10^{-6}
P^m_{H2}/cm^2.Pa^{-1}.s^{-1}	3.8×10^{-12}	4.6×10^{-12}	7.6×10^{-12}	1.2×10^{-11}	2.0×10^{-11}
D_{H2} / cm^2.s^{-1}	3.9×10^{-7}	4.9×10^{-7}	8.7×10^{-7}	1.5×10^{-6}	2.6×10^{-6}
D_{H2}/D_{O2}	1.9	2.0	2.1	2.3	2.4

2.5. Modeling of cross-permeation phenomena

A model of cross-permeation phenomena should provide a quantitative relationship between H_2 concentration in oxygen, temperature and pressure (the level of oxygen contamination is larger since H_2 mobility is about twice that of oxygen). In a first approximation, gas transport across the SPE follows Fick's first law of diffusion :

$$\Phi_i = D_i \frac{\partial C_i}{\partial x} \qquad (8)$$

where Φ_i is the flow of species i in mol.cm^2.s^{-1} and x is the distance coordinate along the membrane

thickness in cm. In stationary conditions of low, Eq. (8) can be rewritten as : $\Phi_i = D_i \dfrac{\Delta C_i}{L}$ **(9)**

Using Eq. (1), Eq. (9) can then be rewritten as : $\Phi_i = \dfrac{D_i}{H_i}\dfrac{(P_1 - P_2)}{L}$ in mol.s^{-1}.cm^{-2} **(10)**

Let j be the current density across the PEM cell in A.cm^{-2}. The mole number of oxygen produced at the anode per second and per cm^2 is $n_{O_2} = j/2\,F$ where F is the faraday. The mole number of hydrogen reaching the anode by cross-permeation is given by Eq. (10). In stationary conditions (constant current density, temperature and pressure), the mole percent of H$_2$ in O$_2$ is $\dfrac{n_{H_2}}{n_{H_2} + n_{O_2}}\,x\,100$ **(11)**

According to Eq. (11), the H$_2$ content in O$_2$ (at constant temperature and pressure) should be inversely proportional to current density. Experiments show that this is not exactly the case, in particular at low current densities (figure 3). This is partly due to the fact that data in figure 3 were obtained using internal gas recombiners to promote the catalytic recombination of gases, as discussed in [7]. This is also due to the faradaic efficiency at the anode, which for a given PEM cell, is a function of current density, temperature and pressure. As can be seen from figure 3 (curves a and b at 2 and 30 bars are bracketing results at intermediate pressures), the efficiency decreases significantly at low current densities. By correcting n$_{H2}$ in Eq. (11) with the experimental values of current efficiencies plotted in figure 3, it is possible to obtain a reasonable fit to the experimental values of H$_2$ concentration in O$_2$ (figure 3, full lines). The reasonable correlation between experimental and model curves support our interpretation of cross-permeation effects and the assumptions used in this simple model. But it should be noted that the current efficiency strongly depends on the structure of the electrode – electrolyte interface and therefore it is difficult to obtain a general relationship applicable to all PEM cells.
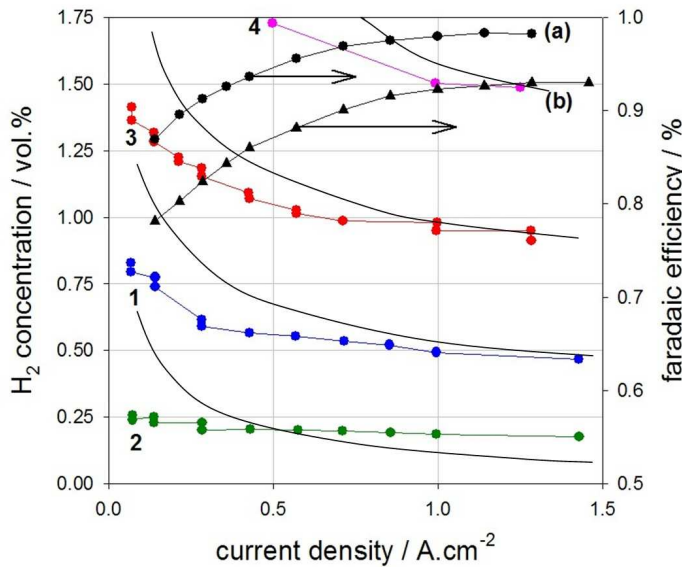

