

HYDROGEN SAFETY ASPECTS RELATED TO HIGH PRESSURE PEM WATER ELECTROLYSIS

Fateev, V.N.¹, Grigoriev, S.A.¹, Millet, P.², Korobtsev, S.V.¹,
Porembskiy, V.I.¹, Pepic, M.³, Etievant, C.⁴, Puyenchet, C.⁴

¹ Hydrogen Energy and Plasma Technology Institute of Russian Research Center “Kurchatov Institute”, Kurchatov sq. 1, Moscow, 123182, Russia, fat@hepti.kiae.ru

² Institut de Chimie Moléculaire et des Matériaux, UMR CNRS n° 8182, Université Paris Sud, bât 420, 91405 Orsay Cedex France

³ DELTA PLUS Engineering & Consulting, Liege Science Park, Avenue Pré-Aily 1, B-4031, Angleur-Liège, Belgium

⁴ Compagnie Européenne des Technologies de l'Hydrogène, route de Nozay, Etablissements Alcatel, 91460 Marcoussis cedex France

ABSTRACT

Polymer electrolyte membrane (PEM) water electrolysis has demonstrated its potentialities in terms of cell efficiency (energy consumption $\approx 4.0\text{-}4.2$ kW/Nm³ H₂) and gas purity (> 99.99% H₂). Current research activities are aimed at increasing operating pressure up to several hundred bars for direct storage of hydrogen in pressurized vessels. Compared to atmospheric pressure electrolysis, high-pressure operation yields additional problems, especially with regard to safety considerations. In particular the rate of gases (H₂ and O₂) cross-permeation across the membrane and their water solubility both increase with pressure. As a result, gas purity is affected in both anodic and cathodic circuits, and this can lead to the formation of explosive gas mixtures. To prevent such risks, two different solutions, reported in this communication, have been investigated. First, the chemical modification of the solid polymer electrolyte, in order to reduce cross-permeation phenomena. Second, the use of catalytic H₂/O₂ recombiners to maintain H₂ levels in O₂ and O₂ levels in H₂ at values compatible with safety requirements.

1.0 INTRODUCTION

Polymer electrolyte membrane (PEM) water electrolysis, which can be used for the production of hydrogen of electrolytic grade, is currently the subject of extensive studies [1, 2]. High purity hydrogen produced from renewable energy sources is expected to be extensively used in a nearby future, for example to feed PEM fuel cells in the so-called “hydrogen economy”. PEM technology provides an example of “zero-gap” configuration, in which electrodes (nano-sized electrocatalyst particles supported by a porous electronic conductor) are in direct contact with the surface of the ion exchange membrane. This cell concept offers some significant advantages compared to more conventional “gap-cells”: (i) no circulating electrolyte is required, pure water being the only reactant supplied to the anodes; (ii) gaseous products H₂ and O₂ are produced at the backside of the inter-polar field, offering the possibility of reducing ohmic drops and increasing current densities. As a result, low energy consumption (4.0-4.2 kW/Nm³ H₂), high specific productivity (current densities up to 2 A/cm²) and high hydrogen purity (>99.99%) are obtained. Although this technology is known to be more expensive than the traditional alkaline electrolysis, significant cost reductions are expected: many materials, catalysts and cell

components used in PEM electrolyzers could benefit from large scale production of PEM fuel cell of similar concept and design.

According to market requirements, high-pressure (up to several hundred bars) electrolyzers are currently needed for direct storage of hydrogen in pressurized vessels. Such levels of pressure would be of particular interest for small-scale (5-50 kW) energy systems powered by renewable energy sources in view of the so-called “hydrogen economy”. In principle, PEM technology offers the possibility of operation at such high pressures, because low permeable membranes are used as solid polymer electrolyte. However, the permeability of Nafion[®] (the most widely used solid electrolyte for such applications) to hydrogen and oxygen, significantly increases with temperature and pressure [3, 4]. This in turn increases the level of cross-contamination and can lead to the formation of explosive H₂/O₂ gas mixtures, either in the electrolyser itself or in the liquid-gas separators. Because of the permeability to hydrogen is larger compared to oxygen, most risks occur on anodic circuit. To maintain adequate safety levels, it is necessary to control contamination levels. Results reported in this communication were obtained mainly during the GenHyPEM STREP project, financially supported by the European Commission in the course of the 6th Framework Research Program [5, 6].

