EXPERIMENTAL PARAMETRIZATION OF STEADY-STATE AND DYNAMIC MODELS REPRESENTED BY AN ELECTRICAL CIRCUIT OF A PEM FUEL CELL

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Abstract – **This work presents a study of parametrization of dynamic and steady-state models of PEM fuel cell from experimental results, since to obtain these parameters using analytical and empirical equation is most of the times very difficulty, due to many variables that have influence to the behavior of the cell voltage, such as water content in the membrane, active area of the electrodes, etc. In this paper an electrical circuit that represents the dynamic response and the equations that represents the steady-state model will be presented, followed by experimental results used to determine the parameters.**

KEYWORDS

Fuel Cell, PEM, Dynamic, Steady-State, Model.

I. INTRODUCTION

In order to obtain power sources that come to supply the difficulties of the actual world energetic system, some alternatives energetic sources have been studied. As one of the most promising power sources, fuel cells arise as an excellent alternative for many applications, as vehicles, portable electronics and small stationary applications.

Although, there are many types of fuel cell, each one differentiated by some characteristics, as electrolyte that is used and temperature of operation, the proton exchange membrane fuel cell (PEMFC) appear as the most interest from the industry, mainly transport, because it can start quickly due to a low operating temperature.

The behavior of PEM fuel cell is difficulty to model analytically, since there are many variables involved, such as temperature, pressure, current, water content of the membrane, etc. Additionally, some of these variables are interdependent, becoming into non-linear model. This problem has leaded some researchers to develop empirical models of PEMFC performance. Many empirical models have been presented, but still difficulty to obtain the parameters, since some of these depends of physic-chemical characteristics that are not available to the designer, such as the charge transfer coefficient, used to calculate the activation voltage loss.

The main aspect in the modeling fuel cell is the cell voltage, due to the behavior of the cell potential changes with different level of load and operating conditions. The cell voltage is found by modeling the maximum theoretical voltage and the mains voltage losses, as activation, ohmic, concentration and internal current. There are many parameters that have to be found in each one of these losses and is not an easy work, since depend of many empirical, physic-chemical and geometrics coefficients.

This paper presents a study of parametrization of dynamic and steady-state models by experimental results. An electrical circuit that models the transient behavior of the fuel cell voltage will be presented. The experimental techniques used are the current interrupt method. Finally, results of simulations will be presented to confirm the model.

II. FUNDAMENTAL OPERATION

Fuel cells are electrochemical devices which convert chemical energy of the reactants into electrical energy and heat. The basic chemical reaction involves the oxidation of hydrogen at the anode electrode and the reduction of oxygen at the cathode electrode, releasing only heat and water.
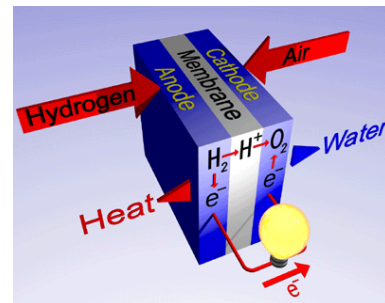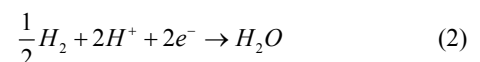

Fig. 1 - Basic PEM Fuel Cell Operation.

Protons H^+, results of hydrogen oxidation (1), are carried from anode to cathode through the proton exchange membrane, that no allow the transport of electrons, which pass through an external circuit to produce useful work. At the cathode the oxygen react with protons and electron taken from anode to produce water and heat (2). Both the anode and cathode contain a catalyst, usually platinum, to speed up the electrochemical process.

$$H_2 \rightarrow 2H^+ + 2e^- \tag{1}$$

$$\frac{1}{2}H_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{2}$$

III. STEADY-STATE AND DYNAMIC MODELS

Although analytical [2,3] model can be used over a long operating range, are most times very difficult to use because it need to know a lot of parameters that are not available to the designer, such as transfer coefficient, internal humidity levels and active area. On the other hand, empirical models [4,5] are usually only refined over a small operating range. In order to solve these difficulties many semi-empirical models have been presented [6,8,9], but it still difficulty to obtain the parametric coefficients.

