Characterization and experimental results in PEM fuel cell electrical behaviour

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ABSTRACT

A control oriented electrochemical static model of a proton exchange membrane fuel cell (PEMFC) stack is developed in this paper. Even though its validation is performed on a specific 7-cell PEMFC stack fed by humidified air and pure hydrogen, the methodology and fit parameters can be applied to different fuel cell systems with minor changes. The fuel cell model was developed combining theoretical considerations and semi-empirical analysis based on the experimental data. The proposed model can be successfully included into a larger dynamic subsystem to complete the power generation system.

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1. Introduction

Fuel cells represent a radically different approach to energy conversion, one that could replace conventional power generation technologies in a wide variety of applications, from mobile and stationary power systems to portable appliances. In particular, a Proton Exchange Membrane (PEM) fuel cell is an electrochemical device that converts chemical energy into electric power, without the intermediate production of mechanical work and with water as the only byproduct [5]. Then, considering that hydrogen production from water electrolysis can be performed using renewable energy (solar, wind, geothermal, etc.), PEM fuel cells emerge as one of the most clean and promising alternatives to reduce fossil fuel dependency.

In this context, improvements in this field require inter-disciplinary work and development of new technologies in many areas. One important issue that recently attracted the research community attention is the model development of fuel cell systems. Among other purposes, accurate system level models are a key requirement to design advanced control strategies, which can improve the efficiency of fuel cell based systems, while avoiding power deterioration and irreversible damages in cells membranes [10]. However, nowadays there is little information in the open literature describing fuel cell models specially suitable for control design purposes. Therefore, to make significant contributions in this area, it is necessary to establish a systematic modeling methodology and develop further reliable models capable to describe the system behavior under different operation conditions.

Therefore, in the current work, the model development of a laboratory fuel cell stack is presented. The test plant under analysis comprises an air compressor, a supply manifold, humidifiers, line heaters and a 7-cell fuel cell stack (Fig. 1). The results presented in this paper are based on a complete gas flow model of the system developed by the authors in [4]. All the work was conducted and organized in a way that the results and methods proposed can be straightforwardly
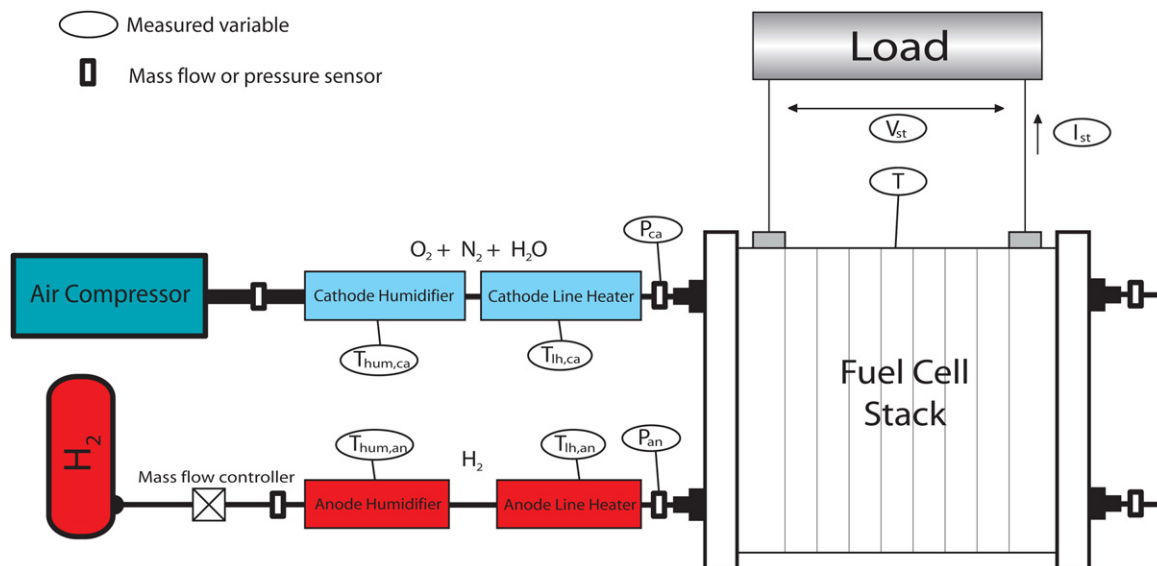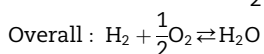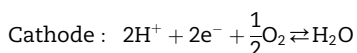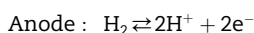
Fig. 1 – Fuel cell system diagram.

extended to different fuel cell stacks. It is also shown that the developed model predictions are in reasonable agreement with the experimental data at different operating conditions of pressure and air flow, indicating that the model can be employed for engineering analysis and included into a larger dynamic subsystem for nonlinear control development.