Figure 3. Data from Ref. [7].
(left) hydrogen content (vol.%) in the anodic oxygen-water vapour mixture, measured at different pressures as a function of operating current density.
50 cm^2 monocell. Pt for the HER, Ir for the OER and Nafion-117 as SPE. T = 85°C. [7]
1 : 1 bar (current collector is platinized).
2 : 1 bar (current collector not-platinized);
3 : 6 bar (current collector is platinized);
4 : 30 bar (current collector is platinized);
Full lines : best fits using Eq. (11) : see text.
(right) current efficiency at the cathode at (a) 2 bar and (b) 30 bar, as a function of operating current density.

To reduce gas transport by cross-permeation through the SPE, different approaches can be followed. First, thicker SPEs can be used. In particular, Nafion-reinforced membranes (in which a PTFE cloth is clamped between two conventional perfluorinated membranes) developed for the chlorine-alkali industry are commercially available. Second, it is possible to reduce either the diffusion coefficient or the solubility of the gas. This can be obtained by dissolving inorganic fillers inside the SPE, such as silica or zirconium oxide. For example, results obtained with zirconium dioxide in the course of the GenHyPEM project show that D$_i$ and H$_i$ can be reduced by a factor varying from 0 to about 10, depending on the filler concentration added to the SPE. Usually, such fillers are incorporated into the SPE by impregnation of cationic precursor species followed by chemical precipitation using an adequate chemical reactant. Third,

it is possible to promote the catalytic recombination of sub-stoichiometric H_2 with O_2 (anodic compartment) and sub-stoichiometric O_2 with H_2 (cathodic compartment) to remove trace amounts of hydrogen and oxygen. This can be done using internal gas recombiners as discussed in [7]. However, the price to pay for such improvements is always a reduction of the ionic conductivity of the SPE, an additional ohmic term during electrolysis and a lower cell efficiency.

3. DESCRIPTION OF THE HIGH PRESSURE PEM WATER ELECTROLYZER

3.1. Stack description

A picture of the GenHy[®]1000 (hydrogen production capacity up to 1 Nm^3 H_2 / hour) PEM water electrolysis stack used for the high pressure experiments is shown in figure 4. Twelve membrane–electrode assemblies (MEAs), 250 cm^2 active area each, are series connected in a filter-press configuration to reach the targeted hydrogen production capacity. Results presented in this communication were obtained using conventional noble metal electrocatalysts (metallic platinum for the HER and metallic iridium for the OER), as described elsewhere [6]. A thick, Nafion-reinforced, membrane was used to reduce gas cross-permeation, as discussed in the previous section. Porous titanium disks (1.2 mm thick, 40% open porosity [17]) were used as current collectors; titanium grids were used as spacers and titanium foils were used as bipolar plates. Carbon-based gaskets were used as cell sealants. Individual cell voltages were measured during electrolysis. For high pressure operation, a stainless steel pressurizing vessel was connected to the front flange of the electrolyser (figure 5). Feed water was introduced directly into the pressurizing vessel for the purpose of heat management and to prevent gas accumulation that would occur from stack leakages.

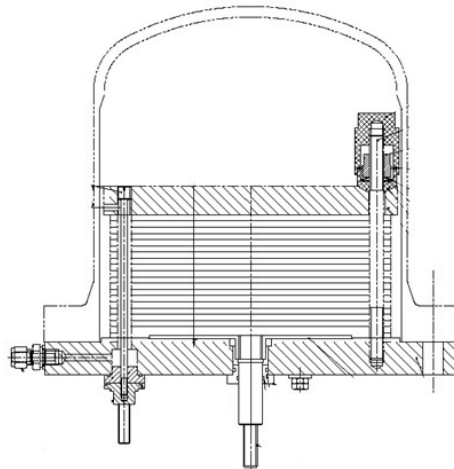**Figure 4.** Photograph of a GenHy[®]1000 PEM water electrolyzer.