This model is represented by subtracting the voltage losses from the reversible voltage as shown in (3), where V_{act}, V_{ohm} and V_{conc} represents the activation voltage loss, ohmic voltage loss and concentration voltage loss, respectively. Another source of losses is the internal currents that acts on all the losses described, mainly in the activation voltage loss, because it occurs at low current densities.

$$V_{stack} = V_{reversible} - V_{act} - V_{ohm} - V_{conc} \quad (3)$$

In this paper the concentration voltage loss will not be used because it occurs at high current densities, and many times it influences are so small to design the control strategy.

A. Reversible Voltage - $V_{reversible}$

Reversible voltage represents the maximum cell potential, it is independent of the load level, just change with temperature and partial pressure of the inlet gases. The analytical model is developed by Nernst equation that represents the change of the cell voltage over a change in partial pressure of the inlet gases. However, the Nernst equation is found to a standard level of temperature (298,15K). To establish a generalized model, which represents the temperature changes, another term has to be included to the model:

$$V_{reversible} = V_{Nernst} + V_T^{change} \quad (4)$$

Where V_{Nernst} is derived from the change in Gibbs free energy:

$$V_{Nernst} = -\frac{\Delta g_{T^0,P^0}}{2 \cdot F} + \frac{R \cdot T}{2 \cdot F} \ln \left(\frac{\dfrac{\overset{*}{p}_{H_2}}{P^0} \left(\dfrac{\overset{*}{p}_{O_2}}{P^0} \right)^{\frac{1}{2}}}{\dfrac{\overset{*}{p}_{H_2O}}{P^0}} \right) \quad (5)$$

And from thermodynamic theory:

$$V_T^{change} = -\frac{\Delta s_{T^0,P^0}}{2 \cdot F}(T - 298,15) \quad (6)$$

$\Delta g_{T^0,P^0}$ represent the molar change in Gibbs free energy of formation at standard temperature and pressure (STP); R is the universal gas constant; F is Faraday's constant; T is temperature (Kelvin); $\overset{*}{p}_{H_2}$ is the partial pressure of hydrogen (atm); $\overset{*}{p}_{O_2}$ is the partial pressure of oxygen (atm); $\overset{*}{p}_{H_2O}$ is the partial pressure of water(atm); P^0 is the standard pressure(atm); $\Delta s_{T^0,P^0}$ is the change in the molar entropy at temperature and standard pressure.

Substituting (5) and (6) in (4), with pressure in atmospheres and using standard values for the constants, the reversible voltage is given by:

$$V_{reversible} = 1.229 + \left(4.308 \cdot 10^{-5}\right)T \cdot \ln\left[\overset{*}{p}_{H_2}\left(\overset{*}{p}_{O_2}\right)^{\frac{1}{2}} \right] - \left(8.453 \cdot 10^{-4}\right)(T - 298.15) \quad (7)$$

B. Activation Voltage Loss

The activation voltage loss is caused by slowness of the reactions taking place on the surface of the electrode [1]. In 1905, Tafel observed that for most value of overvoltage, the graph of voltage loss against natural log of current density can be approximated by a straight line. The equation that better represented the graph is shown below

$$V_{act} = A \ln\left(\frac{i}{i_0}\right) \quad (8)$$

where A is the Tafel slope and i_0 is the exchange current densities.

Although, the coefficient A was observed experimentally by Tafel, later it has been shown with a theoretical basis.

$$A = \frac{R \cdot T}{2 \cdot \alpha \cdot F} \quad (9)$$

where α is the charge transfer coefficient, that is the proportion of the electrical energy applied that is harnessed in changing the rate of an electrochemical reaction [1].

