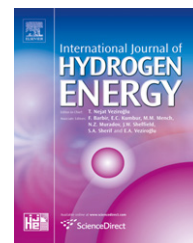


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PEM water electrolyzers: From electrocatalysis to stack development

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ABSTRACT

Proton Exchange Membrane (PEM) water electrolysis can be used to produce hydrogen from renewable energy sources and can contribute to reduce CO₂ emissions. The purpose of this paper is to report on recent advances made in PEM water electrolysis technology. Results obtained in electrocatalysis (recent progresses made in low-cost electrocatalysis offer new perspectives for decentralized and domestic applications), on low-cost membrane electrode assemblies (MEAs), cell efficiency, operation at high current density, electrochemical performances and gas purity issues during high-pressure operation, safety considerations, stack design and optimization (for electrolyzers which can produce up to 5 Nm³ H₂/h) and performance degradations are presented. These results were obtained in the course of the GenHyPEM project, a 39 months long (2005–2008) research program supported by the European Commission. PEM technology has reached a level of maturity and performances which offers new perspectives in view of the so-called hydrogen economy.

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1. Introduction

Proton Exchange Membrane (PEM) water electrolysis can potentially be used for the decentralized production of hydrogen from renewable energy sources [1]. From a historical viewpoint, general principles of PEM technology (Grubb cell) were described in the early fifties, at the dawn of the US space program, in view of electricity production using H₂/O₂ fuel cells in zero-gravity environments [2]. In a PEM cell, a thin (50–250 μm thick) proton-conducting membrane is used as solid polymer electrolyte (SPE) in place of more conventional liquid electrolytes. Several electrolyte-impregnated SPEs were tested at that time. However, direct application to water electrolysis was not possible because available SPEs were lacking

sufficient chemical stability. This was mostly due to the very oxidizing conditions found at anodes of water electrolyzers where oxygen is evolved at high electrode potential values (close to +2 V vs. NHE). Then, in the late sixties, the arrival on the market of more stable sulfonated tetrafluoroethylene based fluoropolymer-copolymer (W. Grot, E.I. DuPont Co., Nafion[®] products [3]) opened the way to water electrolysis applications. Nafion[®] was the first of a class of synthetic polymers called ionomers with ionic properties. These materials were obtained by copolymerization of a perfluorinated vinyl ether comonomer with tetrafluoroethylene (TFE) [4]. Since then, Nafion[®] has received a considerable amount of attention as a proton conductor for PEM fuel cells and water electrolysis applications, because of its high proton

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Nomenclature (List of symbols)			
HER	hydrogen evolution reaction	R	ideal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
MEA	membrane electrode assembly	S	cell surface, m^2
OER	oxygen evolution reaction	T	absolute temperature, K
PEM	proton exchange membrane	U_{cell}	cell voltage, V
SPE	solid polymer electrolyte	V	thermo-neutral voltage, V
STREP	specific targeted research project (European Commission)	W_r	real energy, J mol^{-1} required to split one mole of water
E	reversible cell potential	W_t	theoretical energy, J mol^{-1} required to split one mole of water
E_s	specific energy, kWh Nm^{-3}	μ	chemical potential, J mol^{-1}
F	Faraday constant, 96485 C mol^{-1}	ΔG	Gibbs free energy change, J mol^{-1}
I	current, A	ΔH	enthalpy change, J mol^{-1}
j	current density, A cm^{-2}	ΔS	entropy change, $\text{J mol}^{-1} \text{ K}^{-1}$
\dot{m}_{H_2}	hydrogen production rate, $\text{Nm}^3 \text{ h}^{-1}$	$^\circ$	refers to standard conditions, 298 K, 1 bar
n	number of electron exchanged in a charge transfer process	$\varepsilon_{\Delta G}$	energy cell efficiency (%)
P	pressure, Pa	$\varepsilon_{\Delta H}$	Enthalpy cell efficiency (%)
		ε_j	Faradaic yield or current efficiency (%)

conductivity and its excellent chemical and mechanical stability. Although the large scale production of hydrogen by water electrolysis using PEM technology has been considered from both the technical and financial viewpoints in the early eighties [5], most research papers published in the literature on the subject described small units (up to several cubic meter of hydrogen per hour), mostly used to produce oxygen in anaerobic environments (for example for space and underwater applications). 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. Although still expensive (noble metals are used as electrocatalysts and perfluorinated materials as SPEs), PEM technology can potentially be used to produce hydrogen from renewable energy sources in view of domestic applications. The characteristics of PEM electrolyzers 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 [6,7]. With conversion efficiencies (definition of cell efficiency is given in Section 3 below) above 70% at current densities of 1 A cm^{-2} (this is common good practise, at least at the lab-scale), 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 [8] and the European Commission is actively supporting R&D activities in this field [9]. Currently, small scale systems ($<200 \text{ kW}$) are already available on the market with unit prices in the 10^3 – 10^4 €/kW range for units producing 10 – $1 \text{ Nm}^3 \text{ H}_2/\text{h}$, depending on size and operating conditions. To further bring down unit costs in order to meet market requirements, new materials and improved manufacturing techniques are still needed as well as higher conversion efficiencies. For example, a conventional PEM electrolysis cell operating at 1 A cm^{-2} with a cell voltage of 1.8 Volt (common good practice at the lab-scale) has an efficiency of 80% (based on the enthalpy change of the water splitting reaction). But potential exists for further

process development and optimization of this technology. Would the cell voltage be reduced down to 1.7 V and the current density be doubled, the efficiency would reach 85% and the investment cost would be reduced by a factor of two. For practical applications (both stationary and intermittent), such enhanced electrochemical performances should remain stable and the lifetime of PEM water electrolyzers should be in the upper range of 10^4 – 10^5 h . The involvement of the European Commission in the vision of the “hydrogen society” has led to the GenHyPEM project, a 39 month long and 2.6 M€ STREP programme which started in October 2005 and ended in December 2008. Some significant results obtained in the course of the project are reported in this research paper.