2.0 EXPERIMENTAL

2.1. Experimental setup and membrane-electrode assemblies

In this work, perfluorinated Nafion[®] (and Russian analogue MF-4SK) membranes, with thicknesses in the 100-300 micrometers range, were used as polymer electrolytes. These membranes were modified to reduce gas cross-permeation, using zirconilphosphate, PTFE or polyetherketones. Electrocatalysts (Pt on carbon carrier for cathodes, Ir and mixed oxides (Ir_xRu_yTi_zO₂) for anodes) were synthesized using modified polyol methods. Sintered Ti disks with an open porosity of *ca.* 30-60% were used as current collectors. Different catalysts made from Pt, Pt/C and Pt-PTFE mixtures were disposed at the surface of metallic foam and tested in gas recombiners. All electrochemical experiments were made using either 7 or 50 cm² monocells, operating at a maximum pressure of 70 bar. A schematic diagram of the experimental setup used for the experiments, including the PEM water electrolysis cell and ancillary equipment, is pictured in figure 1.

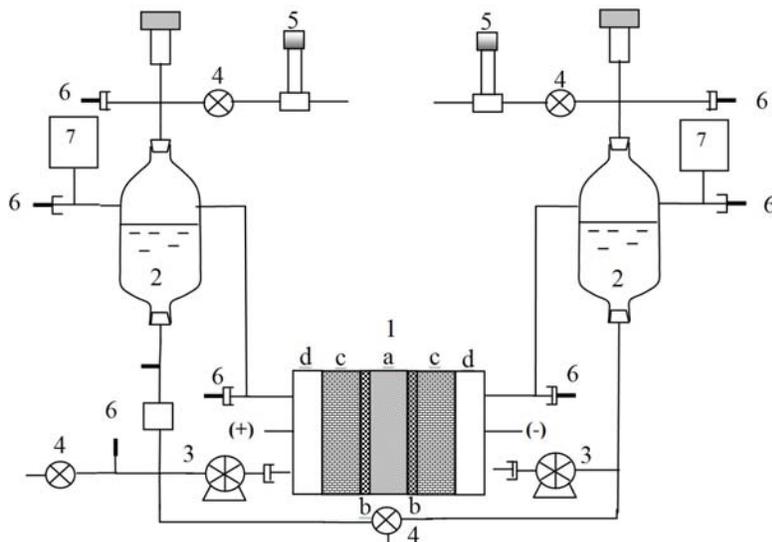


Figure 1. Schematic diagram of the experimental setup including: (1) the PEM electrolysis cell; (1-a) PEM; (1-b) catalytic layers; (1-c) porous titanium current collectors; (1-d) gas collection compartments. Ancillary equipment: (2) liquid-gas separators; (3) pumps; (4) valves; (5) production valves; (6) thermocouples; (7) pressure transducers.

2.2. Risks analysis

During electrolysis, liquid water is circulated on both anodic and cathodic circuits, and biphasic liquid-gas mixtures are separated in liquid-gas separators (figure 1). Whereas liquid water is required only at anodes to fuel the reaction, water is also circulated on the cathodic side for heat management purpose. Solid electrolytes such as Nafion[®] perfluorinated membranes are bi-phasic materials: an organic phase consisting of perfluorinated chains and an aqueous phase made of percolated water clusters, allowing ionic transport [7]. Ideally, only protons should be transported across the membrane thickness during electrolysis, from the anode where they are formed straight to the cathode where they are reduced into molecular hydrogen. But because of the limited permeability of the solid electrolyte, some hydrogen (oxygen) produced at the cathode (anode) permeates through the membrane, the difference of chemical potential (partial pressure) between anodic and cathodic compartments being the driving force to the transfer. Gas transport across the membrane occurs mainly through the aqueous phase and obeys Fick's laws of diffusion. During electrolysis, electro-osmosis (each proton can transport a solvation sheath of several water molecules) can also increase the transport of oxygen. Surprisingly, hydrogen and oxygen reaching opposite sides can cross potential barriers set by the (porous) electrodes. Even hydrogen, which is so easily oxidized at platinum-iridium anodes, can reach the output oxygen stream on anodic circuits. This can be attributed to the fact that these gases are dissolved in water: their reactivity is lowered and/or mass transport limitations occur. Nevertheless, the consequence of cross-permeation is that hazardous H₂/O₂ gas mixtures are formed directly at the surface of the polymeric membrane. From the viewpoint of risk management, since gas permeability increases with pressure, it is necessary to monitor the ratio of H₂/O₂ mixtures in the production streams.

