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## GenHyPEM : an EC-supported STREP program on high pressure PEM water electrolysis

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### Abstract

GenHyPEM (générateur d'hydrogène PEM) is an international research project related to the electrolytic production of hydrogen from water, using proton exchange membrane (PEM) - based electrochemical generators. The specificity of this project is that all basic research efforts are devoted to the optimization of already existing electrolyzers of industrial size, in order to facilitate the introduction of this technology in the industry and to propose technological solutions for the industrial and domestic production of electrolytic hydrogen. GenHyPEM is a three years long research program financially supported by the European Commission, gathering partners from academic institutions and from the industry, in order to reach three main technological objectives aimed at improving the performances of current 1000 Nl/hour H<sub>2</sub> industrial PEM water electrolyzers : (i) Development of alternative low-cost membrane electrode assemblies and stack components with electrochemical performances similar to those of state-of-the-art systems. The objectives are the development of nano-scaled electrocatalytic structures for reducing the amount of noble metals; the synthesis and characterization of non-noble metal catalytic compounds provided by molecular chemistry and bio-mimetic approaches; the preparation of new composite membrane materials for high current density, high pressure and high temperature operation; the development and optimization of low-cost porous titanium sheets acting as current collectors in the electrolysis stack; (ii) Development of an optimized stack structure for high current density (1 A.cm<sup>-2</sup>) and high pressure (50 bars) operation for direct pressurized storage; (iii) Development of an automated and integrated electrolysis unit allowing gas production from intermittent renewable sources of energy such as photovoltaic-solar and wind. Current status of the project as well as perspectives are described in this paper. This project, coordinated by University of Paris XI, has received financial support from the European Commission (STREP n° 019802) and from Région Ile de France.

**Keywords** : electrolytic hydrogen production; PEM water electrolysis.

### 1. The GenHyPEM project

#### 1.1. call description

In 2004, the European Commission released a call related to the production of electrolytic hydrogen using the so-called proton exchange membrane (PEM) technology :

**Advanced concepts for electrochemical hydrogen production.** *The main objective is the development of highly efficient electrochemical systems that allow achieving substantial cost reductions and high current densities compared to the state-of-the-art alkaline water electrolyzers. Research should focus on: synthesis and testing of innovative, low-cost materials to be used in the main components (i.e. electrodes, electrolytes, interconnectors, etc). Final outcome should be the development of low-cost fabrication techniques for all these components and the design, construction and testing of a prototype electrolyser. The target peak efficiency should be higher than 90% and durability exceeding 50.000 hours. The potential integration of the prototype electrolyser with intermittent renewable energy sources should also be assessed with a view to matching characteristics in order to obtain optimally efficient, zero-emission hydrogen production system. Due attention should be given to matching electrolyser performance and durability with expected application and duty cycles. Reversible fuel cell electrolyzers are also be of interest, providing technologies proposed offer real prospects of achieving at least 50% round trip efficiency and comparable durability.*

1.2. historical background

The development of Solid Polymer Electrolyte (SPE) water electrolysis started in France in 1985 at the french Commissariat à l’Energie Atomique (CEA), Centre d’Etudes Nucléaires de Grenoble (CENG) and was then continued in collaboration with various partner laboratories, including the University of Paris-Sud XI (PXI) [1,2]. Patented processes for the production of efficient membrane electrode assemblies (MEA’s) were developed and pressurised (up to 100 bars) small size (1 kW) units were constructed and tested. In parallel, the russian HEPTI RRC “Kurchatov Institute” in Moscow developed PEM water electrolyzers of various designs and capacities (from a few milliliters to tens of cubic meters of hydrogen per hour) [3,4]. Later, a collaboration between the Institut de Chimie Moléculaire et des Matériaux (ICMMO) at PXI, the Kurchatov Institute (KI) in Moscow and the french company “Compagnie Européenne des Technologies de l’Hydrogène” (CETH) was initiated for the development and marketing of PEM-based water electrolyzers with H<sub>2</sub> output capabilities ranging from 100 to 2500 Nliter/hour, rating pressure up to 30 bars, long-term (> 10,000 hours) on-site stable electrochemical performances, power consumption between 4.1 and 4.4 kWh/Nm<sup>3</sup> H<sub>2</sub> depending on the rating current density, and hydrogen gas purity above 99.99 % with oxygen as main impurity. Electrolyzers up to 500 Nliter/hour H<sub>2</sub> using 75 cm<sup>2</sup> squared cells were designed for low current density (< 0.4 A.cm<sup>-2</sup>) and low operating pressure (< 5 bars). Electrolyzers from 1000 Nliter/hour H<sub>2</sub> and above, using 250 cm<sup>2</sup> circular cells, were designed for increased operating current densities (up to 0.6 A. cm<sup>-2</sup>) and higher operating pressure (up to 30 bars). After publication of the call by the European Commission, a consortium with partners of complementary capabilities was built and the submitted GenHyPEM proposal was finally elected. This 2.2 M€ project started by october 2005. Region Ile de France later joined in to support specific actions related to management activities and to dissemination of knowledge.

