Electrochemical Characterization and Optimization of a PEM Water Electrolysis Stack for Hydrogen Generation

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Polymer Electrolyte Membrane (PEM) water electrolysis is considered as a key process for the conversion of zero-carbon electricity into zero-carbon hydrogen in view of different end-uses (in the chemical industry sector but also for energy storage and transport applications). In conventional systems, PEM water electrolysis cell are usually operating at 1.8 V and 1 A.cm^{-2} ($\approx$ 80% efficiency). Low pressure electrolysers (1-50 bars) that can deliver several tens of Nm^3 H$_2$ / hour are appearing on the market. The technology is well-suited for operation using intermittent and fluctuating power sources but still suffers from an elevated cost. Operation at higher current densities could help to bring cost down to market requirements but innovative cell design are needed. The purpose of this communication is to provide some insight on the electrochemical characterization and optimization of PEM water electrolysis stacks. A simple hydrodynamic model has been used to optimize the internal geometry of the PEM cells (selection of cell components, internal design, geometry) from an engineering viewpoint. Cyclic voltammetry measurements have been made to identify the origin of performance limitations and to evaluate the homogeneity of the electrical environment experienced by individual membrane-electrode assemblies during operation. Some issues related to the development of next generation PEM electrolysers equipped with simplified cell structures and operating at higher current densities (in the multi Amp per cm^2 range) in view of future market applications are discussed.

1. Introduction

From a historical perspective, the concept of solid polymer electrolyte (SPE) cell was introduced by Grubb in the early 1950s, at the dawn of the US space program (Grubb, 1959). At that time, compact and highly efficient electrochemical devices were needed to provide electricity for on-board requirements and H$_2$/O$_2$ fuel cell technology was selected because of some inherent advantages, in particular its ability to operate continuously and safely in zero-gravity environments. The concept was later extended to water electrolysis (so-called Polymer Electrolyte Membrane or PEM technology). A significant step forward was made in the 1960s with the development of ionomers of appropriate ionic conductivity and chemical stability. Sulfonated tetrafluoroethylene based fluoropolymer–copolymers, commercialized by the US company DuPont de Nemours under Nafion® trade name became very popular. These materials are characterized by their equivalent weight *i.e.* the mass of one equivalent of chargeTheir microstructure and physical properties have been extensively studied (Mauritz and Moore, 2004). For practical applications, Nafion® membranes offer a good compromise between somewhat incompatible properties: they have an excellent ionic conductivity (equivalent to that of 1 M aqueous solutions of sulfuric acid) and a sufficiently low gas solubility (to limit undesired cross-permeation phenomena), and they also offer good mechanical properties (when appropriately supported, they can sustain high differential operating pressures). Main limitations come from their cost and their water-swelling properties that restrict practical uses to operating temperatures less than 100°C. Above this value, homogeneity and mechanical properties are dramatically lost. PEM water electrolysis cells use thin (150 – 250 μm thick) proton-conducting membranes. The small distance between anode and cathode make these cells very efficient (according to the literature, water electrolysis cells can reach an efficiency (based on the higher heating value of hydrogen) of 80% at 1 A