The technical details of the laboratory fuel cell system under study are as follows: the fuel cell stack is an Electro-Chem® 7-cell stack with Nafion 115 MEAs (membrane electrode assembly), a catalyst loading of 1 mg/cm² of platinum, 50 cm² of active area, 50 W of nominal power and 100 W peak power. A Cellkraft® membrane exchange humidifier is used to maintain proper humidity conditions inside the cells, which is crucial to ensure the optimal operation of a PEM membranes. The air compressor is basically an oil-free diaphragm vacuum pump. The line heaters and stack temperatures are controlled by a power station via decentralized PID controllers, allowing for independent gas conditions to the stack.

The work was firstly focused on obtaining a preliminary structure based on the physical laws that govern the system. Then, the model structures and parameters were adjusted in order to match the experimental data in a broad range of testing conditions.

2. PEM fuel cell operation principle

A proton exchange membrane fuel cell is composed basically of two catalyzed porous electrodes separated by a solid ion conductive electrolyte. The reactions for a PEM fuel cell fed with hydrogen in the anode and oxygen in the cathode are:

$$\text{Anode}: \quad H_2 \rightleftharpoons 2H^+ + 2e^-$$

$$\text{Cathode}: \quad 2H^+ + 2e^- + \frac{1}{2}O_2 \rightleftharpoons H_2O$$

$$\text{Overall}: \quad H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$$

The products of this process are DC electricity, water and heat. The maximum amount of electrical energy generated in a fuel cell corresponds to the Gibbs free energy ΔG of the above reaction. Then theoretical potential of a single PEM fuel cell is:

$$E_0 = -\frac{\Delta G}{nF} \tag{1}$$

where n is the number of electrons involved in the above reaction 2, and F is the Faraday's constant (96,485 C/e-mol). Since ΔG, n and F are all known constants, the theoretical voltage of a single hydrogen/oxygen fuel cell can also be calculated [11]:

$$E_0 = -\frac{\Delta G}{nF} = \frac{237.340}{2 \times 96.485} \frac{\text{J mol}^{-1}}{\text{As mol}^{-1}} = 1.229 \text{ V} \tag{2}$$

at 25 °C and atmospheric pressure.

3. PEM fuel cell nonlinear model

In this section, a nonlinear model is presented in order to characterize the electrical behaviour of a commercial PEM fuel cell stack. The analysis was conducted considering the following assumptions:

- The model is one dimensional, so the gases and reactions are considered uniformly distributed in the cell.
- The electrochemical properties are evaluated at the average stack temperature (60 °C), so temperature variations across the stack are neglected.
- Cathode and anode gas conditions are derived from a previously flow model developed by the authors in [4].
- The water entering to the cathode and anode is only in vapor phase.
- The water activity is uniform across the membrane and is in equilibrium with the water activity at the cathode and anode catalyst layer.
- The effects of liquid water accumulation are not treated.

3.1. Thermodynamic potential

Using standard thermodynamic values of the entropy change, the open circuit voltage of a single cell (Nerst voltage) can be represented by the following expression [1]:

$$E = E_0 + \frac{RT}{2F}\left[\ln\left(P_{H_2}\right) + \tfrac{1}{2}\cdot\ln\left(P_{O_2}\right)\right] \tag{3}$$

where R is the universal gas constant and T is the fuel cell temperature. P_{H_2} and P_{O_2} are hydrogen and oxygen partial pressures, respectively. In this work the fuel cell temperature has been assumed to be constant at 60 °C. The evaluation of the two partial pressures typically involves mass transfer calculations and normally requires averaging over a cell surface, to account for significant changes in the bulk phase partial pressures of the gaseous reactants [7]. This is the reason why in practical issues, correction factors must be considered to fit the experimental data to the governing equations.

Apart from that, it is known that the cell operation voltage of a cell does not remain constant at different load conditions. This is because the current drainage from the cell produces different sorts of losses, which can be divided into three categories: activation, ohmic and concentration or diffusion.