1.3. consortium description

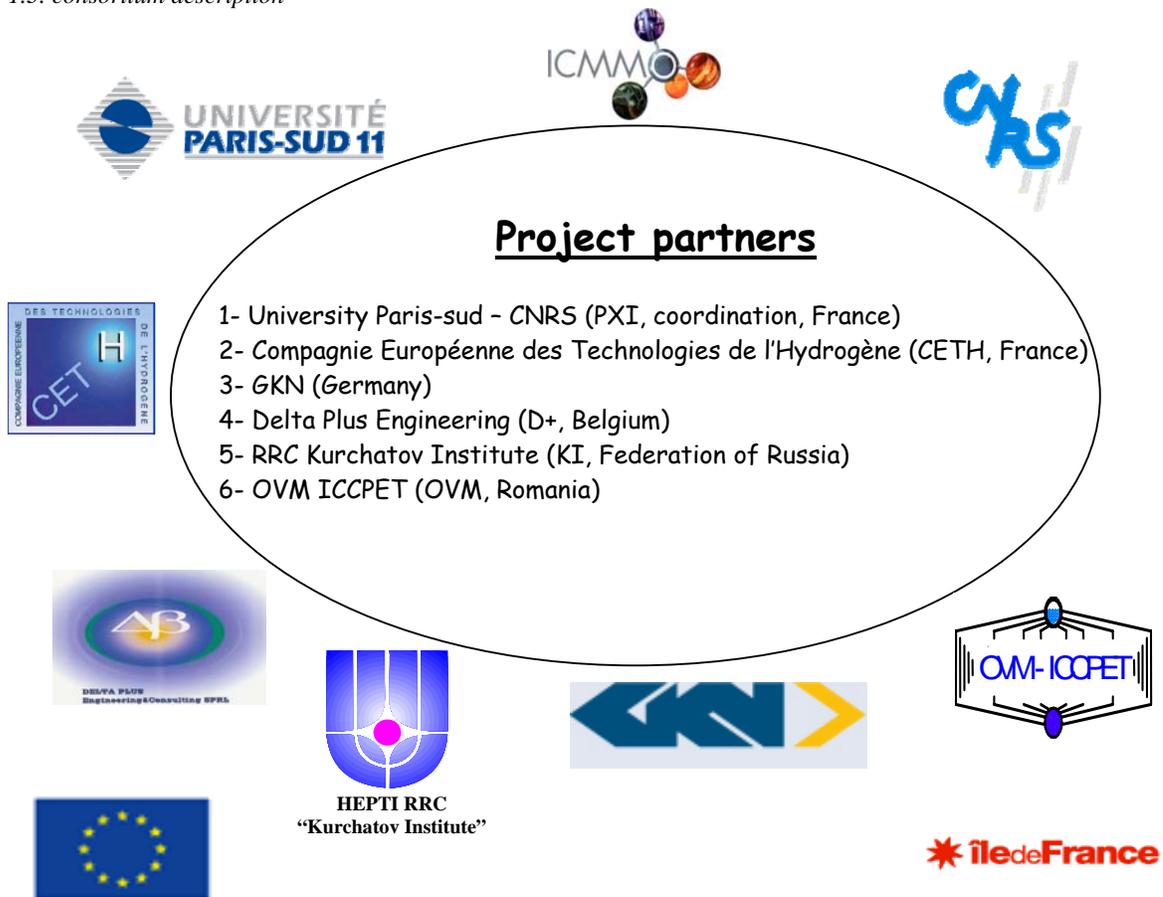


Figure 1 : consortium partners involved in the GenHyPEM project.

