NEW DEVELOPMENTS IN THE APPLICATION OF MULTI-PARAMETRIC SENSITIVITY ANALYSIS IN PEM FUEL CELL MODELING

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Abstract – **Simulation of Proton Exchange Membrane Fuel Cells (PEMFC) may work as a powerful tool in the development and the widespread testing of such alternative energy source. In order to obtain an adequate PEMFC model, which could be used in the analysis of fuel cell generation systems, it is necessary to define the values for a specific group of modeling parameters. The simulation results are strongly affected by the choice of such modeling parameters. Multi-Parametric Sensitivity Analysis (MPSA) is a tool that can be used to define the relative importance of the factors related to the model, because it encompasses the entire parameter space. This paper presents a sensitivity investigation of PEMFC electrochemical models, aiming at to determine the relative importance of each parameter on the model results.**

KEYWORDS

Fuel cell, modeling and simulation, sensitivity analysis.

I. INTRODUCTION

The utilization of fossil fuels has increased, along the years, the concentration of toxic gases in the environment, such as SO_x, NO_x, CO and CO_2. In addition, it can be said that the world is strongly dependent on these energy sources, which are becoming scarcer and even more expensive. Research on alternative and renewable energy sources is a worldwide matter. Such sources should be friendlier to the environment, cleaner and more efficient than the conventional sources. Among the energy sources considered, such as wind power, photovoltaic power and small hydropower, the Fuel Cell (FC) stacks have received more attention in the last few years, especially because of their high electrical and overall efficiency (up to 80% for combined heat and power), low aggression to the environment, excellent dynamic response and superior reliability and durability.

Among the various FC models presently available, the Proton Exchange Membrane Fuel Cell (PEMFC) appears as a more promising source to be used in residences, industries and in small and large scales of distributed generation systems. The main characteristics of PEMFC stacks are: (*i*) they produce water as a residue; (*ii*) they have high efficiency when compared to thermal generation; (*iii*) they operate at low temperatures (up to 90 ^{o}C), which allows a fast start-up; and (*iv*) they use a solid polymer as the electrolyte, which reduces concerns related to construction, transport and safety.

However, the current high costs of the FC stacks make difficult both development and the widespread usage of these systems, especially in developing countries. In order to sort that out, the Group of Micropower Plants Development (NUDEMI) of the Federal University of Santa Maria (UFSM - Brazil) and the Engineering Division of Colorado School of Mines (CSM – USA) have been working with the application of renewable energy sources, mathematical modeling and physical simulation of power sources and, in particular, with PEMFC stacks [1].

The main difficulty to obtain an accurate PEMFC dynamical model is the lack of information about the exact values that should be used for the modeling parameters. These parameters may affect significantly the voltage, power, humidity and temperature characteristics of the stack. There are several papers [1-6, 8] dealing with modeling and simulation of PEMFC, some of them discussing the dynamical behavior of unit cells and stacks [1, 3, 4] and also presenting some aspects related to the modeling parameters [8].

The values used for the parameters are manly based on manufacturing data and on laboratory experiments. However, some aspects of PEMFC operation are still difficult to model accurately and some process are proprietary of the manufacturers. Differences between measurement and calculation arise due to uncertainties stemming not only from experimental measurements but also from ill-defined parameters [10, 11]. The relative importance of the physical and electrochemical processes in a FC can be evaluated using a generalized Multi-Parametric Sensitivity Analysis (MPSA), which encompasses the entire model parameter space. Such analysis is conducted in this paper, using a FC electrochemical model and data from a 500 W PEMFC stack, manufactured by the company BCS Technology [9].

II. PEM FUEL CELL ELECTROCHEMICAL MODEL

This section presents an electrochemical model, which can be used to predict the dynamic behavior of PEMFC stacks. This mathematical model uses a group of parameters, whose definition is essential for the best simulation results. The output voltage of a single cell, V_{FC}, can be defined as follow by Eq. (1); and, for n cells, the stack voltage, V_s, can be calculated by Eq. (2) [1]:

$$V_{FC} = E_{Nernst} - V_{act} - V_{ohmic} - V_{con} \quad (1)$$

$$V_s = n \cdot V_{FC} \quad (2)$$

In Eq. (1), E_{Nernst} is the thermodynamic potential of each unit cell and it represents its reversible voltage; V_{act} is the voltage drop associated with the activation of the anode and of the cathode; V_{ohmic} is the ohmic voltage drop, a measure of the voltage drop associated with the conduction of protons and electrons; and V_{con} represents the voltage drop resulted from the decrease in the concentration of oxygen and hydrogen [4]. The first term of Eq. (1) represents the FC open circuit voltage, while the three last terms represent reduction in this voltage. The resulting voltage, V_{FC}, is the FC useful voltage for a certain operating condition. In addition to the last three terms there is another voltage drop involving the PEMFC operation: this additional drop results from the circulation of electronic currents through the electrolyte or, similarly, from the fuel crossover through the electrolyte [4]. This voltage drop is also modeled, considering a permanent FC current density (J_n), which is added to the main FC current density, even when the FC is operated without any load. Each term of Eq. (1) is defined by [1,2,4]:

$$E_{Nernst} = 1.229 - 0.85.10^{-3}.(T - 298.15) + 4.31.10^{-5}.T.\left[\ln(P_{H_2}) + \frac{1}{2}\ln(P_{O_2})\right] \quad (3)$$

$$V_{act} = -\left[\xi_1 + \xi_2.T + \xi_3.T.\ln(c_{O_2}) + \xi_4.T.\ln(i_{FC})\right] \quad (4)$$

$$V_{ohmic} = i_{FC}.(R_M + R_C) \quad (5)$$

$$V_{con} = -B.\ln\left(1 - \frac{J}{J_{\max}}\right) \quad (6)$$

$$c_{O_2} = \frac{P_{O_2}}{5.08.10^6.e^{-\left(\frac{498}{T}\right)}} \quad (7)$$

$$R_M = \frac{\rho_M.\ell}{A} \quad (8)$$

where P_{H_2} and P_{O_2} are the partial pressures (atm) of hydrogen and oxygen, respectively; T is the cell absolute temperature (K); i_{FC} is the cell operating current (A); c_{O_2} is the concentration of oxygen in the catalytic interface of the cathode (mol/cm^3); the ξ_i (i =1...4) represent the parametric coefficients for each cell [2]; R_M is the equivalent membrane resistance [2]; R_C is the equivalent contact resistance to electron conduction; J_{max} is the maximum current density; B (V) is a constant dependent of the cell type and its operation state [4]; J is the actual cell current density (A/cm^2), including the permanent current density J_n; ℓ is the membrane thickness (cm); and ρ_M is the membrane specific resistivity (Ω.cm), which can be obtained by:

$$\rho_M = \frac{181.6.\left[1 + 0.03.\left(\frac{i_{FC}}{A}\right) + 0.062.\left(\frac{T}{303}\right)^2.\left(\frac{i_{FC}}{A}\right)^{2.5}\right]}{\left[\psi - 0.634 - 3.\left(\frac{i_{FC}}{A}\right)\right].\exp\left[4.18.\left(\frac{T - 303}{T}\right)\right]} \quad (9)$$

where the term 181.6/(ψ-0.634) is the specific resistivity (Ω.cm) at no current and at temperature of 30°C (303 K); the exponential term in the denominator is the temperature factor correction if the cell is not at 30°C. The parametric coefficient ψ is considered an adjustable parameter, with a possible minimum value of 14 and a maximum value of 23 [2].

Equations (1) to (9) represent the fuel cell stack static behavior. An electrical circuit can be used to model the FC dynamical behavior [1,4]. In a fuel cell dynamic model, there is a first order delay in the activation and the concentration voltage components (represented by the resistances R_{act} and R_{con}, respectively). This delay is caused by the charge double layer effect [4], which causes a retard in the dissipation of the electrical charges near the electrolyte/electrode interface. Then, when there is an increase (decrease) in the FC current, there is a delay until the FC voltage decreases (increases). The ohmic overpotential is not affected by the charge double layer effect, and it is directly related to the current. The dynamical equations of the fuel cell dynamic model are represented by:

$$\frac{dv_d}{dt} = \frac{1}{C} i_{FC} - \frac{1}{\tau} v_d \quad (10)$$

$$\tau = C.R_a = C.(R_{act} + R_{con}) = C.\left(\frac{V_{act} + V_{con}}{i_{FC}}\right) \quad (11)$$

where v_d represents the dynamical voltage (associate with V_{act} and V_{con}), C is the equivalent electrical capacitance; τ is the FC electrical time constant; and R_a is an equivalent resistance, related to the activation and concentration voltage drops.