3.2. Activation losses

The activation losses occur because the cell needs energy to produce the electrons transfer, to break and form new chemicals bonds, both in the anode and cathode [6]. This produces a voltage drop in both electrodes of the cell. The activation losses cause the voltage reduction in the low current regions of MEA operation. The steep slope of the initial portion of the curve is an indication of the activation polarization. As the current increases, the slope of the curve becomes less steep. This is a result of the activation polarization becoming less significant due to the increase in other polarization phenomena, specially concentration and ohmic effects [6]. The relationship between the activation voltage and the current density is often described through the Tafel equation:

$$V_{act} = A \ln\left(\frac{i}{i_0}\right) \tag{4}$$

where A is higher for slow electrochemical reactions, i the current density and the constant i_0 is higher if the reaction is faster. The current density i_0 can be considered as the current density at which the overvoltage begins to move from zero. It is important to stress that the Tafel equation only holds true when $i > i_0$. This current density is usually called the exchange current density and its typical values are in the range 10^{-2}–10^{-8} A [5,13].

Although the Tafel was originally deduced from experimental results, it also has a theoretical basis. It can be shown that for a hydrogen fuel cell with two electrons transferred per mole, the constant A is given by:

$$A = \frac{RT}{2\alpha F} \tag{5}$$

The constant α is called the charge transfer coefficient and is the portion of the electrical energy applied that is harnessed in changing the rate of an electrochemical reaction. Its vale depends on the reaction involved and the material of the electrode, but it must be in the range 0–1 [5].

As predicted in [2,5,13], the experimental tests performed in the plant revealed that the values of the parameters α and i_0 do not vary when considering certain changes in operation conditions like pressures and gas flows (see Section 4).

3.3. Ohmic losses

PEM ohmic losses are usually due to both, the resistance that presents the membrane to the protons transfer and the electrical resistance of electrodes and collectors. This is the reason why the voltage drop by ohmic losses remains proportional to the current density drained from the cell:

$$V_{ohm} = i \cdot R_{ohm} \tag{6}$$

where R_{ohm} is the internal resistance of the cell, which has a strong dependence on the membrane humidity and on the cell temperature. Several studies [9,14] show that this resistance is a function of the conductivity of the membrane (σ_m) and the thickness of the dry membrane (t_m), 0.0127 cm in the case of Nafion 115 membranes:

$$R_{ohm} = \frac{t_m}{\sigma_m} \tag{7}$$

In turn, the conductivity of perfluorosulphonicacid ionomer membranes is a strong function of water content (λ_m), defined as the number of water molecules per sulfonate group in the ionomer. Based on different measurements, in [14] the authors correlated the ionic conductivity of a Nafion 117 membrane to its water content and temperature using the following expression:

$$\sigma_m = (b_1 - \lambda_m b_2) \cdot e^{b_3\left(\frac{1}{303} - \frac{1}{T}\right)} \tag{8}$$

In the same work it is stated that the parameters can vary for different membranes, but the general behavior of the model was verified in different operating conditions.

3.4. Concentration losses

Finally, there is another kind of losses called concentration losses that occur when the reactants are rapidly consumed at the electrodes by the electrochemical reactions, then concentration gradients are established. For instance, if the oxygen at the cathode of a fuel cell is supplied in the form of air, it is self-evident that during fuel cell operation there will be a slight reduction in the concentration of the oxygen in the cathode region, as the oxygen is extracted [5]. Due to these losses, there is a sharp drop in voltage when the drained current is too high. However, because of nonuniform conditions over the porous electrode area, the limiting current is almost never experienced in practical fuel cells [2].

To approximate this phenomenon, an empirical equation better describes the concentration loses [3]

$$V_{conc} = m\, e^{(n \cdot i)} \tag{9}$$

where m and n are empirical coefficients with typical values close to 3×10^{-5} V and 8 cm^2/A, respectively [5].

4. Experimental results and discussions

In order to model the static electrochemical behaviour of the fuel cell stack, an approach based on equations (3), (4), (6) and (9) was considered to estimate the polarization curve (V–I) under different operating conditions (air flow rates and pressures). The technique used is based on semi-empirical relationships to model the electrical properties of the stack, derived from the physical processes that occur in the MEA and the phenomena that take place in the channels. The developed model can be successfully included into a larger dynamic subsystem as the one developed in [4], to complete the power generation system model.

Combining the open circuit voltage with the effects of activation, ohmic resistance and concentration, the operation voltage of a PEM fuel cell (V_{fc}) can be described by the following expression:

$$V_{fc} = E - V_{act} - V_{ohm} - V_{conc} \qquad (10)$$

As predicted in [6], good agreement between modelled and experimental data is observed when using the following general expression at constant fuel cell temperature:

$$V_{fc} = V_0 - \frac{RT}{2\alpha F} \ln\left(\frac{i}{i_0}\right) - (R_0 - R_1\lambda_m)i - m\,e^{(n.i)} + b\cdot\ln\left(\frac{P_{O_2}}{a}\right) \qquad (11)$$

where α, i_0, R_0, R_1, m, n, b and a are empirical parameters that take into account the different polarization effects and are adjusted for a specific fuel cell stack, without loss of generality.