1.4. objectives

Four major topics are addressed by the GenHyPEM project :

➤ **Electrocatalysis** (PXI and KI leaders)

Electrocatalysis in current state-of-the-art PEM water electrolyzers requires the use of expensive noble-metals or their oxides (platinum for hydrogen evolution and iridium for oxygen evolution). Thus, cost reductions require either the development of new preparation procedures with lower noble-metals loadings or the use of alternative, non-noble metal catalytic compounds, provided by molecular chemistry and bio-mimetic approaches. These three options are separately addressed within the course of the project.

➤ **solid electrolyte** (OVM leader)

Solid polymer electrolytes in state-of-the-art technology rely on perfluorinated membrane materials such as Nafion® developed in the last 60's by the US firm duPont de Nemours. The objectives of the project are to develop and test alternative low-cost membrane materials for high pressure and high temperature operation.

➤ **current collectors** (GKN leader)

Current distributors in state-of-the-art ( $< 5 \text{ m}^3 \cdot \text{h}^{-1} \text{ H}_2$ ) electrolyzers consist of ca. 1 mm thick porous titanium sheets of uniform porosity. Fabrication costs are in direct relation with the number of units manufactured and for substantially important production, the cost may decrease very significantly. However, depending on the structure of the electrocatalyst layer obtained either by *in-situ* or *ex-situ* means, optimization of the pore structure of the material is of crucial importance in connexion with current distribution at the current collector / membrane interface. Current distributors require pore size optimization. Alternative carbon-based materials are also considered.

➤ **stack optimization and testing** (CETH and D+ leaders)

The objective assigned to this action are stack design modifications to allow higher operating performances (higher current densities and higher operating pressure). The possibility of operating the stack at high ( $1 \text{ A} \cdot \text{cm}^{-2}$ ) current density as nominal rate is considered. High-pressure-operation (50 bars) will be tested in relation with safety considerations. Prototype-scale experiments are performed using  $1000 \text{ Nl} \cdot \text{hr}^{-1} \text{ H}_2$  electrolyzers.

2. PEM water electrolysis technology

2.1. introduction and historical background

The concept of proton exchange membrane (PEM) cells originates in the mid-twentieth century when the first synthetic ion-exchange membranes were discovered [5]. This was the starting point for the development of several electrochemical applications, especially  $\text{H}_2/\text{O}_2$  fuel cells for the US space program [6,7]. As can be seen from figure 2, there are three different ways to use polymeric membrane materials in electrochemical applications. In the first configuration (*gap membrane cell*), the two electrodes are not contacting the membrane. These cells are used for gas evolving reactions with conductive electrolytes. In the second configuration (*zero gap cell*), supported porous electrodes are pressed against the membrane and gaseous products are evolved at the backside of the cell, outside the electric field. In the third configuration (*PEM cell*), the electrodes are directly deposited onto the membrane surfaces and the electrolyte remains immobilized in the membrane. No conducting electrolyte is circulated.