High-pressure electrolysis can also cause new problems associated with the management of the electro-osmotic flux of water. During electrolysis, the level of water in the cathodic liquid-gas separator increases with time, and this must be managed. A first solution would be to purge water from the cathodic circuit but since this is highly de-ionised water, this solution is not always satisfying from an economical viewpoint. A second solution would be to send it back to anodic cells, by applying a pressure difference between cathodes and anodes during operation. But in that case, the hydrogen level in oxygen would increase. So a convenient way is to periodically mix anolyte and catholyte to re-equilibrate the water balance between the two gas separators (figure 1). But since gas solubility increases with pressure, the pollution induced by this operation increases contamination and associated risks.

2.3. Strategies for risk contingencies

To maintain hydrogen contents at levels compatible with safety standards, two different strategies can be followed (i) reduction of hydrogen cross-permeation; (ii) reduction of hydrogen contents in the oxygen-water output stream of anodic cells.

Concerning the reduction of cross-permeation phenomena, the simplest solution of increasing the membrane thickness can be used, but at the cost of an increasing ohmic drop due to higher membrane resistance. Other solutions, such as surface or bulk treatments of the polymeric membrane have been investigated. Experiments using membranes plated with low gas permeability coatings made of PTFE, zirconilphosphate or polyetherketones have been tested. Results show that it is possible to increase current efficiency and decrease contamination levels by a factor of two, without significant impact on the cell voltage. But such treatments can neither totally solve the problem of gases purity nor exclude the possibility of forming explosive gas mixtures by accumulation inside the electrolyser or the liquid-gas separators. It is therefore necessary to act directly on the anodic and cathodic circuits.

Concerning the reduction of hydrogen contents in the anodic oxygen-water stream, an efficient procedure is to promote the catalytic chemical combustion of hydrogen in oxygen using a gas recombiner [8, 9]. Basically, a gas recombiner (figure 2) is a system, which can promote the heterogeneous recombination of gaseous hydrogen and oxygen into water, at the surface of a catalyst. It consists of a vertical case designed to promote natural convection, with either a rectangular or a circular cross-section. The gas mixture to be treated enters at bottom and the hydrogen-free output is released on top. The catalyst is dispersed at the surface of a porous supporting structure of large surface area for higher conversion efficiency. Two protective inlet and outlet grids are positioned at both sides of the case, to prevent ignition of the ambient atmosphere during operation. When the hydrogen content in the gas stream reaches a critical threshold (for hydrogen-air mixtures, the value is 0.7 vol.% at ambient temperature), the activated catalytic element spontaneously starts oxidizing hydrogen. The reaction being strongly exothermic, this results in a spontaneous heating of the catalytic element, increased conversion efficiency and an increasing amount of gas mixture treated through the recombiner.

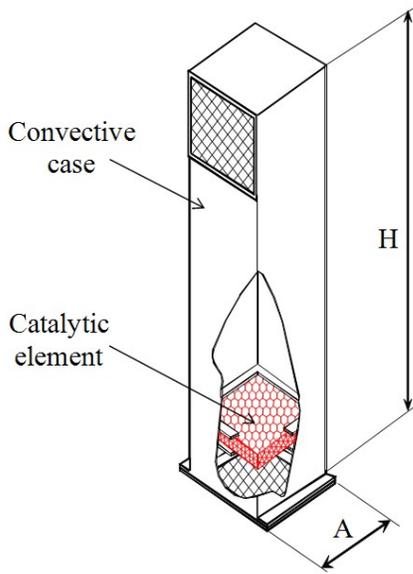


Figure 2. Schematic representation of a catalytic hydrogen-oxygen recombiner.