Note that the model proposed in [6] features the developed terms, representing activation losses and ohmic contributions, as well as incorporating two terms which have appeared only recently in the literature. The exponential term and the pressure ratio logarithm serve to model the effects of gas diffusion at high current densities and concentration losses predominantly at low oxygen stoichiometries, respectively.

Firstly, the term V_0 was taken as $V_0 = E_0 = 1.229$ V, representing the theoretical electrochemical potential of a single hydrogen/oxygen fuel cell. Then, considering that the activation losses do not depend on the pressure and oxygen stoichiometry, the coefficients α and i_0 were determined. To this end, a logarithmic plot of the V–I curve is a helpful tool to better determine the electrical behaviour of the MEAs at low current densities (see Fig. 2).

$\alpha = 0.7$ and $i_0 = 4.5 \times 10^{-6}$ A/cm^2 were the values that better adjusted the experimental data when the cathode air flow rates (W_{ca}) were varied from 1.108×10^{-5} kg/s to 7.707×10^{-5} kg/s, and $P_{H_2} = P_{O_2} = 1$ bar. It is important to stress that in all the experiments presented in this section, the air and hydrogen dew point of 55 °C, while the line heaters and stack temperatures were fixed at 60 °C in order to avoid water condensation inside the stack. Considering these externally regulated temperatures, the relative humidity of the inlet gases was 0.75. The stack current profile was set to vary from 0 A to 12 A, and the anode hydrogen flow was set fixed at 6.483×10^{-6} kg/s (2 slpm of dry H_2), then the hydrogen stoichiometry remains above 5 even in at the highest current (12 A), so the losses due to hydrogen concentration can be neglected. Once anode or cathode flooding occurs, in [8] and
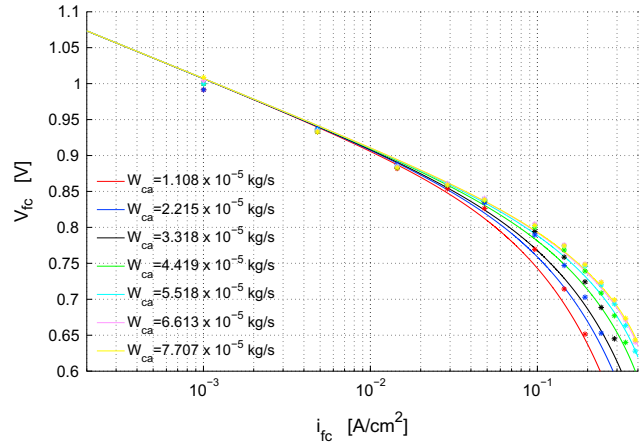

Fig. 2 – Logarithmic polarization curve.

[12] it was stated that the resulting voltage degradation arises from the accumulation of liquid mass in the gas diffusion layers. The accumulated liquid mass is assumed to form a thin film, blocking part of the active fuel cell area A_{fc} and consequently increasing the lumped current density, defining an apparent fuel cell area A_{app} that is approximated as the fuel cell area reduced by the liquid film generated at the interface of the channels and gas diffusion layers. In these experiments there is not a purging schedule and cathode and anode flows are kept constant in every operating conditions, so the effect was modelled with a fixed scaling factor for the membrane effective area. Thus, the approximated value of the apparent fuel cell area was $A_{app} = 20.74$ cm^2 for all the working conditions.

Subsequently, the ohmic polarization was determined in base of the membrane average water content (λ_m). The water content in the membrane, is defined as the ratio of water molecules to the number of charge sites and can be estimated from the membrane relative humidity (RH_m) using the following equation [14]:

$$\lambda_m = 0.043 + 17.81\,RH_m - 39.85\,RH_m^2 + 36\,a\,RH_m^3 \qquad (12)$$

with

$$RH_m = (RH_{ca} + RH_{an})/2 \qquad (13)$$

being RH_{ca} and RH_{an} the gas relative humidity inside the cathode and anode respectively. The following figure (Fig. 3) depicts the profile described by λ_m in the validated model of the stack presented in [4], at different current densities and air flow rates.