C. Ohmic Voltage Loss

The ohmic voltage loss is the addition of the resistance to the flow of the protons through the membrane and the resistance to the flow of electrons through the electrodes. The resistance of the electrodes is practically constant, however the resistance of the membrane change with hydration, temperature and current [6].

A general expression that represents the total resistance is shown below:

$$R_{ohmic} = \varepsilon_1 + \varepsilon_2 \cdot i + \varepsilon_3 \cdot T \quad (10)$$

Therefore, the ohmic oververvoltage is given by:

$$V_{ohmic} = i\left(\varepsilon_1 + \varepsilon_2 \cdot i + \varepsilon_3 \cdot T\right) \tag{11}$$

D. Internal Current

The polymer membrane does not have an ideal behavior, firstly characterized by the presence of a resistance and also by the flow of fuel and electrons through it without producing useful work, what should not occur. This waste of energy is know by internal current, and is significant only at small current, as activation voltage loss.

Internal Current is not modeled as an isolated source of loss, but is in fact included with the nominal current, as can be seen in (12).

$$V_{act} = A \ln\left(\frac{i + i_n}{i_o}\right) \tag{12}$$

where i_n represent the internal current.

E. Dynamic Model

A phenomenon present between the electrodes and electrolyte, called the charge double layer, is the main responsible for the transient behavior. Due to presence of positives and negatives charges on the electrolyte and electrode respectively, this phenomenon can be modeled as an electrical capacitor, which gives the fuel cell a first order dynamic performance, where the voltage moves smoothly to a new value when a step of current is given.

The ohmic resistance is modeled as a resistance R_{ohmic}. The impedance formed by capacitor C_{act} and R_{act} represents the activation voltage loss, where the resistor models the activation voltage drop and the capacitor gives the dynamic behavior.
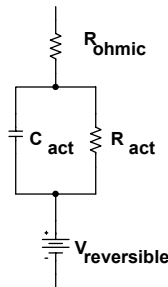
Fig. 2 - Dynamic Model – Equivalent Circuit.

IV. PARAMETERS DETERMINATION OF DYNAMIC MODEL

There are two main experimental methods to determine the parameters of the fuel cell model, *Electrochemical Impedance Spectroscopy (EIS)* and *Current Interrupt*. Although the EIS method reveals more information about the cell, the analysis of the data is more complicated, and demand equipments more accurate.

A. Current Interrupt

The current interrupt method is the simplest experimental procedure to determine the fuel cell parameters when the concentration voltage loss is negligible. The basic procedure is to interrupt the current under constant load conditions. When the current is cut off the immediately voltage drop represent the ohmic loss and the first order response represent the activation voltage loss, or the charge double layer capacitance.
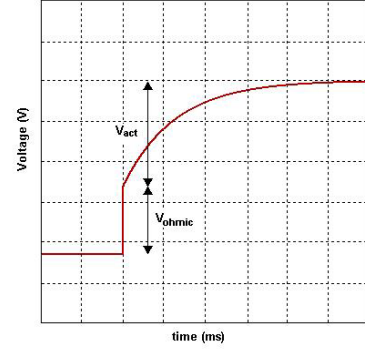
Fig. 3 - Current Interrupt - Theoretical Response.

B. Experimental Results and Parameters

A stack with 48 cells connected in series was used to extract the parameters of the dynamic model. The current immediately before the test was 7.1A, as can be seen in Fig. 4. The measures of ohmic voltage drop, activation voltage drop and the time to the voltage reach at the steady-state value (5τ) are shown in TABLE I.
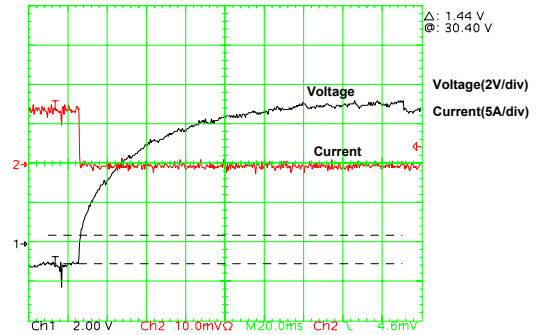
Fig. 4 – Current Interrupt – Experimental Response.