Figure 5. Schematic diagram of the PEM stack and the pressurization vessel used for high pressure tests.

3.2. Hydrodynamics and safety issues

Internal cell design is crucial to reach high stack efficiencies and to manage hazards associated with the production of large amounts of pressurized and stoichiometric H_2 and O_2. Cell geometry must be optimized to insure a homogeneous distribution of water in each individual cell. This is of particular importance (i) to avoid gas accumulation inside the stack during production and (ii) to obtain a regular distribution of current lines across the MEAs and avoid the formation of hot points that would destroy the MEAs, in particular at elevated current densities. As can be seen from figure 6, where the 3D distribution of water flow has been computed in a single PEM cell (mass flow equations were solved using a finite element method and COMSOL[®] multi-physics modelling software), when the conditions of flow are turbulent, some areas inside the cell are not properly hydrated and as a result, the cell is not evenly operating during electrolysis. This can be corrected by adjusting some key geometrical parameters such as

inlet and outlet diameters and positions. The same model can be used to calculate the distribution of pressure inside the stack for different geometries and different water flows. A typical result is plotted in figure 7. When the geometrical characteristics of the PEM stack are properly optimized, a homogeneous distribution of pressure is obtained throughout the stack and as a result, the overall stack efficiency is improved. Also, risks that gases accumulate inside the cells are reduced.
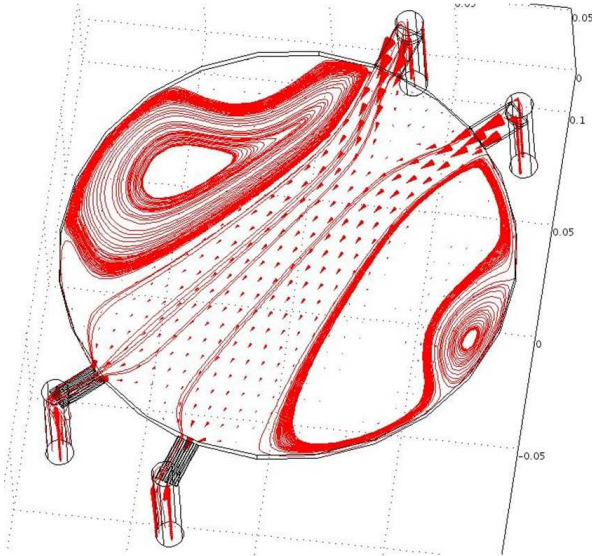

Figure 6. Detailed 3D representation of water mass flow inside a 250 cm^2 PEM mono-cell (360 Nl water / hour).
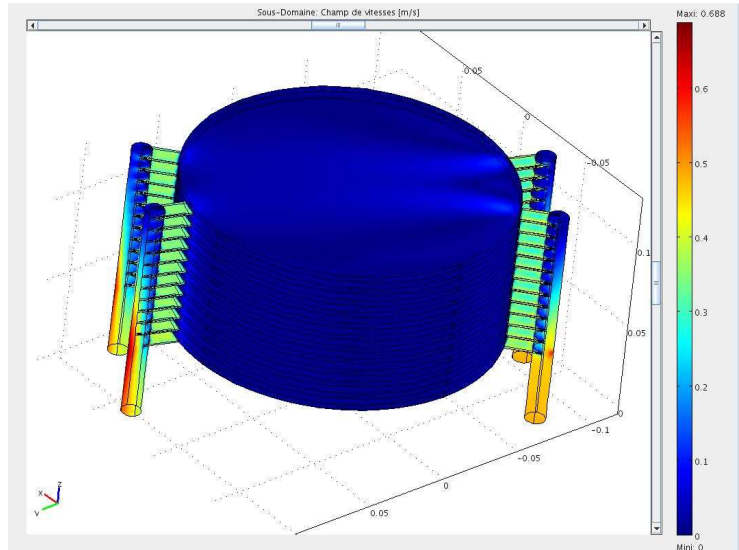
Figure 7. Detailed 3D representation of water mass flow inside the GenHy®1000 PEM stack (360 Nl water / hour).

