

Experimental Study of Proton Exchange Membrane Electrolysis System

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Hydrogen produced through water electrolysis or “Power-to-Hydrogen” can be used as a chemical molecule for heavy oil valorization, directly used as a fuel, or injected into the gas network. The natural gas network and the associated storage sites are important means of energy storage. Oxygen is also produced during electrolysis and can be upgraded. In this work, an experimental study focusing on PEM (Proton Exchange Membrane) electrolysis technology was carried out. The 70 kWe machine was able to produce up to 12 Nm³/h of hydrogen under nominal conditions (i.e. 42 kWt of hydrogen) at 99.9994 % purity level. The test rig includes all sub-systems generally found in a commercial machine. The aim was to find and describe empirical relationships between system variables and responses. These relationships were used to improve numerical model accuracy. In particular, the Design of Experiments (DOE) methodology was introduced and applied to electrolysis system assessment. Afterward, conclusions were drawn with regard to the strengths and weaknesses of this methodology when used to describe electrolysis system behavior.

1. Introduction

Hydrogen produced through water electrolysis or “Power-to-Hydrogen” can be used as a chemical molecule for heavy oil valorization, directly used as a fuel, or injected into the gas network (Kezibri and Bouallou, 2020). The natural gas network and the associated storage sites are important means of energy storage. Oxygen is also produced during electrolysis and can be upgraded. In the context of the present study, we exclusively focus on low temperature electrolysis (e.g. electrolysis of liquid water). The most developed electrolysis technologies are alkaline technologies and PEM (Proton Exchange Membrane) electrolysis (Kezibri and Bouallou, 2017). PEM electrolyzers operate in an acid medium, with a solid electrolyte consisting of a polymer membrane conducting H⁺ protons. This technology has several advantages, including its compactness, simplicity of design, and higher performance than alkaline technology. On the other hand, it is less developed for large-scale applications and is currently more expensive.

2. Experimental test rig

For this experimental analysis, a test rig was made available to us at the Elogen workshop. The PEM electrolysis system is able to produce up to 12 Nm³/h of hydrogen under nominal conditions (i.e., 42 kW_t of hydrogen, see Table 1). The test rig includes all sub-systems generally found in a commercial machine. This includes a reverse osmosis water purification unit, a purified water tank, the anode and cathode water circulation loops, two circulating water purification resins, and a hydrogen purification unit. With regard to system control, the main regulated variables are stack temperature through cooling system regulation; produced gas pressure through control valves; water levels within the separators through a control valve and a lifting pump; stack current density through converter power. For this system (Figure 1), the measured parameters are electrical data (current, potential, and power), temperature data (water and produced gases), pressure data (hydrogen, oxygen and nitrogen), levels in the separator tanks and other data such as water conductivity, flow rate of hydrogen, gas purity, etc. Data acquisition can be done with a minimum sampling period of one second. An average time step

of 10 s seems sufficient to follow the evolution of physical quantities of interest. It is worth noting that the cooling loop ensures heat exchange between the PEM module and cooling utilities.

Table 1: Technical specifications of the used test rig

Number of PEM stacks	up to 2	
Stack nominal power	52.8	kW _e
Hydrogen nominal production	12	Nm ³ .h ⁻¹
Stack nominal potential	101	V
Nominal current density	0,9	A.cm ²
Membrane active area	594	cm ²
Number of cells per stack	55	–
Temperature range	45-65	°C
Anode pressure range	5-14	barg
Cathode pressure range	6-15	barg
Water Circulation flow rate	3.1	m ³ .h ⁻¹