TABLE I

Values of Voltages Drop and Time Constant – Measured

	V_{ohmic}	V_{act}	t_{act}
Measures	1.44V	6.3V	127ms

The parameters of dynamic model can be found by substituting the values of TABLE I in (13), (14) and (15).

$$R_{ohmic} = \frac{V_{ohmic}}{i} \tag{13}$$

$$R_{act} = \frac{V_{act}}{i} \tag{14}$$

$$C_{act} = \frac{t_{act}}{5 \cdot R_{act}} \tag{15}$$

TABLE II

Parameters of Dynamic Model

	R_{ohmic}	R_{act}	C_{act}
Value	203mΩ	887mΩ	0.029F

C. Simulation

In order to prove the extraction of parameters methodology, the simulation of the electrical circuit that model the dynamic response of the stack, Fig. 2, is presented below:
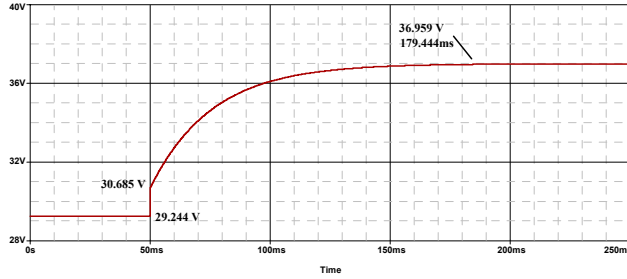

Fig. 5 – Simulation of Parameters of Dynamic Model.

Both the ohmic voltage drop and activation voltage drop are almost the same that the values measured, and the time constant is really next to the experimental value, as can be seen in TABLE III.

TABLE III

Values of Voltages Drop and Time Constant – Simulation

	V_{ohmic}	V_{act}	t_{act}
Simulation	1.441V	6.27V	129.44ms

V. PARAMETERS DETERMINATION OF STEADY-STATE MODEL

In order to determine the parameters of the steady-state model, the current interrupt method also will be used. First, the reversible voltage will be found, than the parametric coefficients of the resistance will be experimentally observed and finally the constants of activation loss, such as Tofel slope (A), exchange current (i_o) and intern current (i_n) will be determined.

Using a stack with 40 cells connected in series, the parameters of the cell, such as temperature, pressure and voltage are measured for a several levels of load, as well as the ohmic losses, by the interrupt current method and finally the cell's resistance using equation (13).

The partial pressure of the oxygen is 0.2095 atm for all measures, since the stack use atmospheric air as a reactant and the oxygen represents 20.95% of the air.

TABLE IV

Measures of the parameters of the stack

I(A)	P_{H2}(atm)	T(K)	V_{cell}(V)	V_{ohmic}(V)	R_{ohmic}(Ω)
0.0	0.408	304.15	32.8	0.0	-
2.85	0.374	306.15	30.4	0.170	0.06
3.82	0.381	306.25	29.6	0.290	0.076
4.91	0.347	306.45	28.8	0.420	0.086
5.59	0.333	307.55	28.3	0.580	0.104
6.46	0.323	307.15	27.8	0.690	0.107
7.45	0.306	306.35	27.3	0.800	0.107
8.39	0.306	306.05	26.8	0.900	0.107
9.62	0.299	303.15	26.1	1.00	0.104
10.6	0.313	307.85	25.8	1.26	0.119
11.3	0.279	303.25	25.2	1.40	0.124
12.4	0.272	303.15	24.6	1.58	0.127
13.1	0.265	303.15	24.3	1.74	0.133
13.9	0.259	303.15	23.8	1.86	0.134
14.9	0.255	303.65	23.3	2.00	0.134
15.3	0.245	303.85	23.0	2.04	0.133
15.6	0.245	303.55	22.5	2.08	0.133

A. Reversible Voltage

The cell reversible voltage is determined by substituting in (7) the experimental measures of cell temperature and the partial pressure of the inlet gases.