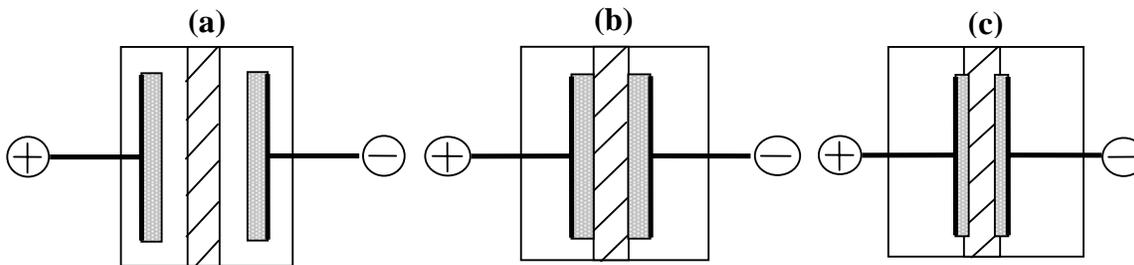


Figure 2 : three different possibilities of using a membrane in an electrochemical cell; (a) gap membrane cell; (b) zero gap membrane cell; (c) PEM cell. —| : current collectors; ■ : electrocatalyst.

The PEM cell is therefore of special interest when : (i) the electrolytic solution is poorly conductive (organic electrosynthesis) or not conductive (electrolysis of pure water) and (ii) the reactants are gaseous (fuel cells). This is exemplified in figure 2 where the similarities between a PEM water electrolysis cell and a PEM fuel cell are outlined. In both cases, the membrane plays the role of a solid electrolyte and acts as a separator to the gaseous reactants or products.

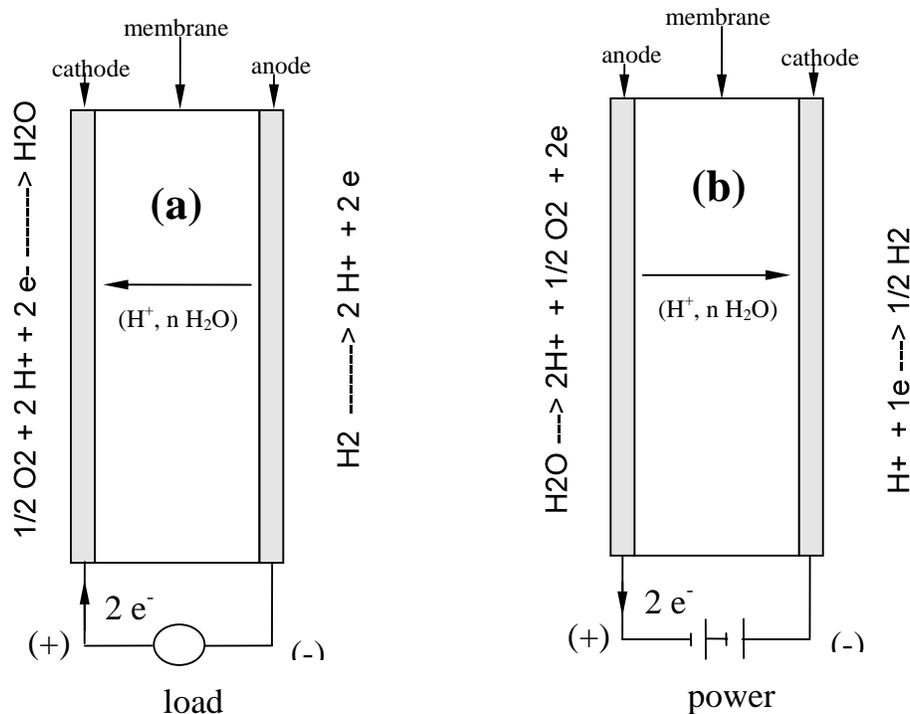


Figure 3 : schematic diagram of (a) a PEM H<sub>2</sub>/O<sub>2</sub> fuel cell and (b) a PEM water electrolysis cell.