cm^{-2}, a value which is common good practice, at least at the lab-scale, Millet, 2011), and capable of operation at high current density (several A cm^{-2} have been reported). The strong acidity of the membrane (pH ≈ 0) requires the use of inert electronic carriers (carbonaceous species, mainly carbon powder, are used at the cathode and electronic conducting oxides at the anode) and platinum-group metals (PGM) electrocatalysts. In the industry sector, water electrolysis technology is dominated by the more mature alkaline process. Because of its cost and some specific operational features (compactness, ability to operate at elevated current density and under severe pressure differences, absence of corrosive electrolyte), PEM technology has been mainly used for some niche markets, in particular for the generation of oxygen in anaerobic environments (underwater for submarines or space). For such applications, PEM offers several decisive advantages: electrolysers are more compact (PEM water electrolysis cells can be operated in the multi A cm^{-2} range), more efficient at high current density (heat management is simplified), safer (no corrosive liquid electrolyte is required) and offers the possibility to operate under pressure difference to release oxygen at atmospheric pressure and pressurized hydrogen for disposal. The situation changed in the 1970s after the first oil crisis. It was then realized that water electrolysis could be the appropriate process for transforming zero-carbon electricity into zero-carbon energy carriers for different end-uses and large scale deployment became a subject of interest (DOE report, 1981). Since then, the need for alternative green energy paths has become more stringent because in addition to the risks associated with the growing scarcity of fossil hydrocarbons, new risks (in particular those associated with increasing concentrations of carbon dioxide in the atmosphere, resulting green-house effects, global warming and climate change) have appeared. Ambitious R&D programs have been implemented in industrial countries to promote the so-called "hydrogen economy", *i.e.* a global organization of the society based on hydrogen as an energy carrier in which the consumption of fossil fuels could be significantly reduced (Cerri *et al.*, 2012). In this context, water electrolysis is expected to take a significant place in emerging markets, those related to transportation (hydrogen refueling stations are being developed to supply hydrogen of electrolytic grade to fuel cell vehicles that are appearing), those related to power grid regulation (PEM water electrolysers are flexible devices that can operate between 10 and 120% power loads without significant harms) and those related to seasonal storage of large amounts of electricity. PEM water electrolysis is an efficient, durable and very flexible technology, that can sustain successive on/off power cycles, and which is therefore well-suited for water splitting using intermittent power sources but also for the production of hydrogen from off-peak nuclear power electricity. However, market requirements are calling for larger, more compact, more efficient, more durable and less expensive systems. Cell design is very critical to reach these goals. In this paper, results related to the characterization and optimization of a twelve-cell PEM stack (internal cell design, geometry, mass flows) are reported, in order to illustrate the challenges faced by electrochemical engineers working on process optimization.

2. Experimental section

2.1 Membrane electrode assemblies

Principles of PEM water electrolysis are pictured in figure 1. Water is split into its elemental components using a thin electrochemical cell made of a central polymer film (SPE = solid polymer electrolyte) surface-coated by to appropriate catalytic layers. Carbon-supported platinum (nanoparticles) are used at the cathode for the hydrogen evolution reaction (HER) and un-supported iridium oxide particles are used at the anode for the oxygen evolution reaction (OER). During electrolysis, liquid water supplied to the anode is oxidized, leading to the formation of gaseous oxygen and protons. Hydrated protons migrate across the solid polymer membrane (SPE) down to the cathode where they are finally reduced into evolving gaseous hydrogen. Half-cell reactions are those of figure 1. The high efficiency of the process comes from the small distance between anode and cathode (typically in the 150 – 250 μm range) and from the use of efficient platinum group metal (PGM) catalysts (Millet *et al.*, 1989). Low cost alternative catalysts can also be used (Dinh-Nguyen et al., 2012) but PGM nanoparticles (carbon-supported platinum at the cathode and iridium dioxide at the anode) are still the most efficient. Nanoparticles are used to increase the surface to volume ratio and to reduce catalyst loadings. Twelve circular membrane-electrode assemblies (MEAs), 250 cm^2 each, were prepared using Nafion 117 SPEs. Catalytic inks containing a suspension of catalytic particles in an alcoholic solution of ionomer chains were ultra sonicated and then automatically sprayed over the surface of the SPE using a catalytic ink printer (figure 2). The thickness of the catalytic layers and the amount of catalyst deposited at the surface of the SPE are directly related to the time of the coating process. 0.5 mg cm^{-2} platinum loadings and 1.0 mg cm^{-2} IrO_2 loadings were used for the experiments. After deposition of the two catalytic layers, MEAs were dried in air to remove alcohols and improve surface adhesion and then mounted in the stack for the electrochemical experiments.
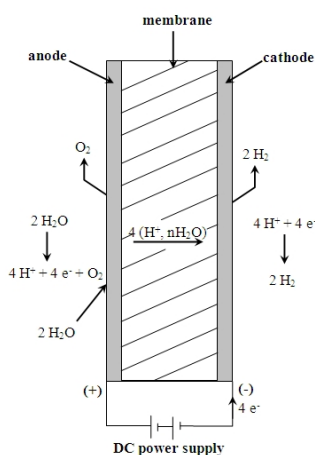
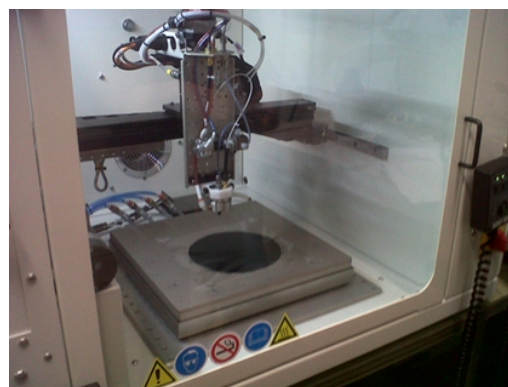Figure 1: principles of PEM water electrolysis.