TABLE V

Reversible Voltage

I(A)	$V_{reversible}$(V)
0.0	48.078
2.85	47.959
3.82	47.965
4.91	47.908
5.59	47.846
6.46	47.844
7.45	47.845
8.39	47.857
9.62	47.953
10.6	47.801
11.3	47.912
12.4	47.903
13.1	47.89
13.9	47.876
14.9	47.85
15.3	47.822
15.3	47.833

B. Resistance Parameters

As already discussed the resistance of the fuel cell change with current and temperature, and therefore can be empirically modeled by:

$$R_{ohmic} = \varepsilon_1 + \varepsilon_2 \cdot i + \varepsilon_3 \cdot T \tag{16}$$

The coefficients ε_1, ε_2 and ε_3 can be determined solving a linear regression of the many measures of resistance when the stack is operating in different level of temperature and current.

The function *LINEST* of the EXCEL calculate a straight line that best fits it data, and returns an array that describes the line using the least square method.

Using the measures of TABLE IV and the function LINEST the coefficients can be found:

$$\varepsilon_1 = -0.7539474$$
$$\varepsilon_2 = 0.00582375$$
$$\varepsilon_3 = 0.00265157$$

C. Activation Loss

Once the reversible voltage and the coefficients of resistance had been calculated, the parameters of activation loss can be determined. The activation voltage loss at determined current when the concentration loss is negligible is the reversible voltage minus the cell voltage minus the ohmic loss:

$$V_{act}(i) = V_{reversible} - V_{cell}(i) - V_{ohmic}(i) \qquad (17)$$

TABLE VI

Activation Losses - Experimental

I(A)	ln(I)	Vact(V)
2.85	1.0473	17.389
3.82	1.3402	18.075
4.91	1.5912	18.688
5.59	1.7209	18.966
6.46	1.8656	19.354
7.45	2.0082	19.745
8.39	2.1270	20.157
9.62	2.2638	20.853
10.6	2.3608	20.741
11.3	2.4248	21.312
12.4	2.5176	21.723
13.1	2.5726	21.85
13.9	2.6318	22.216
14.9	2.7013	22.55
15.3	2.7278	22.782
15.3	2.7472	23.253

A graph of the behavior of the activation voltage against natural logarithmic of the current plus internal current is shown in Fig. 6 . The major approximation here is that the Tafel slope at higher currents without an internal current is approximately the same to the Tafel slope when the internal current is added.

The Tafel slope (*A*) and exchange current (i$_0$) of (12) are calculated from the slope and y-intercept of the graph, respectively, or from a line equation *y=ax+b*, where the Tafel slope is:

$$A = a \qquad (18)$$

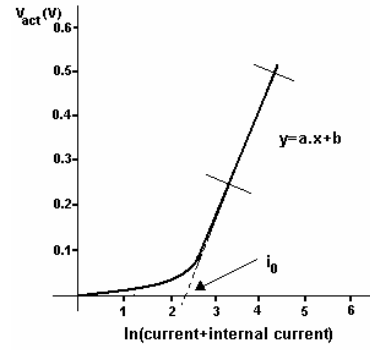$$i_0 = \exp\left(\frac{-b}{a}\right) \qquad (19)$$

Fig. 6 – Graph of Activation overvoltage against natural logarithmic of the current.

Just the activations voltages above 7.45A were used to plot a graph, Fig. 7, which shows the linear behavior of the activation voltage against natural logarithmic of the current.