4. TEST SITE FOR HIGH PRESSURE OPERATION
4.1. General description and safety issues

One of the two test sites used for the experiments in the course of the GenHyPEM project is located at the University of Paris 11, Faculty of Science at Orsay, Institut de Chimie Moléculaire et des Matériaux. The site is divided into three areas : (i) a double door gives access to the main corridor of the building; (ii) a first room is equipped to receive employees and to monitor the HP process; (iii) the high pressure room itself where the GenHy®1000 HP PEM water electrolyser is installed. The test room where high pressure experiments are carried out was designed and constructed following the ATEX directive (ATEX gets its name from the French title of the 94/9/EC directive: *Appareils destinés à être utilisés en ATmosphères EXplosibles*). Since July 2006, organisations in the European Union must follow the ATEX directives to protect employees from explosion hazards in areas with an explosive atmosphere. This is of course the case for H$_2$/O$_2$ production sites. In fact, two **ATEX** directives have been taken into consideration. One for the manufacturer (the ATEX 95 *equipment* directive 94/9/EC, Equipment and protective systems intended for use in potentially explosive atmospheres) and another for the user of the equipment (the ATEX 137 *workplace* directive 99/92/EC, Minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres). Areas where hazardous explosive atmospheres may occur are classified into zones. The classification given to a particular zone, and its size and location, depends on the likelihood of an explosive atmosphere occurring and its persistence if it does. Areas classified into zones (0, 1, 2 for gas-vapor-mist) must be protected from effective sources of ignition. Equipment and protective systems intended to be used in zoned areas must meet the requirements of the directive. Zone 0 require category 1 marked equipment, zone 1 require category 2 marked equipment and zone 2 require category 3 marked equipment. Zones 0 are the zones with the highest risk of an explosive atmosphere being present. The test bench and the electrolyser used in

this work both follow the ATEX directive. To make it short, zone 0 is the water electrolysis test bench itself which is a made of a watertight compartment. A continuous circulation of forced air is provided using an ATEX-certified pump placed on the top of the setup. Fresh air is taken from the outside atmosphere and then released back to the outside. The flow of air is adjusted to the production of hydrogen by the electrolyser. Hydrogen detectors are installed for the monitoring of hazardous atmospheres in real-time conditions.

4.2. Test bench

A general view of the electrolysis unit is provided in figure 8. At bottom, the electrolyser is mounted in its pressurization vessel. The test bench is located close to the wall where a weak mechanical structure has been constructed to manage potential explosion hazards (red square on the wall). Gas circuits are made of stainless steel tubing which can sustain pressures up to 150 bars. Stainless steel liquid – gas separators can be seen at the back of the setup. The system is fully automated. Pneumatic valves are used to manage water and gases flows. Gases produced during electrolysis are depressurized inside the test room down to atmospheric pressure before being evacuated to the exhaust. High pressure pumps are used to inject makeup water in the stack and circulate water in both anodic and cathodic circuits during operation. A 30 kW main dc power supply (600 A, 50 V) is used as power source although the software can manage electric current from intermittent sources such as photovoltaic panels. Web-cams connected to the internet are used for the remote supervision of the process.

Figure 8. General view of the GenHy®1000 high pressure water electrolyzer on the test bench, in the test room.