2. Experimental section

2.1. Chemicals and catalyst synthesis

2.1.1. Noble-metal catalysts

In the course of the GenHyPEM project, Pd- and/or Pt- carbon supported (using carbon nanotubes or carbon powders) electrocatalysts have been synthesized and used as cathodic catalyst for the hydrogen evolution reaction (HER). Catalytic inks were obtained by chemical reduction of precursor salts dissolved in aqueous solution, using a combined impregnation/reduction method and ethylene glycol as reducing agent. Typically, 135 mg of Vulcan XC-72TM (Cabot Co., $250 \text{ m}^2 \text{ g}^{-1}$ BET area) were dispersed in 4.6 cm^3 of 0.1 M solutions of hexachloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Aldrich) or tetrachloropalladic acid hexahydrate (H_2PdCl_4 , Aldrich) in bi-distilled water and 2-propanol (8 vol.%). Then the pH of the mixture was set to ca. 9 by addition of 0.1 M Na_2CO_3 and poured into 60 cm^3 of ethylene glycol to initiate the reduction process. Finally, drop-wise amounts of formaldehyde were added to perform post-reduction of noble-metal particles. After that, the temperature of the mixtures was kept constant at 85°C for 2 h under vigorous stirring and then cooled-down to room temperature for 24 h (completion of the reduction

process). The excess liquid was poured out and the remaining deposits (Pt or Pd on Vulcan) were washed off (8–10 times) using bi-distilled water, dried in an oven at a temperature of 40–50 °C and finally activated in an Ar–H₂ atmosphere (1 bar, 25 °C). TEM analysis revealed that the mean particle size was in the 4–8 nm range. From cyclic voltametry experiments, electrochemical active area comprised between 30 and 50 m² g^{−1} were obtained. Since carbon is not stable under oxygen evolution at anodes of PEM water electrolyzers, it cannot be used as an anodic carrier. In the course of the GenHyPEM project, iridium blacks of high surface area have been synthesized and used as anodic electrocatalysts. Iridium blacks were synthesized by chemical reduction of hydrogen hexachloroiridate(IV) hydrate (H₂IrCl₆·6H₂O, 99.8%, Aldrich) using NaBH₄ (98%, Merck Chemicals) as chemical reducer. In a typical experiment, the Ir-powder was obtained from a 0.1 M H₂IrCl₆ aqueous solution by addition of 0.5 mol l^{−1} KOH solution until a pH of 13–13.5 was obtained. This mixture was stirred at room temperature during the drop-wise addition of NaBH₄ (10 g l^{−1} in 1 M NaOH) until gas evolution ended. Then the remaining deposits (Ir black powder) were washed off (several times) using bi-distilled water until the pH of down-take solution reached a value of 6–6.5. Washed catalyst was finally dried up at 60–70 °C.

2.1.2. Cobalt clathrochelate catalysts

Chemicals used as starting materials for synthesizing boron-capped tris(glyoximate) cobalt complexes in which the metal ion is both coordinatively saturated and encapsulated by a single macrobicyclic ligand [10,11] were obtained from Acros organics and used as received. These cobalt clathrochelates were synthesized as follows [10]: 10 ml of a diethyl ether solution containing boron trifluoride etherate (40 mmol, 5 mL) was drop-wise added to a suspension of Co(OAc)₂·4H₂O (8 mmol, 1 g) and dimethylglyoxime (dmgh₂) (8 mmol, 0.98 g) in diethyl ether (70 mL) under argon at room temperature. Reaction mixture was stirred overnight. Brown crystals were obtained and collected by filtration and then washed several times with diethyl ether. A pure powder of Co(dmgh₂)₂·OAc (1.73 g, 3.6 mmol, 90%) was obtained and then used to prepare the MEAs.

2.1.3. Polyoxometalate catalysts

Commercially available polyoxometalates have been used as cathodic electrocatalysts for the HER. Tungstosilicic acid hydrate (α-H₄SiW₁₂O₄₀, 99.9%, Aldrich) was used as received, without purification.

2.2. Preparation of membrane electrode assemblies

Porous current collectors (1.4 mm thick, porosity of ca. 45%) made of sintered titanium powders of suitable size and geometry [12] have been used as anodic and cathodic current collectors throughout. Membrane electrode assemblies for lab-scale (7 and 23 cm²) and stack (250 cm²) experiments were prepared using a spray technique, as follows. 15 wt.% catalysts (carbon-supported Pt or Pd nanoparticles or cobalt clathrochelates or tungstosilicic acid hydrate) were first mixed with an alcoholic solution of the ionomer (Nafion® 117, Aldrich Co.) and then dispersed in isopropanol for 30 min

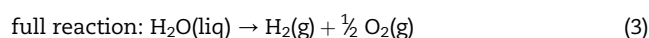
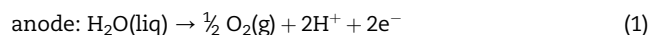
using an ultrasonic bath to produce either homogeneous suspensions (carbon-supported particles) or homogeneous solutions. Catalytic inks were then directly sprayed over the surface of the titanium current collectors using an air gun (lab-scale cells) or a printer (large scale cells). Typical metal loadings of ca. 0.35 mg cm^{−2} (Pt or Pd), 0.5–1.0 mg cm^{−2} (cobalt clathrochelate), and 0.1–1.0 mg cm^{−2} (tungstosilicic acid hydrate) were used. Anodes were prepared using the same procedure but larger iridium loadings (2–2.5 mg cm^{−2}) were used. Current collectors with catalyst layers were then air-dried and finally pressed against the hydrated SPE (Nafion-117 membranes, Ion Power Co.).

2.3. Instrumentation

Polarisation curves using lab-scale cells (7 or 23 cm² active area) have been recorded using a DC Microlab Power supply (10 V–50 A) from Microlab Systems DC. Stack characterization was achieved using a specifically designed and automated test bench developed at CETH in the course of the GenHyPEM project. A 20 kW DC power supply (30 V, 600 A) from Magna Power Electronics Co. has been used to measure polarisation curves.