## 2.2. description of membrane-electrode assemblies

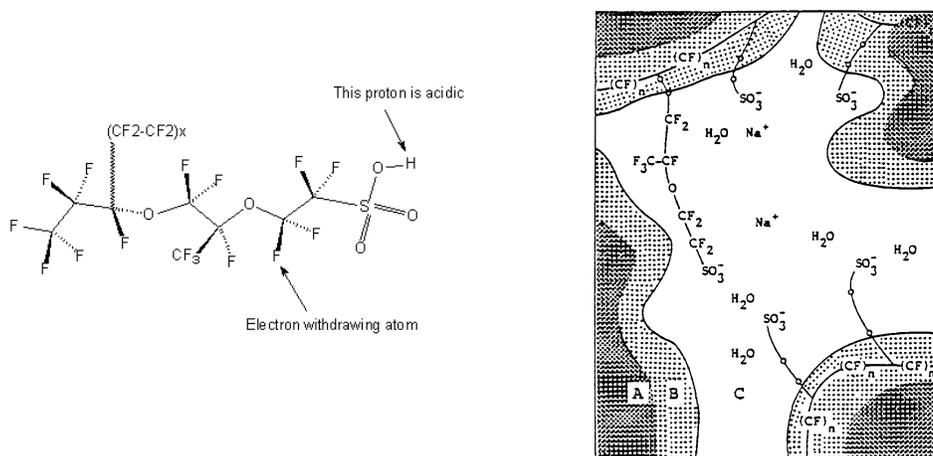
In a PEM water electrolyser, a key component is the so-called membrane electrode assembly (MEA).

### 2.2.1. membrane materials

Candidate membrane for PEM applications must have the following characteristics :

- high protonic conductivity and negligible electronic conductivity
- low solubility of the polymer in water but a strong water uptake by the polymer
- low gas permeability with regard to hydrogen and oxygen
- good chemical and electrochemical stability with regard to the electrocatalysts and the operating cell potential
- adequate microstructure allowing easy and efficient bonding of the electrodes.

A major breakthrough in membrane technology occurred in the late 60's when the US firm Dupont de Nemours introduced its Nafion® products. These materials boosted the development of membrane-based electrochemical applications. Their chemical composition and micro-structure are pictured in Figure 3. The microstructure consists of interpenetrated hydrophylic and hydrophobic domains. Hydrophylic regions containing the hydrated sulfonate groups form a 3-D network of channels-interconnected clusters (diameter 50-100 Å). Much information on the structure on these membrane materials is available in the relevant literature [8,9]. Nafion® membranes have been marketed under various thicknesses and equivalent weight. Nafion® 117 (dry thickness 0.178 mm) is commonly used for PEM research and development.



**Figure 3** : chemical formula (left) and microstructure of a Nafion® membrane (right).  
A = hydrophobic organic region; B = intermediate region; C = ionic region.

### 2.2.2. electrocatalysts

The acidity of Nafion® membranes is similar to that of a 20 wt% sulfuric acid solution. Therefore, acid resistant noble metals such as platinum and iridium or their oxides are used as electrocatalysts. As a result, a major drawback of this technology is its cost. Significant progresses have been reported in the literature over the past decades concerning preparation procedures for lower noble metal loadings and higher operating current densities. Typical current densities as high as 2 A.cm<sup>-2</sup> at 1.7 volt have been reported. Ruthenium, used either as an oxide or a metal, could be an interesting alternative electrocatalyst to more costly platinum and iridium. For the oxygen evolution reaction, metallic ruthenium exhibits the best electrochemical performances but suffers from a lack of chemical stability. Volatile and lethal higher oxides such as H<sub>2</sub>RuO<sub>5</sub> can eventually be formed. Thermally prepared RuO<sub>2</sub> is more stable but cannot be easily plated to the membrane.