Including the dynamic behavior (Eq. (10)), the resulting fuel cell voltage is then defined by:

$$V_{FC} = E_{Nernst} - V_{ohmic} - v_d \quad (12)$$

III. PARAMETRIC SENSITIVITY ANALYSIS

The model presented in Section II needs definition of several parameters, prior to computer simulation. In order to investigate the influence of such parameters in PEMFC analysis, a 500 W BCS stack was simulated, and the base parameter set is presented in Table I. These values are based on literature data, for similar stacks [2,4], and also on the manufacturer data [9].

The parameters presented in Table I have the following meaning:

- n: number of cells used in the stack
- A: cell active area (cm^2)

- ℓ: membrane thickness (μm)
- T: cell operating temperature (K)
- P_{O_2} and P_{H_2}: oxygen and hydrogen partial pressures (atm)
- R_C: contact resistance (Ω)
- ξ_i and ψ: parametric coefficients
- J_n: no-load current density (A/cm^2)
- J_{max}: maximum current density (A/cm^2)
- C: equivalent electrical capacitance (F)

TABLE I - PARAMETER SET OF A 500 W BSC STACK

Param.	Value	Param.	Value
n	32	ξ_1	-0.948
A	64 cm^2	ξ_2	0.00286+0.0002.ln (A)+ (4.3.10^{-5}).ln (c_{H_2})
ℓ	178 μm	ξ_3	7.6.10^{-5}
T	333 K	ξ_4	-1.93.10^{-4}
P_{O_2}	0.2095 atm	ψ	23.0
P_{H_2}	1 atm	J_n	3 mA/cm^2
R_C	0.0003 Ω	J_{max}	469 mA/cm^2
B	0.016 V	C	3 F

Using the parameter set presented in Table I, Fig. 1 shows the simulated polarization curve, obtained with the electrochemical model (Section II). Fig. 1 also shows the polarization curve presented in the manufacturer data [9]. As it can be seen, the simulated results present a good agreement with the real data, except at the very beginning and at the very end of the polarization curve.

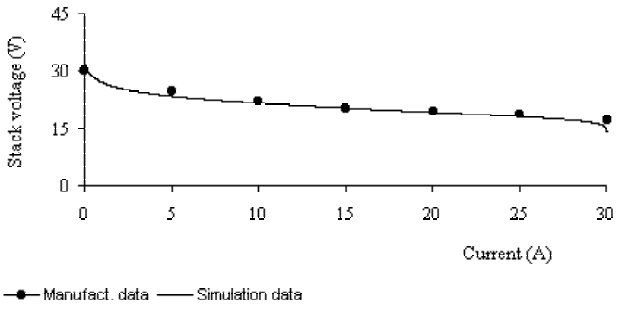


Fig. 1. 500 W BCS stack polarization curve

The discrepancies observed in Fig. 1 are mainly caused by the difficulty to obtain the exact parameter values. As seen in Table I, there are various parameters to be defined, before an accurate simulation could be obtained. In addition, even though there were good agreement between the observed and simulated results, it is not possible to identify the relative importance of each parameter used in the model. Then, in order to investigate that, the parametric sensitivity of the fuel cell electrochemical model can be tested, using the approach of Multi-Parametric Sensitivity Analysis (MPSA) [10]. In order to apply the MPSA to the fuel cell electrochemical model, Fig. 2 presents a block diagram of the model inputs, outputs and feedback signals. The input parameters showed in Fig. 2 will be evaluated in order to define their relative importance on the model results. Only the number of cells (n) will not be evaluated, because it is a constant number with 100% of certainty.

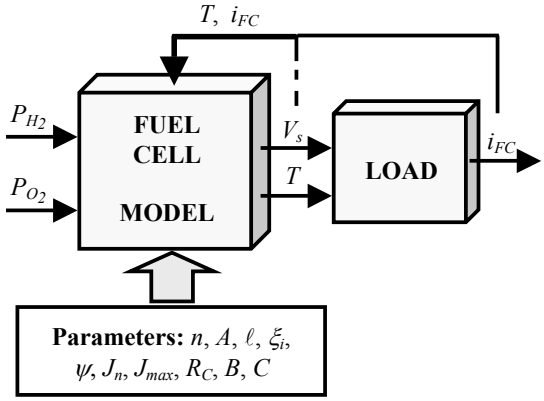


Fig. 2. Block diagram of the fuel cell model

To apply MPSA, the following steps may be followed t for a certain set of parameters [10]:

1. Select the parameters to be tested.
2. Set the range of each parameter.
3. For each parameter, generate a series of independent random numbers with a uniform distribution within the defined range.
4. Run the model using the selected series and calculate the objective function (Eq. (13)) for each value of cell current.
5. Determine the relative importance of each parameter for each value of current, using Eq. 14.
6. Evaluate parametric sensitivity (to define the sensitive and insensitive parameters).