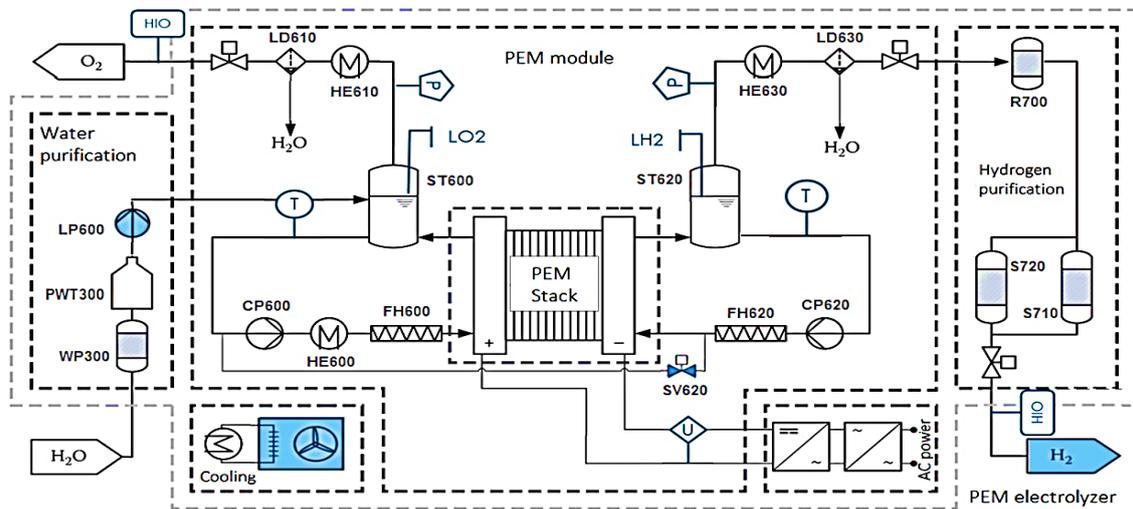


Figure 1: Measurement points for stack current and potential (I , U), temperature (T), pressure (P), vessel levels (LO_2 , LH_2), and gas purity (OIH , HIO)

2.1 Design of experiments methodology

Design of Experiments (DOE) is a statistical tool deployed in various types of systems, process and product design, development, and optimization. It is a multipurpose tool that can be used to solve various engineering problems. It aims to obtain the maximal results from data while minimizing inputs in terms of experiments required. Durakovic (2017) explored historical aspects of DOE and provided state of the art on its application, guided researchers on how to conceptualize, plan, and conduct experiments, and how to analyze and interpret data, including examples. In the last year's application of DOE has been growing rapidly in manufacturing as well as non-manufacturing industries, especially for the most promising technologies for a complete transition to sustainable energies. Thus, Rom an-Ramírez and Marco (2022) were interested in its application to the evaluation of lithium-ion batteries (LIBs) which is only just beginning to be recognized, and Lee et al. (2022) are interested in a comprehensive review of the Design of Experimental (DOE) for water and wastewater treatment by examining key concepts, methodology, and its contextualized application.

2.2 DOE terminology

There are a few terms that are often used in the DOE field, which we would like to define before applying this methodology to the studied system. The influencing factors are the set of decision or control variables involved in the study. They are commonly noted x_i . These factors are suspected to have an impact on system behavior. The system responses R_j are the parameters of interest or the objective functions to be optimized. By varying the levels of the influencing factors x_i , we examine the impact on the values of these responses and measure

the change's order of magnitude. To link factors to system responses, we can use a DOE procedure that follows a polynomial form. We write that each response R_j is a function of the set of influencing factors x_i . We have:

$$R_j = a_0 + \sum a_i x_i + \sum a_{ij} x_i x_j \quad (1)$$

Here the a_i coefficients measure each x_i factor's contribution to response variation while a_{ij} denotes the impact of each x_i and x_j interaction. By solving the polynomial form for these coefficients, we can quantify the impact of each factor or combination of factors on system responses.

2.3 DOE applied to PEM electrolysis

Santarelli et al. (2009) are the first authors to apply the DOE methodology to produce a simple and comprehensive mathematical model for stack potential and water permeation through the membrane (Medina and Santarelli, 2010). The results from quadratic formulas that the authors obtained are in agreement with the experimental behavior of the PEM stack. However, these formulas remain exclusive to the studied system for which they were generated. The aim of such an approach is to create, in a fast and simple way, a dataset that will be translated into expressions describing the behavior of a specific phenomenon in an electrolysis system within a limited domain.

Using the test rig, we carry out steady-state measurements of two system responses at different operating conditions of current density, cathodic pressure, and temperature. The DOE post-processing methodology requires a minimum of $3^3 = 27$ tests to achieve a full factorial plan. Each factor is varied within a set range where three levels are chosen. These levels are shown in Figure 2.