### 2.3. plating procedures

Electrocatalysis in state-of-the-art PEM water electrolyzers require noble metals (Pt on the cathodic side and Ir-based compounds on the anodic side), Nafion® membrane materials and porous Ti-based current collectors. Several plating procedures have been reported in the literature [10,11]. The electrocatalyst active layer can be either plated onto the current collector which is then pressed onto the membrane or directly deposited at the membrane surface using either chemical or electrochemical routes. For example, a process which is used in the GenHyPEM project for the preparation of membrane-electrode assemblies (MEAs) is using frequency-modulated galvanostatic pulses. The technique can be illustrated as follows for the preparation of Pt-based MEAs. In a first step, the membrane is mounted in an electro-plating cell and clamped between two Ti current collectors. A solution containing a cationic Pt salt is then circulated on both sides and the membrane, initially in H<sup>+</sup> form, incorporates a given amount of precursor salt. Impregnation solution is then removed and water is circulated. 100 cycles of 60 sec long galvanostatic pulses are used for the electro-plating. As a pulse is applied, the cell voltage gradually rises (figure 4). The galvanostatic pulse is reversed when either (i) the cell voltage becomes higher than a pre-determined value ( $\pm 2.5$  V in figure 4), or (ii) once a pre-determined duration (60 sec) is reached. This results in the production of frequency-modulated galvanostatic pulses (figure 5). In the first stages of the reduction process, the frequency is elevated because overvoltages are high. The nucleation process is favoured. As the active area increases, overvoltages decrease and the frequency is relaxed. Thus, highly dispersed electrocatalytic structures can be obtained.

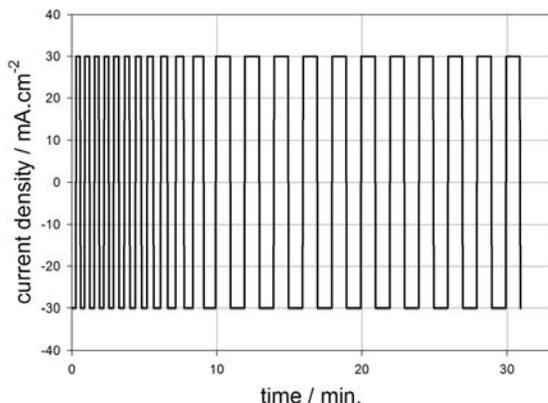


Figure 4 : frequency-modulated galvanostatic pulses used for the electro-plating of fractal electrocatalysts.

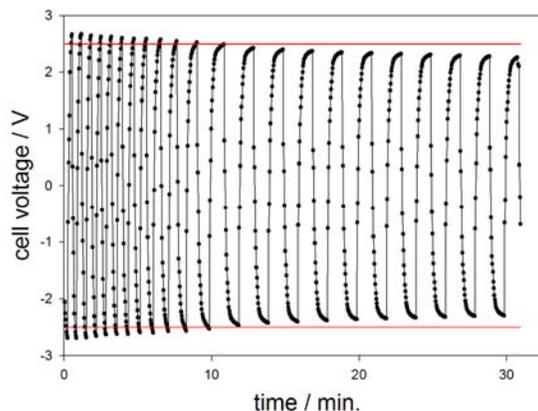


Figure 5 : potential response measured during the plating process.

Anodisation of nano-scale nuclei further favours the production of highly dispersed structure with elevated surface area. This can be seen from figure 6 where lab-scale ( $2\text{ cm}^2$ ) i(E) curves are plotted at two different operating temperatures. A substantial improvement in cell voltage is observed when two successive electro-plating cycles are made. At larger scale (Figure 7), homogeneous Pt deposits are obtained. The MEAs thus obtained are then mounted in electrolysis stacks.

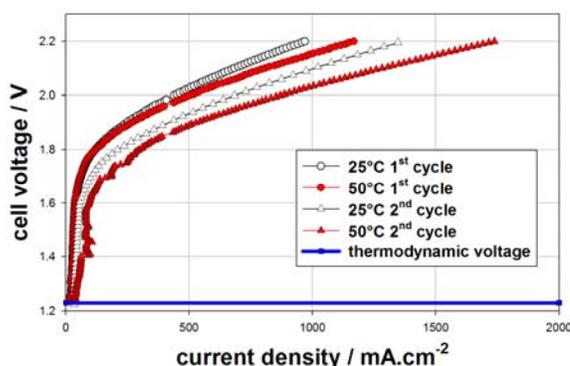


Figure 6 : electrochemical performances measured after electroplating.



Figure 7 : photograph of a  $250\text{ cm}^2$  MEA Nafion®117/Pt kept in water after Pt deposition.