5. RESULTS OBTAINED DURING HIGH PRESSURE TESTS

5.1. Electrochemical performances

As can be seen from figure 9, the electrochemical performances of the stack are directly related to the operating temperature and current density, not to the pressure as previously reported [7]. At 0.5 $A.cm^{-2}$ and *ca.* 50°C, a conversion efficiency $\varepsilon_{\Delta H}$ (based on the enthalpy change of the water decomposition reaction [6]) close to 80 % and a mean cell voltage value of 1.88 V were obtained. During production, stable electrochemical performances were measured as soon as the temperature of the system was stabilized. High operating temperature (> 75°C) could be obtained by insulating water circuits in order to reduce heat transfers to the surroundings and adding electrical heat sources. At 85°C, the same 80% efficiency was obtained at a current density of about 0.8 $A.cm^{-2}$. Above 50 bars, thick Nafion-reinforced membranes are required to prevent gas cross-permeation, and as a result, the ohmic drop across the SPE is higher and the efficiency of the stack is slightly reduced. Several thousand hours of intermittent operation have been satisfactorily performed without noticeable degradation of electrochemical performances. The

main cause of performance degradation was a slow increase of individual cell voltage, resulting from the incorporation into the SPEs of metallic cations (iron, chromium, nickel) formed in the water circuit by dissolution of some steel components (sensors). Such metals are prone to form UPDs (Under Potential Deposits) at the surface of platinum electrodes and as a result, the cathodic overvoltage increases. The process, which is slow and reversible, can be significantly reduced by using online cartridges of ion-exchangers or managed through periodic maintenance operations.
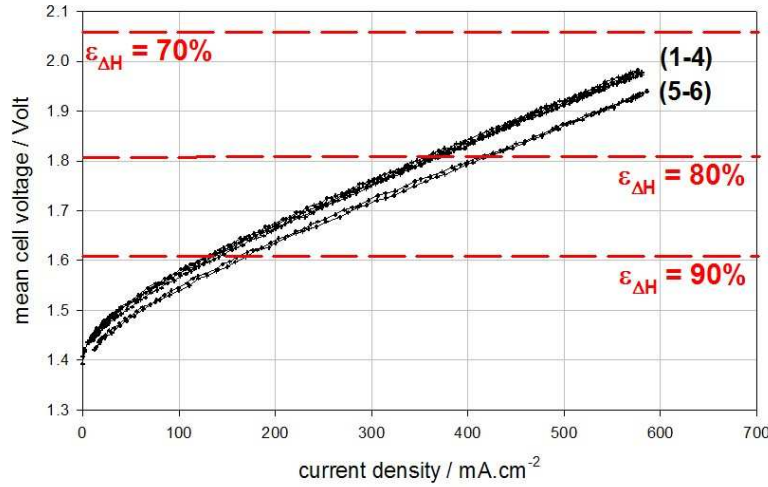

Figure 9. Polarization curves measured on the GenHy1000 stack at CETH at different operating pressures and temperatures :

1 : 3 bars, 40°C
2: 4 bars, 40°C
3: 5 bars, 40°C
4 : 6 bars, 40°C
5: 7 bars, 50°C
6 : 8 bars, 50°C

5.2. Gas purity during high pressure operation

In the course of the GenHyPEM project, some experiments have been made at operating pressures above 50 bars, using only eight thicker and reinforced SPEs and gas recombiners in the circuitry. Results obtained with the GenHy®1000 PEM stack in the 1-130 bars pressure range are compiled in Table 2.

Table 2. Main test results obtained with the high-pressure PEM water electrolysis stack under stationary operating conditions.

Parameter	Unit	Measured value at operating pressure, bar					
		1	25	50	75	100	130
Electric current	A	123.5	126.5	125.5	124.5	125.0	124.0
Operating temperature	°C	86	87	85	89	84	88
H_2 production rate	Nm³/hr	0.42	0.43	0.42	0.40	0.38	0.36
H_2 purity before recombiner	% vol.	99.98	99.76	99.18	98.56	98.01	97.34
H_2 purity after recombiner	% vol.	99.999	99.999	99.997	99.995	99.993	99.991
Individual cell voltage	V						
1		1.70	1.70	1.71	1.71	1.72	1.73
2		1.68	1.69	1.70	1.71	1.71	1.72
3		1.71	1.71	1.71	1.72	1.71	1.71
4		1.70	1.71	1.71	1.73	1.74	1.74
5		1.71	1.70	1.71	1.71	1.73	1.74
6		1.69	1.69	1.70	1.71	1.73	1.73
7		1.70	1.69	1.69	1.70	1.72	1.73
8		1.68	1.70	1.70	1.73	1.74	1.74
Stack voltage	V	13.57	13.59	13.63	13.72	13.80	13.84
Power consumption	kW	1.68	1.72	1.71	1.71	1.73	1.72
Specific power costs	kWh/Nm³	4.06	4.07	4.08	4.11	4.13	4.14
Current efficiency	%	99.98	99.68	98.13	96.57	92.91	90.45