Recombiners can be used in the vicinity of industrial electrolyzers to treat hydrogen-air mixtures and to manage security risks associated with hydrogen leaks during production. The rate of hydrogen combustion Q (in $\text{m}^3 \text{H}_2/\text{hour}$), for a given gas recombiner, can be expressed by the following empirical relationship [8]:

$$Q = S \cdot \left(\frac{\rho_o g}{A} \right)^{1/n} H^{1/n} \cdot C \frac{(\alpha c)^{1/n}}{T_o \left(1 + \frac{\alpha c}{T_o} \right) \cdot (1 + \beta \alpha \cdot c)},$$

where S , A and H are geometrical parameters of the recombiner's case, C is the hydrogen concentration at the inlet side (at the outlet, it is assumed to be close to zero), ρ_o and T_o are density and temperature of ambient hydrogen-air mixture, α and β are experimental coefficients related to the temperature sensitivity of the catalyst as a function of hydrogen concentration.

For risk prevention in PEM water electrolyzers, gas recombiners should be located as close as possible to the electrolysis cell where hazardous H_2/O_2 mixtures are formed. However, since liquid

water is circulated in the electrolyser, this is not always possible because optimal operation requires dried gases. Also, to increase the conversion efficiency of these systems, it is necessary to increase the volume of the convective case, a solution, which is not always acceptable, especially at high pressure. A first approach which was investigated during the GenHyPEM project was to adapt the concept to water electrolysis by plating porous PTFE/Pt coatings at the backside of the porous current collectors (element 1-c in figure 1), in order to promote chemical recombination directly in the electrolysis cell. A second approach was to introduce a gas recombiner along the production line, after the liquid-gas separators, to produce hydrogen-free oxygen and oxygen-free hydrogen.

3.0 RESULTS AND DISCUSSIONS

3.1. Effect of operating pressure on thermodynamics, kinetics and faradaic yield

As can be seen from figure 3, when the operating pressure is increased, the thermodynamic voltage of the electrolysis cell also increases (following Nernst equation). But at high current densities (in the 0.5-1.0 A/cm² range), the kinetics is improved, as a result of a reduction of the size of gaseous bubbles with pressure. Although these bubbles are not produced in the interpolar domain (as in conventional the alkaline process), gas accumulation between porous current collector and membrane can produce a screen effect. On anodic sides, this effect can stop the transport of liquid water up to the electrocatalytic layer through the porous current collectors and increase anodic overvoltage and parasite ohmic drops.