Figure 2: preparation of MEAs by ink printing.

2.2 PEM water electrolysis cell and stack

The cross-section of a typical PEM water electrolysis cell showing individual cell components is provided in figure 3. The central MEA is clamped between two porous current distributors made of sintered titanium particles. Their porosity is adjusted to facilitate mass transport of liquid and gaseous species through the pores during operation. Two titanium end-plates delimit the cell which is rather compact, typical thicknesses ranging between 5 and 7 mm. Grid spacers were introduced between end-plates and current distributors to manage open porosity areas where liquid water can be pumped and gas production can be collected.
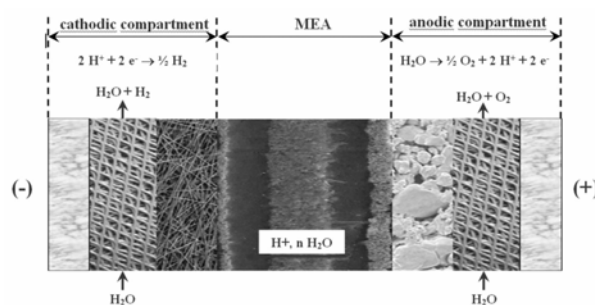

Figure 3: cross-section of a PEM water electrolysis cell.

Figure 4: PEM water electrolysis stack.

In order to increase the production capacity of the electrolyser, individual PEM cells are stacked together in a filter-press configuration. Results reported here were obtained using the 12-cell stack of figure 4. The cells are mounted on a thick stainless steel front flange which can receive a pressurization vessel for operation above atmospheric pressure. A test bench available in our group can be used to perform experiments up to 50 bars and 2 A cm^{-2}.

2.3 Characterization tools

Mass flow equations have been solved by finite element analysis (Comsol Multiphysics$^{®}$ software). The PEM stack has been characterized electrochemically using a Modulab (Solartron Analytical) potentiostat equipped with a 50A amperometric booster.

3. Results and discussion

3.1 Numerical model

The internal design of a PEM water electrolysis cell is very critical because it determines the electrochemical performances. The most stringent requirement is that water should be homogeneously distributed in each cell over the entire active area. The modeling of hydrodynamics in PEM water electrolysers can be a very tough problem. The level of complexity depends on the level of detail and accuracy that is needed. There are two main categories of physical problems that are difficult to handle