The **Vact** line represents the experimental points and the **Linear** line the trend-line that represents the linear behavior of the graph.
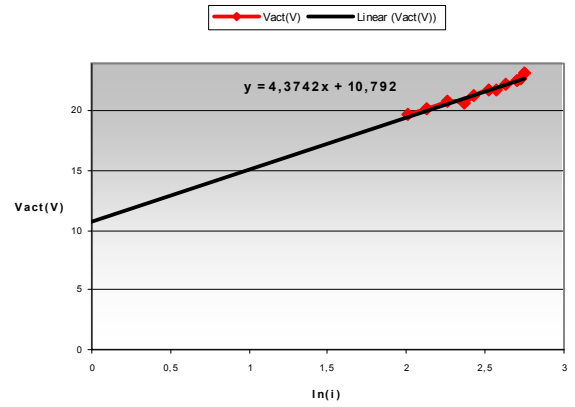

Fig. 7 – Activation Voltage against natural logarithmic of the current.

The line equation that better represents the trend line is:

$$y = 4.3742x + 10.792 \qquad (20)$$

Therefore, substituting the coefficients of the line equation into (18) and (19), the Tafel slope and the exchange current can be calculated:

$$A = 4.3742$$

$$i_0 = 0.085A$$

To complete the model the internal current can be estimate, from the activation voltage at open circuit, where *i* is equal to zero.

Since A and i_0 are already determined the internal current can be calculated from:

$$i_n = i_0 \cdot \exp\left(\frac{V_{act}(open-circuit)}{A}\right) \quad (21)$$

The open circuit activation loss is also calculated by (17), however the ohmic loss is zero since the current across the cell is also zero. Therefore:

$$V_{act}(open-circuit) = 15.278$$

Using the coefficients already calculated in (21):

$$i_n = 2.789$$

D. Polarization Curve

After all the parameters have been calculated the polarization curve that represents the static behavior of the cell can be determined from:

$$V_{stack} = V_{reversible} - A\ln\left(\frac{i_n + i}{i_0}\right) - \left(\varepsilon_1 + \varepsilon_2 \cdot i + \varepsilon_1 \cdot T\right)i \quad (22)$$

The Fig. 8 shows the theoretical and experimental polarization curves, that prove the efficiency of the model, since the difference between these data are small.
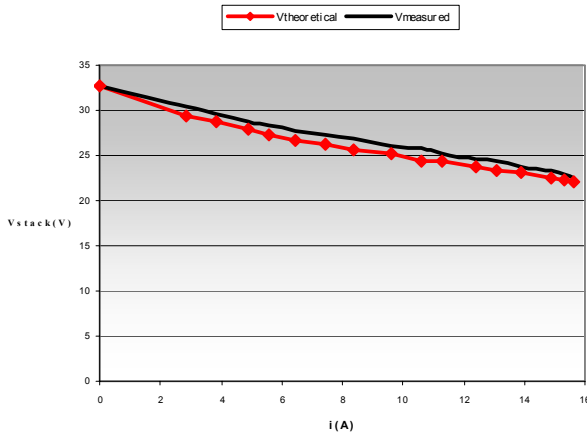

Fig. 8 – Polarization Curve – Experimental x Theoretical.

VI. CONCLUSION

This study presented simple but accurate dynamic and steady-state models to the proton exchange membrane fuel cell (PEMFC). Since the concentration overvoltage is negligible, the parameters of the whole model can be determined by experimental results, except the reversible voltage that is calculated from an analytical equation, but it still simple.

The parameters of an electrical circuit that represents the dynamic model of a stack with 48 cell operating in series was extracted experimentally using the interrupt current method. By simulation, the behavior of the cell voltage was approximately equal to the experimental results that prove the efficiency of the procedure.

The parameterization of the static model was also presented, where the coefficients of the ohmic loss and activation losses were calculated by experimental results, and proved a good efficiency when compared with experimental curve.

This model arises as a good alternative to predict a steady-state behavior of the fuel cell when some chemicals and physics parameters are not available.

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