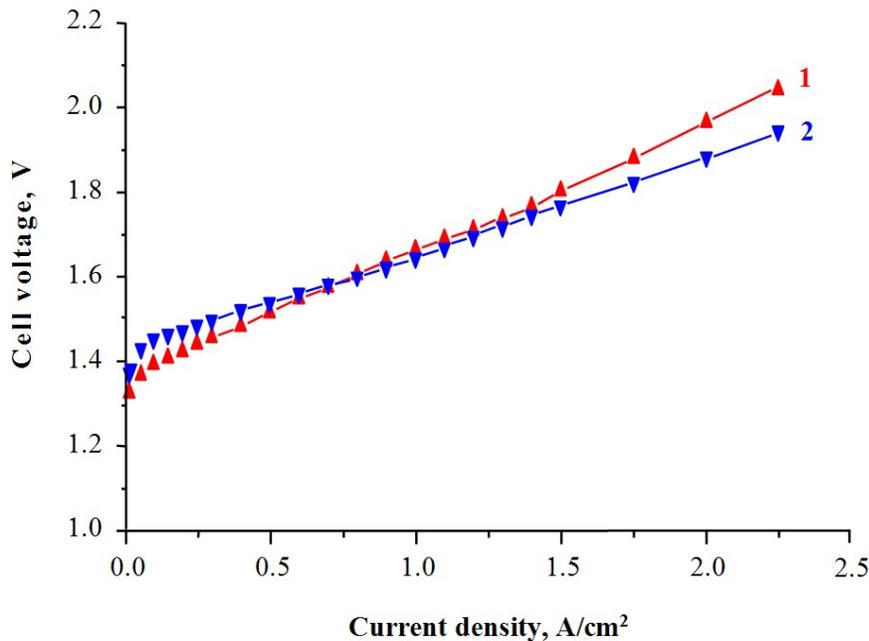


Figure 3. Lab-scale polarization curves measured during PEM water electrolysis at T = 90°C and different operating pressures:
 1 – P = 1 bar;
 2 – P = 50 bar.

Therefore, higher operating pressure has a positive effect in terms of kinetics and conversion efficiency. This is counter-balanced by a negative effect on current (faradaic) efficiency with pressure (figure 4), because of gas cross-permeation phenomena. This negative effect is larger at low current densities, when the production rate of gases is low. This is because the solubility of H₂ and O₂ in the solid electrolyte (of constant thickness) being constant, the flow of gas is constant according to Fick's first law of diffusion. As the current density is increased, the relative weight of parasite cross-phenomena decreases.

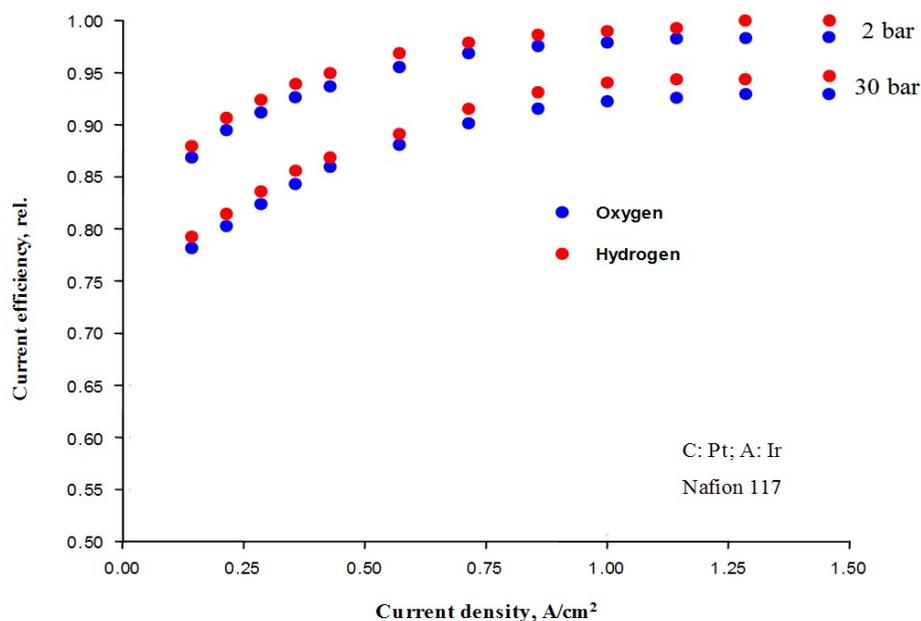


Figure 4. Lab-scale measurements of anodic and cathodic cell current efficiencies as a function of current density at 2 and 30 bar.

3.2. Effect of operating pressure on gas purity

a- Hydrogen concentration in oxygen

As can be seen from figure 5, hazardous levels of hydrogen in oxygen are reached as the operating pressure is raised, especially at low current densities. In the 30-70 bar range, hydrogen contents continuously increase with pressure up to unacceptable levels of 10 vol.% at 0.1 A/cm² and 3-4 vol.% at 0.5-1.0 A/cm².