and that are calling for simplifying assumptions. The first one comes from the fact that liquid-gas biphasic mixtures are in circulation. The second one comes from the intentionally porous nature of current distributors, through which complex (possibly non-stationary) mass transport phenomena are taking place. These difficulties can be somewhat circumvented by firstly considering monophasic liquid flows. Results obtained under such simplifying assumptions can significantly help the designer to reach a proper cell design. This is what was done here. Considering the pumping of liquid water across anodic cell compartments, what is needed is to adjust the internal cell design in order to distribute water homogeneously over the entire operating surface. Several models of turbulent flow can be used to solve that kind of problem, depending on the number of differential equations required to evaluate turbulent viscosity. Most popular ones are so-called Prandtl and k-ε models. Results reported in this work were obtained using the second one, because it offers the opportunity to take into account the dissipation of kinetic energy of the turbulent flow from large to small swirls. The turbulence kinetic energy k and its dissipation function ε are convected, diffused, created or destroyed during the process. Transfer equations for k and ε are derived from Navier-Stokes equations, integrated over given time intervals, taking into account some product terms of fluctuating kinetics. Assuming that the fluid under consideration is not compressible, the description of transport phenomena is obtained by solving a set of differential equations including modified Navier Stokes equations (taking into account swirling viscosity), continuity equations (1,2) and k- ε equations (3,4).

$$-\vec{\nabla} \bullet \left[\left(\eta + \rho C_\mu \frac{k^2}{\varepsilon} \right)(\vec{\nabla} \bullet \vec{U}) + (\vec{\nabla} \bullet \vec{U})^T) \right] + \rho(\vec{U} \bullet \vec{\nabla})\vec{U} + \vec{\nabla}p = \vec{0} \tag{1}$$

$$\vec{\nabla} \bullet \vec{U} = 0 \tag{2}$$

$$-\vec{\nabla} \bullet \left[\left(\eta + \rho \frac{C_\mu}{\sigma_k} \frac{k^2}{\varepsilon} \right)\vec{\nabla}k \right] + \rho\vec{U} \bullet \vec{\nabla}k = \rho C_\mu \frac{k^2}{2\varepsilon} \cdot (\vec{\nabla} \bullet \vec{U} + (\vec{\nabla} \bullet \vec{U})^T)^2 - \rho\varepsilon \tag{3}$$

$$-\vec{\nabla} \bullet \left[\left(\eta + \rho \frac{C_\mu}{\sigma_\varepsilon} \frac{k^2}{\varepsilon} \right)\vec{\nabla}\varepsilon \right] + \rho\vec{U} \bullet \vec{\nabla}\varepsilon = \rho C_{\varepsilon1} \frac{k}{2} \cdot (\vec{\nabla} \bullet \vec{U} + (\vec{\nabla} \bullet \vec{U})^T)^2 - \rho C_{\varepsilon2} \frac{\varepsilon^2}{k} \tag{4}$$

where : C_μ , $C_{\varepsilon1}$ et $C_{\varepsilon2}$ are model constants ; σ_k is the turbulent Prandtl number of energy k; σ_ε is the turbulent Prandtl number of function ε. The stack shown in figure 4 has been digitalized and above-mentioned mass flow equations have been solved with appropriate boundary conditions using COMSOL Multiphysics® software. A global view of the digitalized PEM stack and details of an individual PEM cells are provided in figures 5 and 6 respectively.
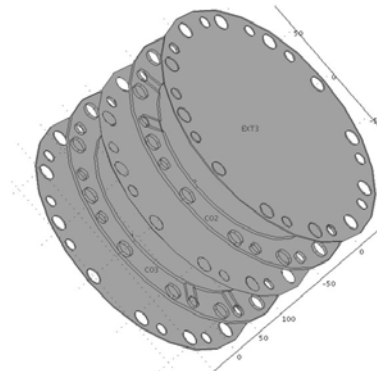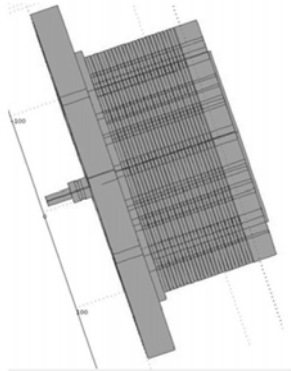

Figure 5: numerical representation of the PEM stack.   *Figure 6: numerical representation of a PEM cell.*