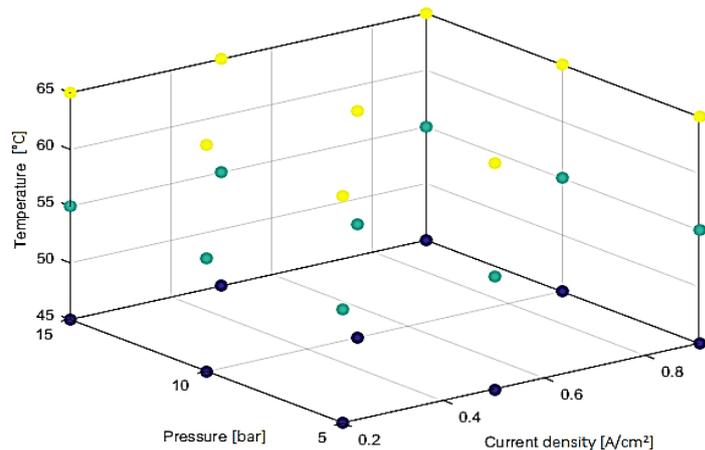


Figure 2: presentation of the levels considered for influencing factors: stack temperature [°C], cathode side pressure [bar], and current density [A.cm⁻²]

The type of response targeted during this experimental measurement will mainly concern the average cell potential and the hydrogen permeation. Nevertheless, other kinds of responses could be considered by applying the same approach, such as the amount of water permeation, stack degradation phenomena, or specific consumption of BOP equipment. However, specific test rigs need to be set up to meet the requirements of measured response.

2.4 Design of experiments for cell potential

Following the DOE plan described earlier, we model the voltage of the cell through this plane of experiments which gives us a rapid evaluation of its behavior according to the operating conditions applied. The direct result of this approach is the generation of the first-order model applied to the cell voltage Eq(2).

$$U_{cell} = 1.68 + a_i i - a_T T + a_P P - a_{iT} iT - a_{iP} iP - a_{TP} TP \quad (2)$$

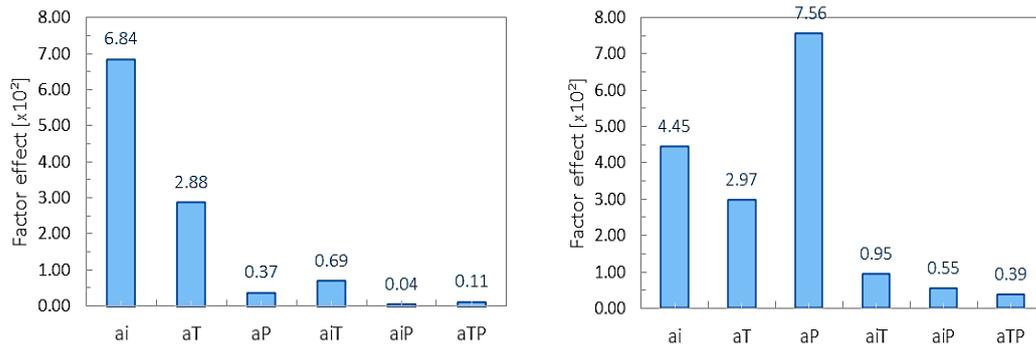


Figure 3: (a) Coefficients of the DOE plan for cell potential (b) Coefficients of the DOE plan for hydrogen crossover

Figure 3a shows the contribution of each term in formula (2) to the variation of the average cell potential. The sign in front of each coefficient indicates the direction of evolution of the response with respect to a variation of the associated factor. If we merely compare the individual effect of the factors, it seems natural that current density contributes the most to this variation, followed by temperature and then pressure, with a much smaller contribution. It is also important to emphasize the existence of a strong interaction between current density and operating temperature, which seems to play a significant role in cell potential value.

Lastly, it is important to mention that these findings are only valid inside the considered domain (i.e., Figure 2). Indeed, when low values of current density are applied, the correlation between cell potential and influencing factors no longer follows a linear behavior (i.e., the nonlinear part of the polarization curve). In practice, PEM electrolyzers are operated outside these singular cases to allow a production closer to nominal power with less impact on the energy efficiency of the process.

2.5 Design of experiments for hydrogen crossover

We apply the same approach to evaluate the impact of operating conditions variations on hydrogen permeation through the membrane. This phenomenon is the main reason behind production losses and also presents a challenge to the safety of the process. The system response, in this case, is the molar fraction of hydrogen in produced oxygen at the anode side (denoted HIO). The same DOE plan is applied to obtain the following statistical model:

$$HIO = 0.38 - a_i i - a_T T + a_P P - a_{iT} iT + a_{iP} iP - a_{TP} TP \quad (3)$$

Likewise, the evaluation of model coefficients allows identification of each individual factor's impact on hydrogen fraction in produced oxygen as well as factors interaction impact. Pressure seems to have the highest effect on hydrogen fraction, followed by current density and then temperature. An increase in pressure causes a larger fraction of hydrogen to cross the membrane and increases its fraction on the anode side. This outcome is in agreement with experimental observations (Grigoriev et al., 2009). On the other hand, current density and temperature have a reverse effect on hydrogen crossover (negative sign for coefficients a_i and a_T). The impact of binary interactions on this response is more difficult to determine because of the small difference between respective coefficients. For this specific phenomenon, there are other influencing factors that can impact its behavior, in particular, the thickness of the membrane or the addition of a catalyst on the anode side to react with permeated hydrogen. Experimental investigation of the influence of these other parameters requires dedicated test rigs and additional setup.