3. Thermodynamics of PEM water electrolysis and definitions

In a water electrolysis cell, electricity is used to split water molecules into gaseous hydrogen and oxygen. In an acidic PEM cell, liquid water splitting occurs according to the following half-cell reactions:



Solvated protons formed at the oxygen-evolving anode of the PEM cell migrate through the SPE membrane to the cathode where they are reduced into molecular hydrogen. Liquid water is consumed at the anode but also released at the cathode (so-called electro-osmosis drag). At equilibrium, the amount of electricity (n.F.E) required to split one mole of water is equal to the change of Gibbs free energy ΔG_d of the water dissociation reaction (3):

$$\Delta G_d - n F E = 0 \quad \text{and} \quad \Delta G_d > 0 \quad (4)$$

where n = 2 (number of electrons exchanged during the electrochemical splitting of water); F is the Faraday; E is the thermodynamic voltage associated with the water dissociation reaction (3) and ΔG_d is the free energy change associated with the water dissociation reaction (3). ΔG_d is a function of both operating temperature and pressure and thus:

$$\Delta G_d(T, P) = \Delta H_d(T, P) - T \Delta S_d(T, P) > 0 \quad (5)$$

ΔH_d(T, P) et ΔS_d(T, P) are respectively the enthalpy change (J mol^{−1}) and entropy change (J mol^{−1} K^{−1}) associated with the water dissociation reaction (3). To split one mole of water, ΔG_d

(J mol⁻¹) of electricity and $T \cdot \Delta S_d$ (J mol⁻¹) of heat are required. The thermodynamic electrolysis voltage E in Volt is defined as:

$$E(T, P) = \frac{\Delta G_d(T, P)}{n F} \quad (6)$$

The thermo-neutral voltage V in Volt is defined as:

$$V(T, P) = \frac{\Delta H(T, P)}{n F} \quad (7)$$

In standard conditions of temperature and pressure ($T^\circ = 298 \text{ K}$, $P^\circ = 1 \text{ bar}$), water is liquid, H_2 and O_2 are gaseous. Standard free energy, enthalpy and entropy changes for reaction (3) are:

$$\Delta G_d^\circ(\text{H}_2\text{O}) = 237.22 \text{ kJ mol}^{-1} \Rightarrow E^\circ = \Delta G_d^\circ(\text{H}_2\text{O}) / 2F = 1.2293 \text{ V} \approx 1.23 \text{ V}$$

$$\Delta H_d^\circ(\text{H}_2\text{O}) = 285.840 \text{ kJ mol}^{-1} \Rightarrow V^\circ = \Delta H_d^\circ(\text{H}_2\text{O}) / 2F = 1.4813 \text{ V} \approx 1.48 \text{ V}$$

$$\Delta S_d^\circ(\text{H}_2\text{O}) = 163.15 \text{ J mol}^{-1} \text{ K}^{-1}$$

A voltage term $T \cdot \Delta S_d^\circ / (2F) = 0.25 \text{ V}$ must be added to the thermodynamic voltage E to provide the heat required by reaction (3). It should be noted that splitting of water vapour in place of liquid water requires less energy, the difference being the enthalpy change associated with water vaporisation. This is referred to in the literature as low and high heating values of H_2 formation.

The efficiency of a PEM water electrolysis cell relates the theoretical amount of energy W_t required to split one mole water to the real amount of energy W_r . Due to various irreversibilities appearing when a current flows across the cell (ohmic drops, electrochemical overvoltages), $W_r > W_t$. The cell efficiency is defined as the dimensionless ratio:

$$\varepsilon = \frac{W_t}{W_r} \quad (8)$$

$\triangleright W_r = (U_{\text{cell}} \cdot I \cdot t / n_{\text{H}_2})$, U_{cell} is the actual cell voltage in Volt, I is the current in A and t is the duration of the experiment in seconds.

$\triangleright W_t$ can be defined from the thermodynamic voltage E : $W_{t,\Delta G} = (E \cdot I \cdot t) / n_{\text{H}_2}$

$\triangleright W_t$ can also be defined from the thermo-neutral voltage V : $W_{t,\Delta H} = (V \cdot I \cdot t) / n_{\text{H}_2}$

Therefore, two different definitions can be used to calculate the efficiency of a PEM cell. Since E and V are both function of operating temperature T and operating pressure P , and since U_{cell} is also a function of the operating current density j , the two different cell efficiencies can also be expressed as a function of T , P , j :

$$\varepsilon_{\Delta G}(T, P, j) = \frac{E(T, P)}{U_{\text{cell}}(T, P, j)} \quad \varepsilon_{\Delta H}(T, P, j) = \frac{V(T, P)}{U_{\text{cell}}(T, P, j)} \quad (9)$$

At low current densities, cell efficiencies close to 100% are obtained. The efficiency of a PEM water electrolysis cell is a critical parameter responsible for the energy cost of the process. Operation at high current density is necessary to

reduce investment costs but since efficiency decreases when current density increases, a compromise has to be found between energy and investment costs. In conventional PEM water electrolyzers, $\varepsilon_{\Delta H} \approx 70\%$ at 1 A cm^{-2} , $T = 90^\circ \text{C}$ and $P = 1 \text{ bar}$. The challenge is to improve this value with lower noble-metal contents. The specific energy consumption E_s is the amount of electricity (in kWh) required for the production of a given amount (for example one cubic meter) of hydrogen. It is expressed in units of kWh/Nm³. E_s is also a function of operating temperature, pressure and current density:

$$E_s(T, P, j) = \frac{U_{\text{cell}}(T, P, j) \times I}{\dot{m}_{\text{H}_2}} \quad (10)$$

where I is the cell current in Amp and \dot{m}_{H_2} is the hydrogen production rate in Nm³/h. In standard conditions, $E_s^\circ = 2.94 \text{ kWh/Nm}^3$. It should be noted that the ratio $E_s^\circ / E_s(T, P, j)$ is equal to $\varepsilon_{\Delta G}$. Finally, the faradaic yield or current efficiency ε_j is defined as the dimensionless ratio of the hydrogen mole number n_{H_2} formed during a given time interval Δt to the amount of electricity passed through the cell during the same period times the Faraday:

$$\varepsilon_j = \frac{n_{\text{H}_2}}{j S \Delta t} 2 F \quad (11)$$

The current efficiency is strongly impacted by gas-cross-permeation phenomena. Hydrogen formed at the cathode diffuse across the cell to the anode where it is oxidized back into protons and oxygen formed at the anode diffuse across the cell to the cathode where it is reduced back into water. As a result, the gas production is reduced and electricity is dissipated as heat in the cell.