3.2 Optimization of cell design
Our main concern during this work was to find the conditions that would insure a proper distribution of water flow from one cell to the other but also inside each individual cell. The solution to the first problem is dominated by the geometry and disposition of water inlets and outlets. The model allows us to calculate local flow rates across individual cells. Integration over the entire surface and over all the cells yields the

relationship between flow rates and pressure drops across individual cells and across the entire stack. Results cannot be discussed in details within the limited format of this communication but main results have been summarized. Figure 7 shows the quasi-stationary situation when liquid water is pumped across a stack equipped with pairs of inlets and outlets. By adjusting their diameter, all cells can be fed homogeneously.
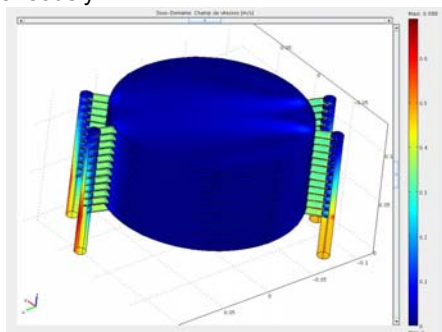

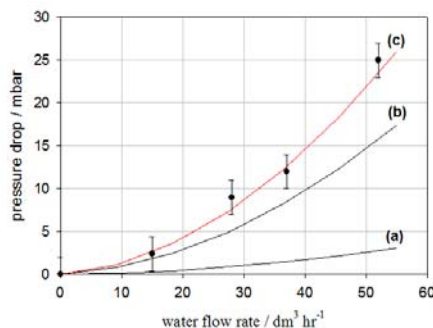Figure 7: numerical representation of the PEM stack.

Figure 8: pressure drop versus water flow rate : experimental (●) and model (−) relationships.

The second problem (homogenous distribution of flow rates inside each cell) is more critical. The void fraction, turbulences and the pressure drop across each cell must be adjusted so that water can be evenly distributed. Even when pairs of inlets/outlets are used, there is a tendency for the liquid to flow directly across the cell, leaving aside some areas where quasi-stagnant conditions of flow prevail. This is of course not acceptable during electrolysis. Addition of current distributors (see figure 3) does not significantly improve the situation. In fact, what matters is the design of the spacers placed between bipolar plates and current distributors and the diameter of cell outlets. They both contribute to increase the pressure drop across the cell at nominal flow-rates and to improve homogeneity of flow across the cells. Experimental and modelled pressure drop versus water flow rate relationships are plotted in figure 8. Curve (a) is the result obtained for the empty cell. Curve (b) was obtained by adding the current collectors and curve (c) by adding the spacer. When experimental curves are appropriately fitted with model equations, this is a good indication that main hydrodynamic features of the cell are taken into account. The situation at local scale can be analyzed and the effect of turbulence promoters inside the cell can be evaluated.

3.3 Electrochemical performances

Cell performances are evaluated by measuring polarisation curves. To enhance performances, the conclusion was reached that there is a need (i) to use MEAs with large roughness factors (to improve efficiency) and (ii) to use proper cell design so that MEAs can operate homogeneously. In-situ information can be gained using some specific electrochemical techniques. For example, cyclic voltammetry can be used to measure the roughness factor of individual cells. Although an internal reference electrode is required to separately measure cathodic and anodic roughnesses, implementation of such reference in a PEM stack is not an easy task. Therefore, we measured cyclic voltammograms (CVs) without the help of a reference, by cycling the cell voltage at constant scan rate (50 mV/s) between ± 1 V. Integration of the CVs yields electric charges that were then compared to a reference charge measured in a reference cell with two smooth platinum and iridium electrodes immersed face-to-face in a aqueous solution of sulfuric acid. The dimensionless ratio of both charges gives the desired roughness factor which can then be plotted as a function of cell number in the stack. Two sets of results obtained with the same MEAs mounted in cells with two different designs are plotted in figure 9. When the cell design is not appropriate, two kinds of negative effects are usually encountered. First effect, roughness factors are low and data-points are significantly scattered (figure 9, bottom). This is a clear indication that MEAs are not operating in the same electrochemical environment. This is usually due to the fact that compression forces over the cells are not homogeneous. As a result, current distributors (see figure 3) do not homogenously contact the surface of active layers. This may come from stacking problems when the cells are assembled, or from a misconception of cell design. When the cells are appropriately mounted and the electrochemical environment is homogeneous, roughness factors are usually higher and values less scattered (figure 9, top). Second effect, mass transport limitations are sometimes observed on polarization curves. An example is provided in figure 10. In such cases, performances differ from one cell to the other and there is a tendency to reach limiting current values. This is usually due to gas screening effects, *i.e.* the formation of a more or less continuous gaseous film at interfaces between catalytic layers and current distributors (see figure 3). Most of the time, the problem comes from anode compartments were liquid water and