These tests have been performed at a constant current density of 500 mA.cm^{-2} and at a mean operating temperature of 88°C. The purpose of these tests was to determine the level of contamination (O_2 in H_2) by cross-permeation and the current efficiency, the main operating parameter being the pressure. Individual cell voltages were stable and remained homogeneous throughout the stack during operation. A mean stack efficiency $\varepsilon_{\Delta H}$ = 85% was measured. The major impact of the high operating pressure was found on hydrogen purity which dropped down to 97% at 130 bars and faradaic (current) efficiency which dropped down to 90% at 130 bars (figure 10). It can be assumed that oxygen purity in the PEM cells which has not been measured was even lower than 97%. In such conditions, the use of internal gas recombiners is necessary. The stack has been used for about 1000 hours of intermittent operation at different high operating pressures without significant performance losses.
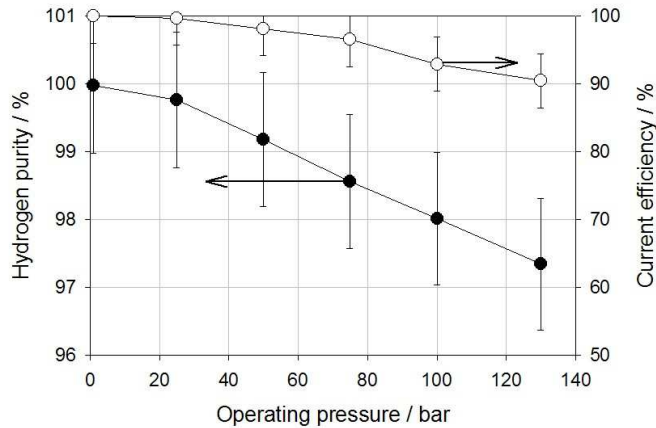

Figure 10. Hydrogen purity (vol.%) in the cathodic compartment as a function of operating pressure.

6. CONCLUSION

PEM water electrolysis technology provides a safe and efficient way to produce hydrogen and oxygen from water and electricity using intermittent energy sources. Gases can be produced at high pressure for direct storage in pressurized vessel, at no significant extra cost. However, high pressure operation raises a number of safety considerations which must be properly managed to reduce production risks. Results presented in this communication were obtained in the course of the GenHyPEM project, a research program supported by the European Commission. Experiments have been performed in the 1-130 bars pressure range, offering the possibility to quantify different hazards. One of the most challenging problems which has been identified during the project is the management of gas cross-permeation phenomena which can lead to significantly high level of contamination. A simple model has been used to account for experimental data obtained at the lab-scale in the 1-30 bars pressure range. It is shown that data on hydrogen solubility and mobility are sufficient to account for the experimental data, but that the faradaic efficiency of the anode must also be considered. A GenHy®1000 PEM water electrolyser which can produces up to 1 Nm^3 H_2 / hour has been designed, optimized and tested in the extended 1-130 bars pressure range. Values of hydrogen purity and current efficiency are reported, showing that the contamination level of hydrogen by oxygen can be significantly high, even when thick membranes are used. In terms of perspectives, higher operating current densities (in the 1-5 A.cm^{-2} current density range) and higher operating pressures (in the 150-300 bar) are still being investigated among the GenHyPEM consortium to further bring down the price of PEM water electrolysers and extend their field of application.

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