4. Results and discussion

4.1. Electrocatalysis

4.1.1. Results obtained with conventional noble-metal electrocatalysts

In conventional PEM water electrolyzers, metallic platinum is used as electrocatalyst for the hydrogen evolution reaction (HER) and iridium (metal or oxide) is used for the oxygen evolution reaction (OER) [13]. This is due to the highly acidic environment found in proton-conducting SPE (non-noble metals would be rapidly oxidized and would dissolve in the solid electrolyte). Best electrolysis efficiencies ($\varepsilon_{\Delta H} \approx 70\%$ at 1 A cm^{-2}) can be obtained using noble-metal loadings of ca. 0.5 mg cm^{-2} of Pt for the HER and ca. 2 mg cm^{-2} of Ir (or iridium oxide) for the OER. To a certain extent, PEM water electrolysis remains an expensive technology due to the use of noble metals. As for PEM fuel cell technology, noble-metal loadings must be reduced because of cost requirements. Concerning the HER, platinum loadings can be significantly lowered by coating Pt nanoparticles at the surface of electronic carriers of large surface areas. Pt can be coated over carbon nanotubes or over carbon powders. Typical polarisation curves obtained using different MEAs at 90°C and in the $0\text{--}2 \text{ A cm}^{-2}$ current density range, are plotted in Fig. 1.

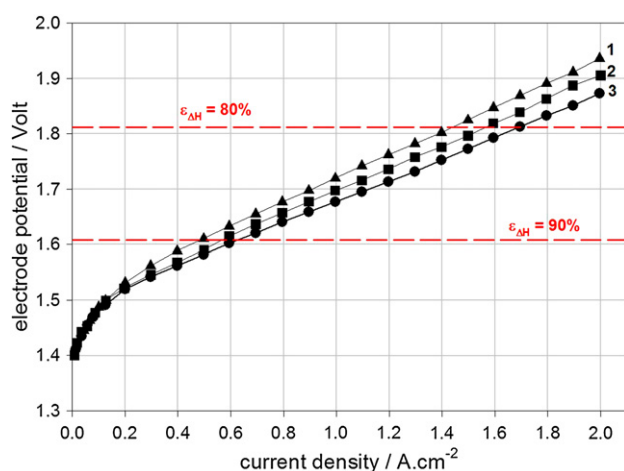


Fig. 1 – Current-voltage performances measured on a single cell (operating area of 7 cm²) with different noble-metal catalysts. Cathode: 1 – Pd20/Vulcan XC-72 (0.35 mg cm⁻² of Pd), 2 – Pd40/Vulcan XC-72 (0.7 mg cm⁻² of Pd), 3 – Pt40/Vulcan XC-72 (0.7 mg cm⁻² of Pt). Anode: black Ir (2.0 mg cm⁻²). Nafion®-115 SPE membrane. Operating conditions: $T_{\text{cell}} = 90^{\circ}\text{C}$, $P = 1$ bar.

Pt40/VulcanXC-72 denotes a catalyst made of Pt nanoparticles (40 wt.%) deposited onto Vulcan carbon powder XC72. Electrochemical performances measured using Pt and Pd nanoparticles deposited at the surface of Vulcan XC72 are compared. Slightly more efficient results were obtained using Pt in place of Pd at the cathode. A cell efficiency $\epsilon_{\text{AH}} \approx 90\%$ is obtained at 0.6 A cm^{-2} and $\epsilon_{\text{AH}} \approx 80\%$ is obtained at 1.6 A cm^{-2} . Slightly more efficient results can be obtained by using thinner SPEs, thus reducing the ohmic drop across the membrane. However, gas-cross-permeation effects increase more rapidly when the operating pressure is raised and such membranes should be used only for operation at atmospheric pressure. Noble-metal loadings can also be reduced at the anode by using mixed oxides [14] but in view of the large scale application of PEM water electrolysis technology, cheap electrocatalysts are required for both HER and OER.

4.1.2. Results obtained with cobalt clathrochelates for the hydrogen evolution reaction

As discussed in the previous section, expensive noble metals are used as electrocatalysts in conventional PEM technology. This is a major drawback, detrimental to the widespread utilization of that technology. Cost considerations require the use of less expensive electrocatalysts. In recent years, different compounds have been identified as possible electroactive materials which could be used in place of platinum for the HER [10,11]. Following the work of Espenson and colleagues [15], boron-capped tris(glyoximate) cobalt complexes (referred to as Co(dmg) in the followings) have been tested at the cathode of PEM water electrolysis cells in the course of the GenHyPEM project. In these compounds classified as clathrochelate complexes, the metal ion is locked in a close-knit structure, inhibiting ligand exchange in the more labile oxidation states of the encapsulated metal ion.

This, in turn, explains why the chemical activity of this family of stable complexes is particularly low and explains their chemical stability. Also, it is worth noting that these compounds are not electron conductors. Therefore, it is more convenient to adsorb them at the surface of an electronic carrier of large surface area (again, Vulcan XC-72 was used for that purpose) after solubilization in isopropanol and to plate the mixture directly onto the electrode after addition of Nafion (5 wt.%). Co(dmg) crystals tend to crystallize separately. Therefore the challenge here was to obtain an homogeneous coating of carbon particles by Co(dmg) to increase active area. Some typical results obtained during PEM water electrolysis are plotted in Fig. 2.