2.6 Stack heat capacity

The aim behind this step is to determine the variation of stack heat capacity C_{th} as a function of temperature. Under steady-state conditions, the adopted macroscopic approach consists in considering the stack as a single homogeneous mass with a constant mean temperature. In practice, to determine the thermal capacity, we apply the so-called "double slope" approach commonly used in calorimetry techniques. First, the stack temperature is gradually increased through heating of circulating water by applying a heating power of $\dot{Q}_h = 500$ W until a steady state is reached. During this phase, no hydrogen production is performed, and the current density is set to naught. Then, electric heating is interrupted to allow cooling of the stack and return to room temperature. During both the heating and cooling phases, stack temperature is recorded. Considering a constant temperature

variation ΔT around a given stack temperature at both heating and cooling phases, stack thermal capacity at this temperature is determined through time intervals Δt_h and Δt_c for each phase slope according to the expression given by Eq(4):

$$C_{th}(T) = \frac{\dot{Q}_h}{\Delta T(T)} (\Delta t_h - \Delta t_c) \quad (4)$$

Figure 4a gives the experimental heating and cooling curves obtained for the test rig. While electric heating is enabled, the stack takes a little over 3 h to reach a stable temperature of about 46 °C. The cooling phase lasts a little more than 6 h to reach a room temperature of 31 °C. The numerical regression of the chosen hot and cold points makes it possible to link stack heat capacity with operating temperature (see Figure 4b).

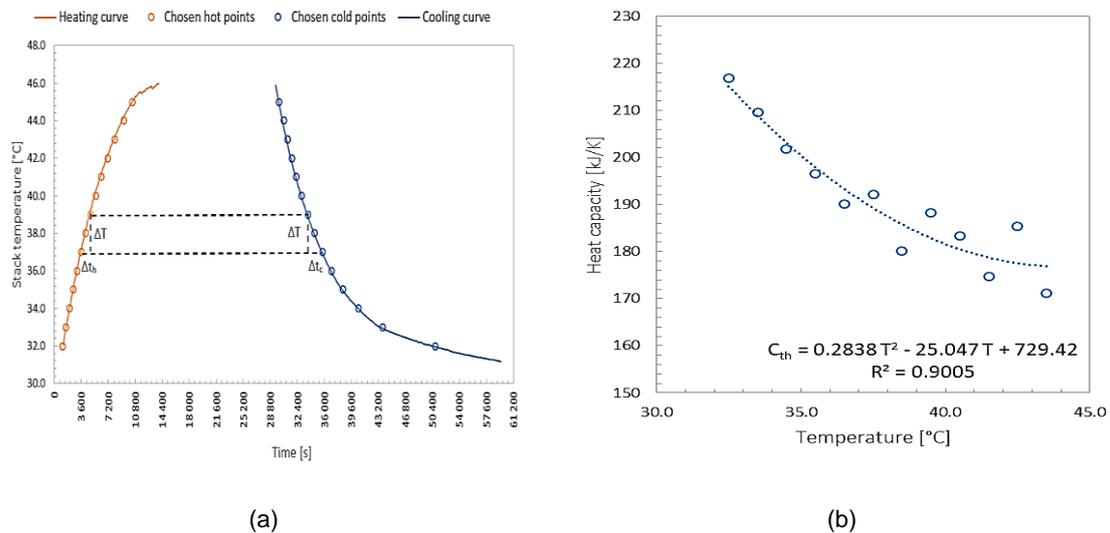


Figure 4: (a) Experimental curves for stack heating and cooling phases (b) Stack overall heat capacity as function of temperature

2.7 Experimental analysis at rated power

In order to assess the steady-state electrolyzer behavior, the test rig was run for a period of 45 h under nominal operating conditions (see Table 1). The experimental data acquisition is performed every 10 s. A satisfactory delay to thoroughly describe the quasi-stationary behavior of the system's responses.