The first solution, which was investigated to maintain hydrogen contents below 2 vol.%, was to platinize the backside of the porous current collectors. Direct application of platinum (using physical means such as pulverization) produced efficient coatings but their specific surface was too low (*ca.* 5 m²/g). In the course of the GenHyPEM project, a procedure was developed to improve the recombination efficiency of these catalytic layers. With noble metal loadings of *ca.* 0.1 mg/cm² at the backsides of anodic current collectors, oxygen purity was significantly increased (from 96 to 99.1%). As can be seen from figure 5, by using platinized current collectors, it was possible to maintain such levels below 2 vol.% but a pressure of 30 bar is a limit beyond which other treatments are required. It should be noted that an indirect benefit of this platinization process was to prevent titanium oxidation and to maintain good electrical contacts with the external circuit.

Higher oxygen purities were obtained by adding a gas recombiner in series with the anodic liquid-gas separator. This solution was useful to produce hydrogen-free oxygen but not to manage safety problems in the anodic circuit. Two major differences were observed, compared to operation with dried gases. First, the start-up of the recombination process was systematically delayed after starting production, sometimes by up to 10 minutes. Second, the conversion efficiency of the recombiner was significantly altered, yielding lower gas purities. This was attributed to water screening effects resulting either from the condensation of water droplets issued from the main stream, or by the formation of a liquid water film at the surface of the catalyst resulting from the recombination process. By adding a dryer (or hydrophobic PTFE particles in the Pt catalyst of the gas recombiner), it was possible to reduce the start-up time down

to 1-2 minutes for hydrogen concentration of about 1-2% and to improve conversion efficiency. Optimization of housing design is still required to avoid water splashing of the catalytic element.

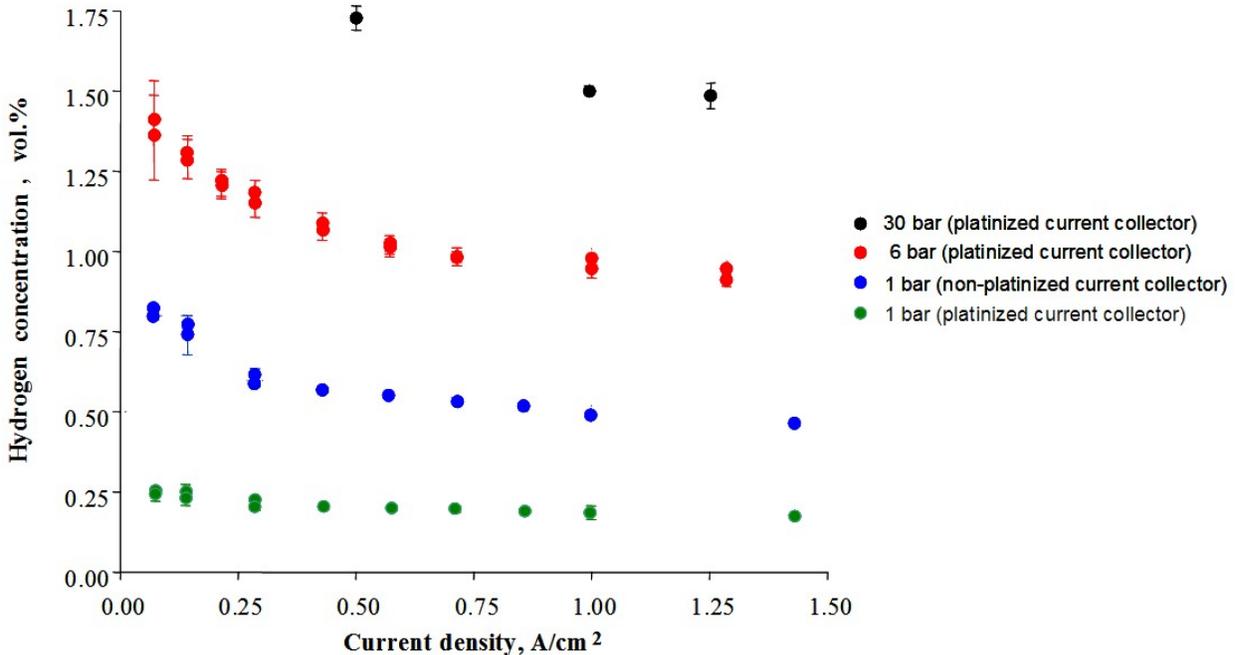


Figure 5. Hydrogen content (vol.%) in the anodic oxygen-water vapour mixture, measured at 1, 6 and 30 bar in the liquid-gas separator as a function of operating current density. 50 cm² monocoell. Pt as cathodic catalyst, Ir as anodic catalyst and Nafion[®]-117 as PEM.