In all cases, iridium black (2.5 mg/cm²) was used at the anode. First (curve 1), a mixture of bare Vulcan XC-72 and Nafion (5 wt.%) was used as catalyst for the HER. Then (curve 2), a mixture of Co(dmg) and Nafion (5 wt.%). Then (curve 3), a mixture of Co(dmg) adsorbed onto Vulcan XC-72 and Nafion (5 wt. %). For comparison, a conventional polarisation curve measured with Pt for the HER and Ir for the OER is also plotted (curve 4). Comparison of curves 3 and 4 reveals that, although the cobalt clathrochelate remains significantly less efficient than Pt for the HER, interesting electrochemical performances are nevertheless obtained. A cell efficiency $\epsilon_{\text{AH}} \approx 80\%$ is obtained at a current density of 500 mA cm^{-2} and 90°C . EIS analysis of cell impedance (not shown here) reveals that diffusion-controlled transport of molecular H₂ produced during water electrolysis, away from the cathode, significantly contributes to the overall cell impedance. Electrode structure requires further optimization and addition of hydrophobic additives, currently tested, are expected to further improve electrochemical performances.

4.1.3. Results obtained with polyoxometalates for the hydrogen evolution reaction

Electroactivity of polyoxometalates (POMs) with regard to the HER in liquid electrolytes has been reported in the literature a few decades ago [16,17]. These catalysts have been

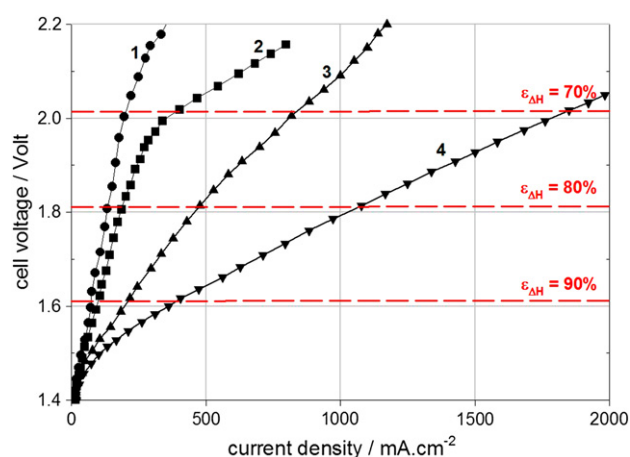


Fig. 2 – Polarisation curves measured at 90°C using different AMEs (23 cm² PEM cell). Anode: 2.5 mg cm^{-2} Ir°. (1) 1 mg cm^{-2} Vulcan XC72/Nafion115/Ir°; (2) 1 mg cm^{-2} Co(dmg)/Nafion115/Ir°; (3) 1 mg cm^{-2} Co(dmg)/VulcanXC72/Nafion115/Ir; (4) 1 mg cm^{-2} Pt/Nafion115/Ir.

successfully tested at the cathode of PEM water electrolyzers in place of platinum for the HER. Some typical polarisation curves, obtained with the simple and commercially available tungstosilicic acid hydrate ($\alpha\text{-H}_4\text{SiW}_{12}\text{O}_{40}$) adsorbed at the surface of the cathodic titanium current collector, are plotted in Fig. 3. On top (black circles) is plotted a reference curve obtained when Pt is used for both the HER and the OER. At bottom (green circles) is plotted a second reference curve obtained when platinum is used at the cathode for the HER and metal iridium is used at the anode for the OER. Between these two limiting curves are plotted three additional curves (red circles, curves label 1, 2, 3) obtained with increasing loadings of $\alpha\text{-H}_4\text{SiW}_{12}\text{O}_{40}$ for the HER and Ir metal for the OER. Although the electrochemical performances are not as good as those obtained with Pt at the cathode, those obtained with optimized POMs (curve 3) cathodes are already very efficient: $\varepsilon_{\text{AH}} \approx 70\%$ has been obtained at 1 A cm^{-2} , significantly higher than those obtained with above mentioned clathrochelates. These results offer new and interesting perspectives to PEM water electrolysis technology. By getting rid of noble metals, substantial cost reductions can be expected, opening the way to new applications in the industry.

4.2. Stack design and optimization

In the course of the GenHyPEM project, a GenHy[®]1000 PEM water electrolyzer (hydrogen production capacity up to $1 \text{ Nm}^3 \text{ H}_2/\text{h}$) operating in the 1–50 bar pressure range has been developed as main project deliverable and tested. A stack efficiency of 80% at 1 A cm^{-2} was initially targeted (efficiency of ancillary equipments and water vapour losses are not considered in the calculation of the overall stack efficiency).

4.2.1. Stack description

The GenHy[®]1000 stack is pictured in Fig. 4. Twelve circular MEAs (250 cm^2 active area each) are series connected in



Fig. 4 – Photograph of a GenHy[®]1000 PEM water electrolyzer.

a filter-press configuration to reach the targeted hydrogen production capacity. Results presented here were obtained using conventional noble-metal electrocatalysts (Pt° for the HER and Ir° for the OER). Porous titanium disks (1.2 mm thick, 40% open porosity [12]) were used as current collectors; titanium grids were used as spacers and titanium foils were used as bipolar plates. Carbon gaskets were used as cell sealant. Individual cell voltages were measured during electrolysis. For high-pressure operation, a stainless steel pressurizing vessel was connected to the front flange. Feed water was introduced directly into the pressurized vessel for the purpose of heat management and to prevent gas accumulation that would occur from stack leakage.