### 3. Project achievements

#### 3.1. experimental results

Main academic results obtained so far concern electrocatalysis using non-noble metals as well as plating procedures. Some of these results are published in different communications during this 16<sup>th</sup> WHEC 2006 in Lyon. Main achievements obtained so far concern the development of moncell test benches of nominal scale ( $250\text{ cm}^2$ ) used to characterize various MEAs at different operating (current density, temperature and pressure) conditions (figure 8), stack development from the GenHy®100 to the GenHy®1000 scale (figure 9), automated GenHy®100 production units (for laboratory applications, figure 10) and automated GenHy®1000 test benches for stack qualification up to 10 bars (figure 11). Potential applications of these automated GenHy®1000 production units concern hydrogen refueling stations. Specific test benches are developed for high pressure testing. Different tests are performed at CETH's test site as well as at KI's. D+ from Belgium provides engineering support for the design of test benches and automated procedures for continuous high pressure operation and testing. Special attention will be paid to the structure of the MEAs for high pressure operation at which significant cross-permeation of gases is known to occur.



**Figure 8** : typical monosell of nominal scale used to test MEAs performances (CETH).



**Figure 9** : GenHy®1000 stack (CETH).



**Figure 10** : automated GenHy®100 system (CETH).



**Figure 11** : automated GenHy®1000 system (CETH).



**Fig. 12.** 1.5 m<sup>3</sup>/hour hydrogen generator operated up to 30 bars (KI).

### 3.2. cost analysis

A major difficulty faced by manufacturers for the dissemination of PEM technology in the industry concerns production cost. Cost reduction is a key issue in the GenHyPEM project, in relation with the Strategic Research Agenda (SRA) of the European Commission. SRA references are 1.00 €/Kg for non-energy costs and 1.9-3.8 €/Kg for energy cost. The following figures provide some information on cost analysis for a GenHy<sup>®</sup>1000 stack unit, from which it appears that platinum group electrocatalysts account for less than 25% of the global cost. Therefore, reduction costs can be expected from the different constituents of the stack and not only from electrocatalysts.

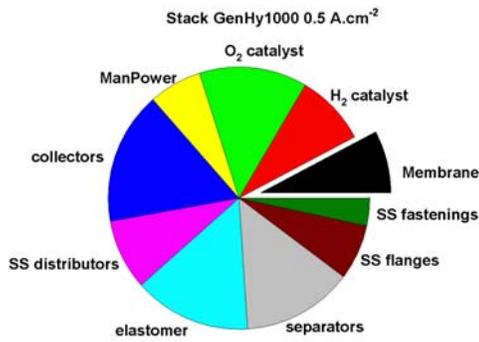


Figure 13 : cost analysis for a GenHy<sup>®</sup>1000 operated at 500 mA.cm<sup>-2</sup>.

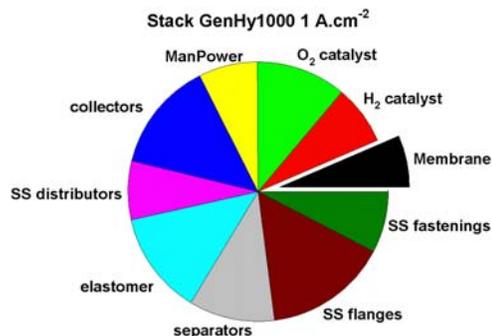


Figure 14 : cost analysis for a GenHy<sup>®</sup>1000 operated at 1000 mA.cm<sup>-2</sup>.

### 3.3. dissemination of knowledge

Several tools are used to insure the dissemination of knowledge in relation with this project :