The objective function of the sensitivity analysis usually is calculated from the sum of square errors between observed and modeled values [10]:

$$f = \sum_{i=1}^{k} \left[x_0(i) - x_c(i) \right]^2 \tag{13}$$

where f is the objective function value, $x_0(i)$ is the observed value, $x_c(i)$ is the calculated value and k is the number of elements contained in the random series (Step 3). The observed values used were obtained from simulations that use the base value for each parameter (Table I). The range for each parameter to be evaluated is presented in Table II, for the 500 W BCS stack.

The evaluation of the relative importance of each parameter, independently, on the stack voltage can be obtained by:

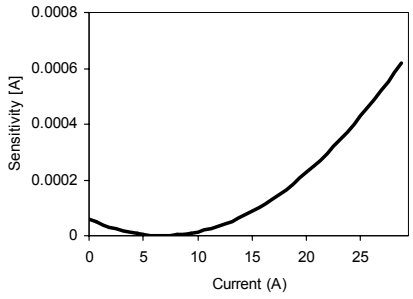
$$\delta_h = \frac{f_h}{x_{0(h)}} \tag{14}$$

where *h* represents each current point.

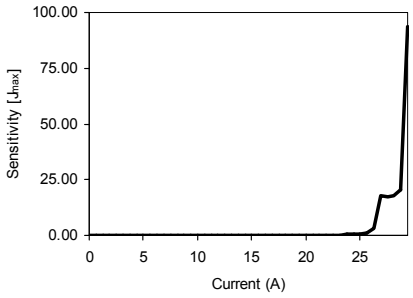
TABLE II – RANGE OF PARAMETER USED IN MPSA

Param.	Test range	Param.	Test range
A	64 ±5% [cm^2]	ξ_1	-0.948 ±10%
ℓ	178 ±5% [μm]	ξ_3	$7.6.10^{-5}$ ±10%
R_C	0.0003 ±15% [Ω]	ξ_4	$-1.93.10^{-4}$ ±10%
B	0.016 ±15% [V]	ψ	15 – 24
J_n	3 ±25% [mA/cm^2]	C	1 – 5 [F]
J_{max}	469 ±10% [mA/cm^2]		

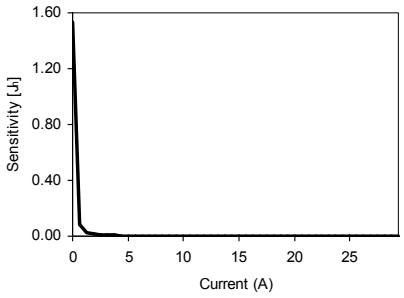
By applying the described procedure to the PEMFC model, using a series of 500 data for each current value, the results presented in Fig. 3 were obtained, for selected parameters. As it can be seen from Fig. 3, the relative effect of the parameters on the model can be classified as (not all parameters are shown due to the paper size restriction): 1) Insensitive: A, ℓ, R_C; 2) Sensitive: J_n, B, ξ_4, ψ; 3) Highly sensitive: J_{max}, ξ_1, ξ_3.