4.2.2. Hydrodynamics

Internal cell design is crucial to reach high stack efficiencies. On one hand, parasite ohmic losses due to surface contact points between titanium stack components must be reduced down to values lower than $100 \text{ m}\Omega \text{ cm}^2$ to maintain parasite ohmic losses at values less than 0.1 V at 1 A cm^{-2} . On the other hand, the hydrodynamics inside the stack requires geometry optimization to insure a homogeneous distribution of water in each individual cell. This is of particular importance to insure a regular distribution of current lines across the MEAs and avoid the formation of hot points, especially at elevated current densities. Whereas the modeling of biphasic liquid–gas mixtures can be extremely complicated, in particular transport processes across porous current collectors, simpler models related to the hydrodynamics of liquid water are also useful. In the GenHyPEM project, water distribution inside the stack was optimized by solving mass flow equations using

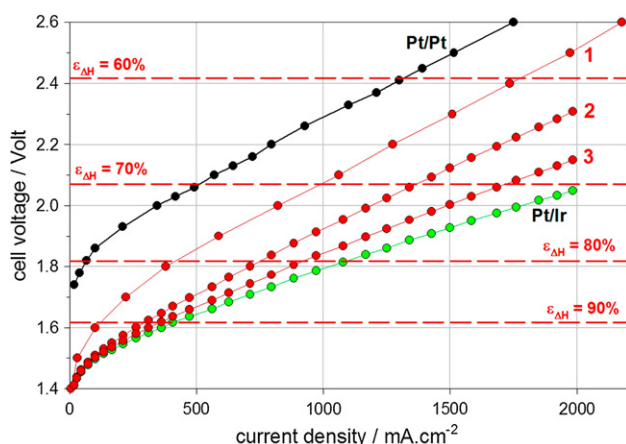


Fig. 3 – Polarisation curves measured on lab-scale (7 cm^2) PEM cells at 90°C . (●) reference curve with Pt for both HER and OER; (●) reference curve with Pt for the HER and Ir for the OER; (●) $\alpha\text{-H}_4\text{SiW}_{12}\text{O}_{40}$ for the HER: 1–0.2 mg cm^{-2} ; 2–0.5 mg cm^{-2} ; 3–0.8 mg cm^{-2} . Ir[°] for the OER (2.5 mg cm^{-2}).

a finite-element method (COMSOL multiphysics modeling). First, single cell experiments have been performed and internal geometry of individual cells has been optimized. By adjusting the diameter of cell outlets, it is possible to obtain a homogenous distribution of water flows over the entire MEA surface. A typical result is pictured in Fig. 5, where the 3-D distribution of water mass flow across an empty PEM cell is plotted. Two water inlets and two water outlets have been used to homogenize water distribution. The model has been used to calculate internal pressure drops as a function of overall water mass flow (Fig. 6). Model results obtained for different cell geometries have been satisfactorily compared to experimental ones. Then, the entire stack has been digitized and the overall stack geometry has been optimized to insure a homogeneous distribution of liquid water in each individual cell. Geometrical characteristics of PEM cells have finally been optimized to improve overall stack efficiency, as discussed in Section 4.3.

4.2.3. Current distribution

Using the same finite-element approach, internal cell design has also been optimized to reduce parasite ohmic losses and insure a homogeneous distribution of current lines across each individual PEM cell. Special attention has been paid to the design of current collectors, their microstructure and the distribution of current lines at the microscopic scale, at collector-catalyst interfaces and inside catalytic layers [12].

4.3. Electrolyzer performances

4.3.1. Electrochemical performances

The GenHy[®]1000 PEM electrolysis stack and its test bench are pictured in Fig. 7. As can be seen from Fig. 8, the stack efficiency is directly related to the operating temperature and current density. At 1 A cm^{-2} and ca. 85°C , a conversion efficiency ε_{AH} close to 80% and a mean cell voltage value of 1.88 V were obtained. During production, stable electrochemical

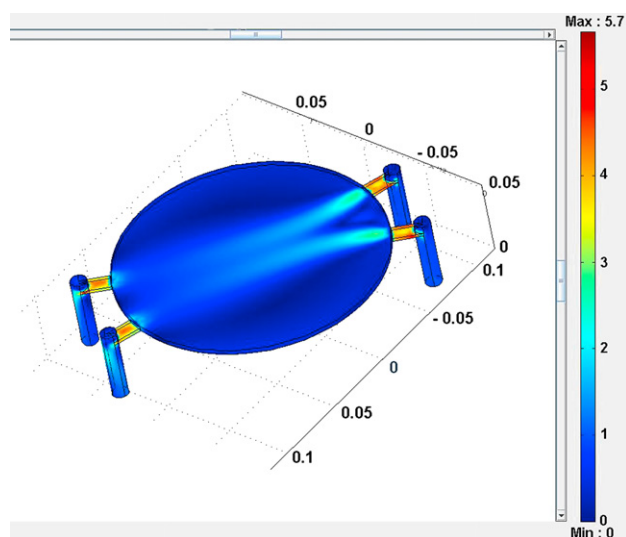


Fig. 5 – Detailed 3D representation of water mass flow (in arbitrary units) inside a 250 cm^2 PEM cell (360 Nl water/h).

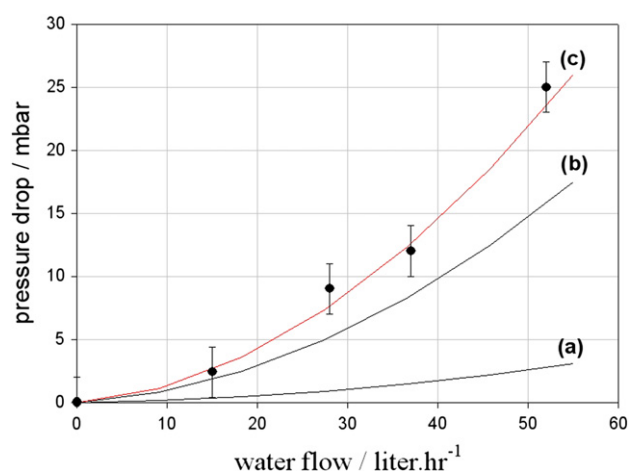


Fig. 6 – Experimental and model pressure – mass flow relationship obtained for a 250 cm^2 moncell at room temperature. (•) experimental datapoints.: (a) empty cell; (b) empty cell + current collector; (c) empty cell + current collector + spacers.

performances were obtained after a few hours of continuous operation, when the temperature of the system was stable. To reach high operating temperature, water circuits had to be properly insulated to reduce heat transfers to the surroundings. The electrolyzer could be powered either by a dc power



Fig. 7 – Photograph of the GenHy[®]1000 PEM water electrolyzer.