- **Website** : a website under construction (<http://www.genhypem.u-psud.fr/genhypem.htm>) will be used for communication purposes. A public section will be open and an intranet section will be available to partners. The public section is open to all interest groups and will announce public meetings, workshops and the like as well as it will give access to generated (public) knowledge and deliveries as well as information on the project status. The intranet will be accessible only to project partners and act as an instrument to co-ordinate the consortium. This web site intends to be an informal and public forum enabling groups of interest to be in close touch with the developments and activities of the consortium.
- **Conferences and fairs** : dissemination of results are also ensured through technological exhibition during industrial fairs. Prototype systems have been exhibited in various International Conference and Fairs such as the Hannover Fair Meeting (Germany) in 2005 and 2006, and the Salon International des Véhicules Ecologiques et des Energies Renouvelables, 30 mars – 02 avril 2006, Monaco.
- **Interaction with EU H2/FC Technology Platform**: the project interacts, follow up the developments of the H2/FC Technology Platform, provides and exchanges information in view of steering the work and aligning the deliverables with the priorities and targets of the platform to the extent possible. The project reports to the Commission the necessary information to assess progress in view of technology watch and planning exercise that will be carried out as part of the Roads2 HyCom project.

### 3.4. raising public participation and awareness

Concerning dissemination of information beyond the research community, specific actions are planned. Several partners of the consortium are involved in educational affairs and wish to promote the ethical values related to GenHyPEM to a more general public, and especially to the young generations. Technological and environmental related aspects will be presented and the benefit of international collaboration between EU state members and non-EU neighboring countries will be outlined. An exhibition has been organised at the french Palais de la Découverte in early 2006 to introduce energy problems and promote hydrogen-related applications as well as the use of renewable sources of energy. With the support of Région Ile de France, a specific demonstration PEM water electrolysis cell (GenHyOne<sup>®</sup>, CETH) has been developed and presented to the public. A video film related to the hydrogen economy has also been realized on this subject and released by the Palais for educational

purposes. It is planned to present these pedagogical productions in different Colloquiums along the three years duration of the project.

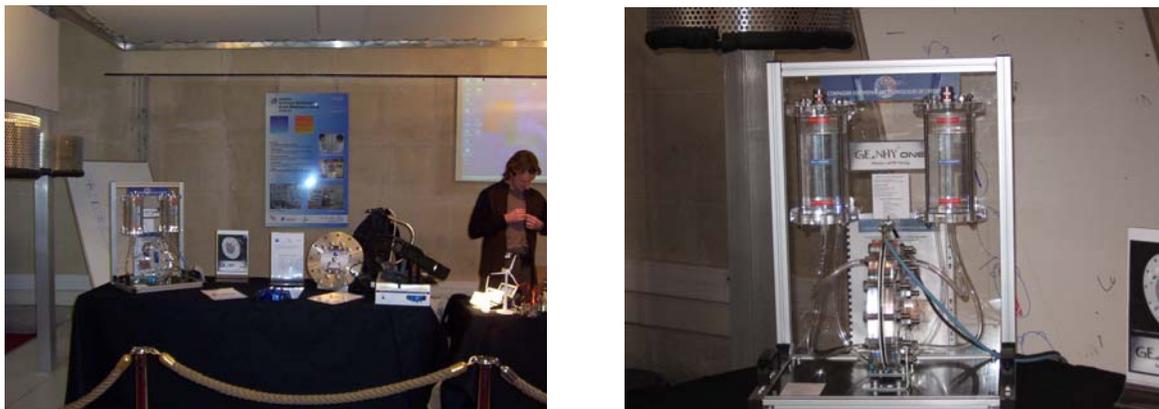


Figure 15 : public exhibition at the French Palais de la Découverte in Paris (01/03 - 15/05 2006).

#### 4. conclusions and perspectives

Since the pioneering work of General Electric Company in the USA, suggesting in the 50's the possibility of using ion-exchange membranes as solid electrolyte, many R&D programs have been launched in industrialized countries to develop the use of PEM technology. Most of the research work has been devoted to the development of H<sub>2</sub>/O<sub>2</sub> fuel cells and water electrolyzers. In these times of growing environmental problems and repeated oil crisis, the hydrogen economy offers fascinating perspectives. PEM technology has an important role to play, especially to provide adequate technological solutions aimed at promoting the use of renewable sources of energy, both for industrial and domestic applications. The GenHyPEM project is participating to this international research effort. Optimized electrolytic generators producing up to 2500 Nliters H<sub>2</sub> per hour will be developed by industrial partners and commercialized for miscellaneous industrial applications.

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