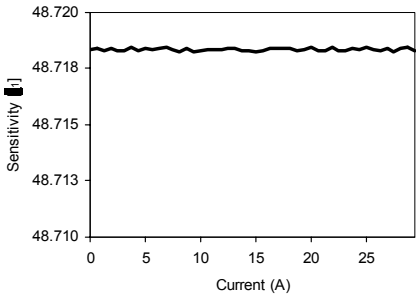
(a) Cell active area



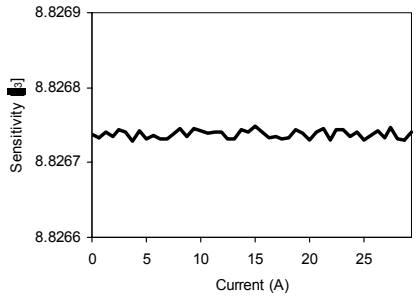
(b) Maximum current density



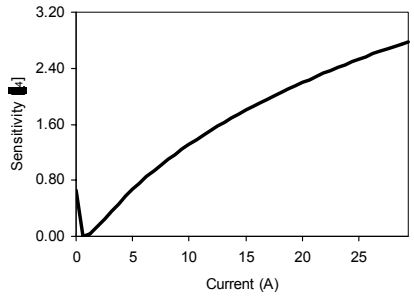
(c) Internal current density



(d) Parameter ξ_1



(e) Parameter ξ_3



(f) Parameter ξ_4

Fig. 3. Relative importance of the modeling parameters

The insensitive parameters are basically the ones related to the cell construction: their influence on the model accuracy is not critical and it is not necessary to know their exact values to have a good response. Parameter J_n only affects the simulation results at low current values, because its value will define the resulting open-circuit voltage, considering the internal current and crossover effect [4]. Parameters B, ξ_4 and ψ also have more influence on the stack voltage for high current values. However, their effect is less accentuate than J_{max}. The parameter B defines the form of the polarization curve, especially in its final portion (near the maximum stack current). The final portion of the polarization curve is characterized by a fast decrease in the voltage, as shown in Fig. 1. For the parameter J_{max} the model results are also more affected for high current values. This can be explained by the logarithm term in Eq. (6): when the current density is close to the maximum value, the logarithm term tend to zero as well the concentration voltage. This, by its turn, changes the resulting stack voltage.

However, for parameters ξ_1 and ξ_3 the model results are affected for all current values in a same order. Their electrochemical exact definition is [2]:

$$\xi_1 = -\frac{\Delta G_a}{2 \cdot F} - \frac{\Delta G_c}{\alpha_c \cdot n \cdot F} \quad (15)$$

$$\xi_3 = \frac{R \cdot (1 - \alpha_c)}{\alpha_c \cdot F} \quad (16)$$

where: ΔG_a is the free activation energy (Gibbs energy) for the standard state (J/mol), referred to the anode; ΔG_c is the free activation energy for the standard state (J/mol), referred to the cathode; α_c is a parameter for the anode chemical activity; F is the Faraday constant; R is the gases universal constant; A is the cell active area (cm^2); c_{H_2} is the hydrogen concentration (mol/cm^3); and c_{H_2O} is the water concentration (mol/cm^3). All this elements are related to the electrochemical process needed for electrode activation and they are difficult to be determined with great accuracy. The values used in the presented model are based on calculation and measured results [2].

Taking the results presented in Fig. 3 into account, the process to define the fuel cell stack parameters is not a simple task and once the parameter set is defined, it is only valid for that specific stack. Considering the relative importance of ξ_1 and ξ_3 on the simulation results, Fig. 4 presents the stack polarization curve, assuming that their values are not well known. It can be seen from this figure that the stack voltage changes considerably, making the polarization curve far from similar to the real data.

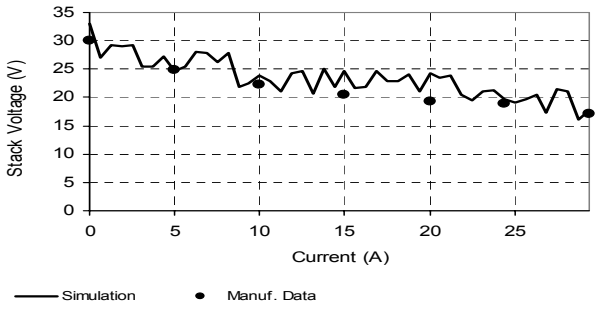


Fig. 4 – Influence of the uncertainty of parameters ξ_1 and ξ_3 on the model results

IV. CONCLUSION

In this paper, an investigation of the influence of the modeling parameters on the dynamical performance of PEMFC simulations is conducted. It shows the effects of some key parameters, using an electrochemical model to evaluate the stack polarization curve based on the dynamic behavior of a 500 W BCS stack and some data from the literature. A basic parameter set is used to shown how the choice of the parameters can influence the initial curve.

The parameters are analyzed using a Multi-Parametric Sensitivity Analysis (MPSA). As a result, the parameters were classified according to their influence in the model results as: insensitive (A, ℓ and R_C), sensitive (J_n, B, ξ_4 and ψ.) and highly sensitive (J_{max}, ξ_1 and ξ_3). For the most sensitive parameters (ξ_1 and ξ_3) it has been shown that the polarization curve can present results that are not similar to the real data. In addition, the results do not present a fixed tendency but they are dispersed along the real curve. As shown in this paper, the definition of the values for the fuel cell simulation parameters is not a simple task and, moreover, once the parameter set is defined, it is only valid for a specific cell or stack. To simulate other fuel cells, almost all the values must be defined again. Using the data presented in this paper, it is possible to evaluate the importance of each parameter in the simulations accuracy and, then, correct the parameters values to obtain the best results.

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