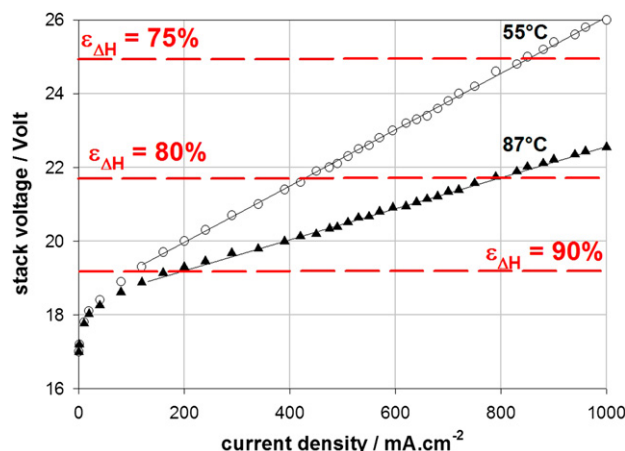


Fig. 8 – Stack voltage – current density measured on the GenHy®1000 PEM water electrolysis stack.

supply connected to the main power supply or using photo-voltaic panels. Several hundred hours of intermittent operation have been satisfactorily performed without noticeable degradation of electrochemical performances.

4.3.2. High-pressure operation

High-pressure operation is potentially interesting for the direct storage of hydrogen in pressurized vessels. Some applications require storage pressures up to several hundred bars. Whereas the absolute pressure of operation in itself raises different safety issues, the main challenge comes from gas-cross-permeation phenomena which take place across the SPE membrane during electrolysis. Hydrogen cross-permeation effects are critical in PEM cells because the concentration threshold of H_2 in H_2 – O_2 gas mixtures, responsible for explosion hazard, is rather low (4%). Hydrogen and oxygen solubility and diffusivity in Nafion® membranes are such that gases significantly diffuse between anode and cathode compartments. The mobility of molecular hydrogen being larger than the mobility of oxygen, most operating hazards appear in the oxygen production flow where large hydrogen concentrations can be measured. Typical values are plotted in Fig. 9 [6,7]. As can be seen, both operating pressure and current density play a major role in the level of contamination. The pressure difference between cathode and anode generates a gradient of chemical potential of hydrogen across the SPE which in turn leads to hydrogen transport by diffusion. At the microscopic level, there are different mechanisms responsible for the overall hydrogen transport across the membrane. Diffusion which takes place in both aqueous and organic phases of the polymer has a negative effect, leading to higher contamination level. Two other effects tend to counter-balance cross-permeation phenomena. First, the electro-osmotic drag of water from the anode to the cathode (each proton formed at the anode and migrating to the cathode carries several water molecules, the exact number being a function of the equivalent weight of the polymer) has a positive effect on cross-permeation phenomena by dragging dissolved H_2 molecules back to the cathode. Also, molecular

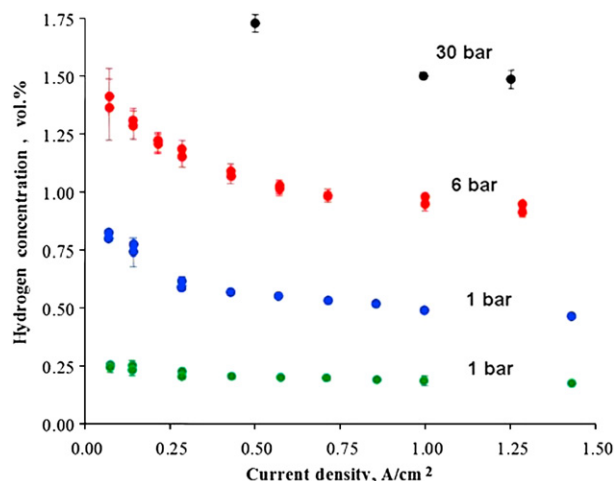


Fig. 9 – Hydrogen content (vol.%) in the anodic oxygen–water vapour mixture, measured at 1, 6 and 30 bar as a function of operating current density. 50 cm² monocell. Pt for the HER, Ir for the OER and Nafion-117 as SPE. (●): 30 bar (backside of current collector is platinized); (○): 6 bar (backside of current collector is platinized); (●): 1 bar (backside of current collector not-platinized); (○): 1 bar (backside of current collector is platinized).

hydrogen reaching the anode can be partly oxidized back into protons. This is detrimental to the faradaic yield ϵ_f of the water electrolysis reaction but has a positive effect on oxygen purity. For this purpose, the structure of the anode (porosity, thickness) must be optimized and addition of isolated platinum particles inside the SPE can promote the catalytic oxidation of diffusing H_2 into protons. Different mitigation strategies can be used to reduce the risks related to H_2 in O_2 . First, thicker SPE membranes can be used to reduce permeation rates (based on Fick's first law of diffusion) but this leads to higher ohmic drops across the SPE during electrolysis and reduces the overall cell efficiency. Also, internal gas recombiners can be used as described elsewhere [7] to promote the catalytic recombination of H_2 and O_2 in the gas phase (Fig. 9).

In the course of the GenHyPEM project, some experiments have been made at high operating pressure using a stack of cells made of PTFE-reinforced SPEs (Nafion® 1100). Some results obtained in the 1–130 bar pressure range are compiled in Table 1. Tests have been performed under stationary conditions at 500 mA cm^{−2} and at a mean operating temperature of 88 °C. The main operating parameter was the operating pressure. As can be seen from Table 1, individual cell voltages were stable and remained homogeneous during operation. Some differences between individual cells are directly related to the distribution of current lines which are not perfectly homogeneous over the active area. A mean stack efficiency $\epsilon_{AH} = 85\%$ was measured at 500 mA cm^{−2} using thick (PTFE-reinforced) SPEs. This is a significant improvement compared to conventional systems. The major impact of the high operating pressure was found on gas purity (as reported elsewhere [7]). For example, hydrogen purity steadily decreased with pressure due to oxygen cross-permeation and

Table 1 – Main test results obtained with the high-pressure PEM water electrolysis stack under stationary operating conditions.