In particular, we focus on stack temperature impact on its potential. Figure 5 shows the profiles of both these values. As expected, we note that the evolution of the voltage is inversely proportional to that of temperature. This important input will allow the comparison of the different approaches used for cell potential prediction. The simplest way to numerically assess cell potential at different current densities is to use a regression model at constant temperature and pressure. However, when the system undergoes a change in operating conditions, this approach can quickly become limiting. This is directly linked to the fact that the considered regression parameters (exchange current densities, ohmic resistance and charge transfer coefficients) also depend on operating conditions, particularly on temperature.

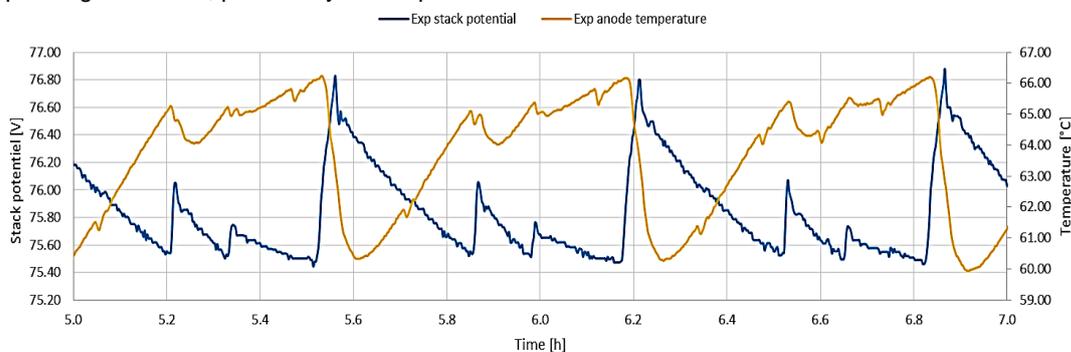


Figure 5: Experimental stack potential and temperature at rated power

Figure 6 shows a comparison between three approaches: the above-described simple regression model, the multi-regression model, and the DOE model. A simple regression model (i.e., established only from a single polarization curve) fails to correctly predict temperature impact on potential variation. On the other hand, both multi-regression and DOE models show this change and can reproduce the measured behavior of stack potential. The observed difference between the DOE model and experimental measurement is due to the fact that the model was based on average cell potential, which is then multiplied by the number of cells to estimate stack potential. In addition, the experimental temperature is measured at the outlet of the gas separator tanks. Both models do not reproduce the recorded potential peaks, which follow the actual stack temperature. To improve this numerical prediction, a measurement of stack outlet temperature should be considered in the used test rig.

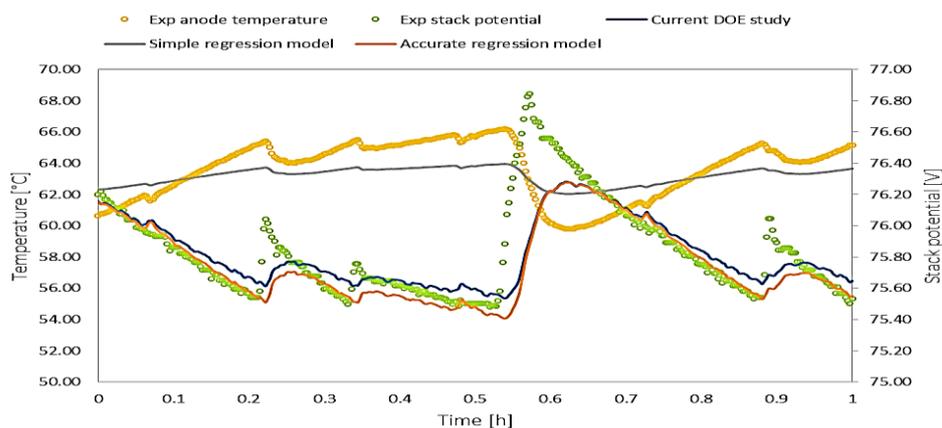


Figure 6: Comparison between numerical regression methods and DOE methodology

3. Conclusion

Clearly and objectively, experimental analysis plays an important role in achieving the semi-empirical approach chosen in this study. The results were encouraging and confirmed the utility of this approach, which prevents a precise designation of specific contributions of each physical phenomenon because of its abstract mathematical formulation. This methodology could serve as a quick and easy diagnostic tool to implement either while monitoring the system evolution after several hundreds of operational hours or simply to reduce the number of fitting parameters and complexity of governing equations usually used in literature work. The Design of Experiments methodology was applied to a limited number of PEM electrolysis responses, and as a perspective, we can suggest extending this methodology to examine other phenomena of interest.

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