gaseous oxygen are flowing in opposite directions across the current collectors. An oxygen film tends to form at a critical current density and then water cannot reach the interface. There is in turn a risk of SPE de-hydration and irreversible degradation. The situation can be improved by a better control adjustment of compression forces and by adjusting the porosity of current collectors (Grigoriev *et al.*, 2009).
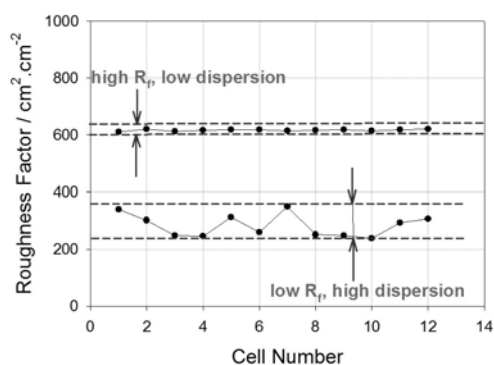

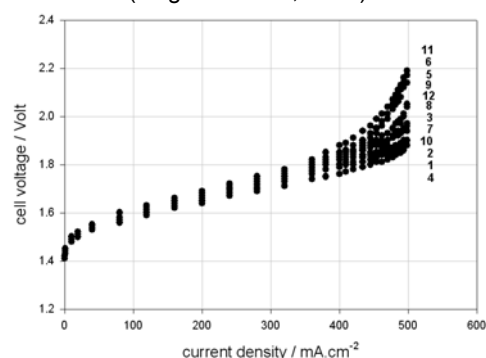Figure 9: Roughness factors of two series of MEAs and cell design.

Figure 10: Polarization curves of individual cells.

4. Conclusions

Polymer Electrolyte Membrane (PEM) water electrolysers of increasing capacity are developed for the chemical industry sector but also for energy storage and transport applications. The technology is well-suited for operation using intermittent and fluctuating power sources but still suffers from elevated costs. Market requirements are calling for more efficient, more compact, more durable and less expensive systems. Operation at elevated current densities offers some promising perspectives to reduce capital expenses but the internal geometry of the cells must be optimized to ensure homogeneous distribution of flow and efficient operation. Results reported in this communication were measured on a prototype PEM water electrolysis stack equipped with twelve membrane – electrode assemblies (MEAs), 250 cm^2 each. First, a simple hydrodynamic model has been used to optimize the internal geometry of individual cells and to ensure a homogeneous distribution of liquid water to all the cells. Then, mean cell roughness factors have been measured. It is shown that they provide a valuable information on the situation that prevails inside the stack during operation and that individual MEAs can experience quite diverse electrochemical environments, a situation detrimental to performances, durability and safety. Heterogeneous electrical environments and distributions of compression forces across the stack can also lead to uneven polarization curves and/or to mass transport limitations which in turn can dry the membranes and ultimately destroy the cells. Such issues are of increasing importance when cells of larger surface are used. Next generation PEM electrolysers equipped with simplified cell structures and operating at higher current densities (in the multi Amp per cm^2 range) are requied. Engineering optimization of such stacks require the solution of combined fluid mechanics, mechanics, heat transfer and electrochemical problems.

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