Parameter	Unit	Measured values 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	Nm ³ /h	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	1.676	1.719	1.711	1.708	1.725	1.716
Specific energy consumption E _S	kWh/Nm ³	3.99	4.00	4.07	4.27	4.54	4.77
Current efficiency	%	99.98	99.68	98.13	96.57	92.91	90.45
Energy efficiency ε _{AG}	%	72.5	72.4	72.2	71.7	71.3	71.0

vice-versa. As a side effect of gas-cross-permeation, the current efficiency ϵ_j dropped down to 90% at 130 bars. Consequently, the specific energy consumption tends to increase with operating pressure. When gas recombiners are used in the circuitry, the mean gas purity can be maintained at values well-above the thresholds of explosion mixtures. As already pointed out, this is a simple and efficient way to manage explosion hazards. In the course of the project, the stack has been used for about 1000 h of intermittent operation at different operating pressures without significant losses in performances. The use of platinum at the cathodes makes them more sensitive to poisoning effects by under potential deposition of trace amounts of metallic cations. The use of alternative non-noble catalysts is expected to reduce this effect. Current and temperature cycling may have a deleterious effect but on the long term.

4.3.3. Long time performances and degradations

PEM water electrolysis technology has demonstrated its ability to operate in the upper range of 10^4 – 10^5 h. Performances measured during the first 800 h of operation of the GenHy[®]1000 stack at constant stack voltage of 22.5 V (mean cell voltage = 1.88 V) and 40 °C are plotted in Fig. 10. A mean current density close to 500 mA cm^{−2} is obtained. A larger current density close to 1 A cm^{−2} would be obtained if the stack was operated at nominal (80–90 °C) temperature. Over longer periods of time, two main causes of performance degradation have been observed. The first one is reversible. It is directly related to the purity of the feed water used in the process. Circulation of highly de-ionized water in the stainless steel circuitry of the electrolysis unit increases the concentration of various metallic cations (iron, chromium, nickel) in the feed water. As a result, ion-exchange processes take place in the PEM cells between circulating water and SPE, and metallic cations enter into the SPE, leading to a gradual decrease of current at constant stack voltage. This is mainly

due to the high sensitivity of platinum used at the cathode for the HER to under potential deposition of metals, at the potential of operation of the cathodes. The second one is irreversible and due to the degradation of the MEAs. As in PEM fuel cells, different degradation mechanisms have been identified to explain performance losses. The first one is related to the polymer: at high current density, uneven distribution of current lines may lead to the formation of hot points and uneven membrane swelling. The second one is

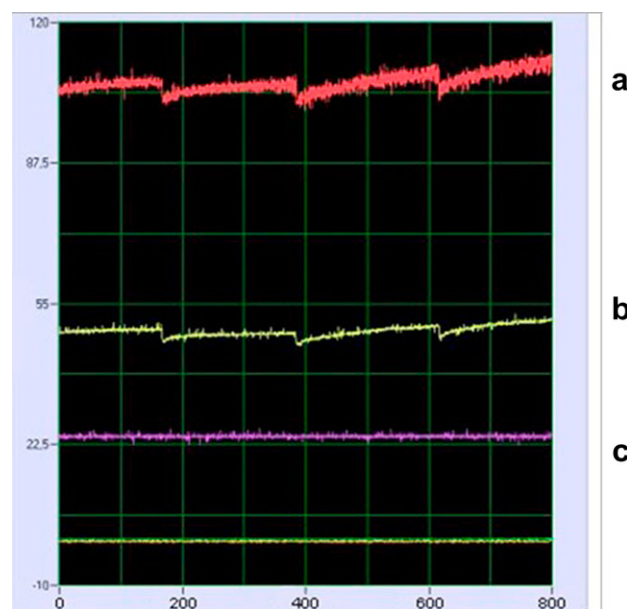


Fig. 10 – (a) Stack current vs. time measured during the first 800 h of operation of the GenHy[®]1000 electrolyzer operating at (b) a temperature $T \approx 40$ °C and (c) constant stack voltage (≈ 23 V). $P = 3$ bars.

related to the Pt catalyst at the cathode: the stability of platinum nanoparticles adsorbed onto carbon carriers is critical and efficiency losses come from either coalescence of nanoparticles or loss of nanoparticles which are released in the circuitry. These effects are directly proportional to the temperature of operation and to the duration of electrolysis. As a result, a gradual and irreversible loss of electrochemical active area can be measured.

5. Conclusion

PEM water electrolysis technology provides a safe and efficient way to produce electrolytic hydrogen and oxygen from renewable energy sources. In the course of the GenHyPEM project, stack efficiencies close to 80% ($\epsilon_{\Delta H}$) have been obtained using 1 Nm³ H₂/h capacity electrolyzers operating at high (1 A cm⁻²) current densities. Experiments have been made in the 1–130 bar pressure range, offering the possibility to store hydrogen directly in pressurized vessels. In view of the so-called “hydrogen society”, PEM technology can potentially be used for the development of miscellaneous applications ranging from auxiliary power units (APU) for domestic end uses to hydrogen refueling stations, but higher operating pressures, in the 150–300 bar range, are still required. Although cost considerations still limit the large scale development of PEM electrolyzers, some breakthrough results have been obtained using cheap catalyst carriers of large specific area and a new generation of low-cost and efficient catalytic structures for both hydrogen (HER) and oxygen (OER) evolution reactions and this opens the way to a new range of applications. The purpose of the GenHyPEM project was to take advantage of these new potentialities to develop low-cost PEM electrolytic hydrogen generators. PEM electrolyzers with optimized designs, allowing hydrogen production up to 5 Nm³ H₂/h have been developed so far and tested by industrial partners within the GenHyPEM consortium. Some of them are commercially available for miscellaneous industrial applications. 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 consortium to further bring down the price of these systems and extend their field of application. R&D on low-cost electrocatalysts is also still active and new families of cheap compounds are expected to appear in the short-term.

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