b- Oxygen concentration in hydrogen

Compared to hydrogen reaching oxygen in the anodic compartment, the amount of oxygen reaching the hydrogen cathodic stream by permeation is much lower because of the reduced oxygen permeability. During electrolysis from atmospheric pressure up to 6 bar, oxygen was not detected in hydrogen (less than 5 ppm was measured even with un-platinized current collectors), at operating current density $i > 0.5 \text{ A/cm}^2$. But as the operating pressure was increased (up to 50 bar), the oxygen concentration in hydrogen roused up to 2-4 vol.%, especially at low ($< 0.4 \text{ A/cm}^2$) current densities. By using a recombination catalytic layer at the backside of the cathodic current collector, the problem was mostly solved and hydrogen purities of *ca.* 99.99% (water vapour excluded) were measured.

4.0 CONCLUSIONS

PEM water electrolyzers, operating at pressures up to 70 bar, can be used to produce hydrogen and oxygen of electrolytic grade, with high efficiencies. However, because of increasing rate of gas cross-permeation with pressure, the concentration of hydrogen in oxygen and the concentration of oxygen in hydrogen can reach critical levels. To avoid the formation of explosive gas mixtures, it is necessary to reduce gas cross-permeation. This can be done to a certain extent by surface modifying the solid electrolyte, for example by coating low-permeability protective layers. Contaminant concentration in the produced gases can also be

reduced by adding catalytic gas recombiners, directly in the electrolysis cell or along the production line. By using gas recombiners inside the electrolysis cell, it was possible to maintain hydrogen contents below 2 vol.% at an operating pressure of 30 bar, with Nafion[®] 117 as solid electrolyte.

ACKNOWLEDGEMENT

Financial support from the European Commission within the 6th Framework Programme (GenHyPEM, STREP n° 019802) and from the Council for Grants at the President of the Russian Federation (grant n° MK-4218.2006.8) are gratefully acknowledged.

REFERENCES

1. Millet, P., Andolfatto, F. and Durand, R., Design and performance of a solid polymer electrolyte water electrolyzer. *Int. J. Hydrogen Energy* 21, 1996, pp. 87-93.
2. Grigoriev, S.A., Porembsky, V.I. and Fateev, V.N., Pure hydrogen production by PEM electrolysis for hydrogen energy. *Int. J. Hydrogen Energy* 31, 2006, pp. 171-175.
3. Ogumi, Z., Takehara, Z. and Yoshizawa, S., Gas permeation in SPE method. *J. Electrochem. Soc.* 131, 1984, pp. 769-773.
4. Ogumi, Z., Kuhore, T. and Takehara, Z.I., Gas permeation in SPE method. *J. Electrochem. Soc.* 132, 1985, pp. 2601-2605.
5. <http://www.genhypem.u-psud.fr>
6. Millet, P., Fateev, V., Grigoriev, S., Deschamps, A., Etievant, C. and Puyenchet C., GenHyPEM: a research program on PEM^l water electrolysis supported by the European Commission, Proceedings of the 2nd International Workshop on Hydrogen, Ghardaïa, Algerie, 27-29 October 2007, in press.
7. Mauritz, K.A. and Moore, R.B., State of understanding of Nafion. *Chemical Reviews* 104(10), 2004, pp. 4535-4586.
8. Baronov, G.S., Grigoriev, S.A., Kalinnikov, A.A. and Fateev, V.N., Development of hydrogen sensors and recombiners, Proceedings of the 1st International Conference on Hydrogen Safety, Pisa, 8-10 September 2005, p. 78.
9. Kalinnikov, A.A., Baronov, G.S., Grigoriev, S.A. and Fateev, V.N., Hydrogen energy. Safety problems, Proceedings of the 11th International Symposium on Loss Prevention and Safety Promotion in the Process Industries, Praha, 31 May - 3 June 2004, p. 148.