Considering that above a certain value of i the relationship between λ_m and i remain fixed, it is natural to predict that the ionic conductivity of the membrane remain practically unaltered at different air flow rates. This assumption conducts to select a small value of R_1 and R_0 close to the average resistance of the MEA, according to the data. In this particular case, the most representative values for the system were $R_1 = 0.005$ Ω/cm^2 and $R_0 = 0.22$ Ω/cm^2.

The next set of parameters to be estimated are a and b, which consider the effect of low oxygen stoichiometries in the cathode. As it can be seen in Fig. 4, in all polarization curves there is a significant voltage drop at certain current densities.
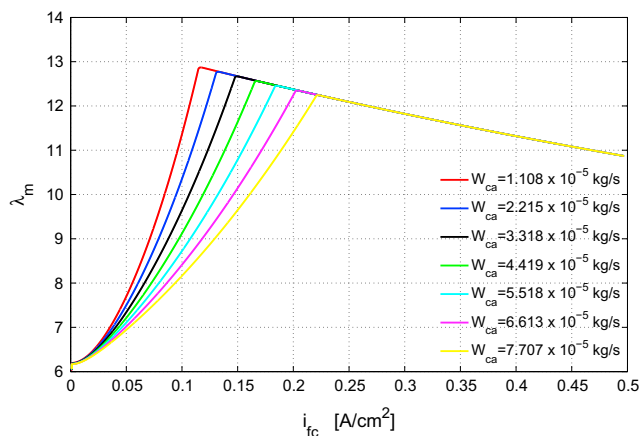
Fig. 3 – Membrane water content.

Fig. 5 – Polarization curve of the fuel cell stack (constant airflow and different levels of cathode pressure).

In fact, the values of current densities where voltage drops start vary with the air mass flow. Then, the parameter a can be associated to the value of oxygen partial pressure that produces the steep effect of the concentration loss. The parameter b represents the sensitivity of the polarization curve at different air flow rates, so it can be adjusted depending on the data obtained from the polarization curves at the minimum and maximum air flow rates (red line and yellow line in Fig. 4). For the tested fuel cells stack, the estimated values of these parameters were $a = 0.2$ bar and $b = 0.06$ V.

Lastly, values m and n where adjusted in order to respect the general gas diffusion loss at high stack currents. The obtained values were $m = 8.1 \times 10^{-5}$ V and $n = 15.2$ cm^2/A.

The following figure (Fig. 4) represents the polarization curves obtained at constant pressure (1 bar) and different levels of air flow (1.108×10^{-5} kg/s to 7.707×10^{-5} kg/s).

Fig. 5 depicts the polarization curves obtained at constant air flow (7.707×10^{-5} kg/s) and increasing levels of working pressures (1–2.35 bar).

In Figs. 4 and 5 it can be appreciated that the presented model based on equation [11] and its parameters adjustment, satisfactory predicts the fuel cell static V–I behaviour under different tested conditions of air flow rates and cathode pressures.
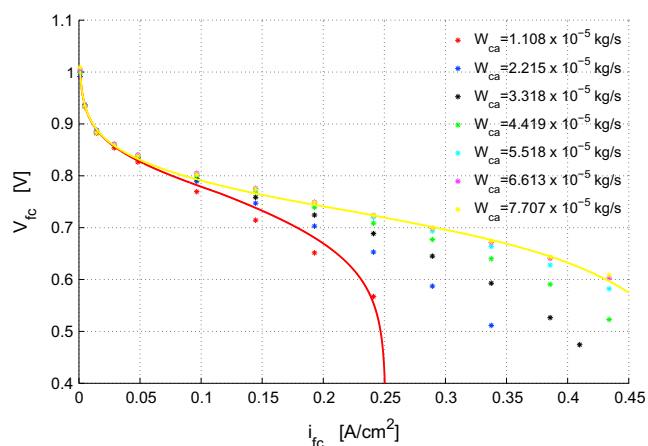
5. Conclusions

An experimental model of a PEM fuel cell stack was developed. Using theoretical considerations about the physics of the system, static equations that describe the nonlinear multi-valued voltage characteristics of the system was obtained. Subsequently, analyzing the data obtained from tests and measurements in the laboratory, the equations were slightly modified and its parameters were adjusted to obtain a final model that confirms its experimental validity under different pressure and air flow working conditions.

The model was primarily developed for control studies, so it can be incorporated in a larger dynamic subsystem to complete the power generation system model.

Finally, it should be stressed that all the modeling methods and physical considerations can be extended to other PEM fuel cell systems.

Acknowledgments

Fig. 4 – Polarization curve of the fuel cell stack (constant cathode pressure and different levels of airflow).

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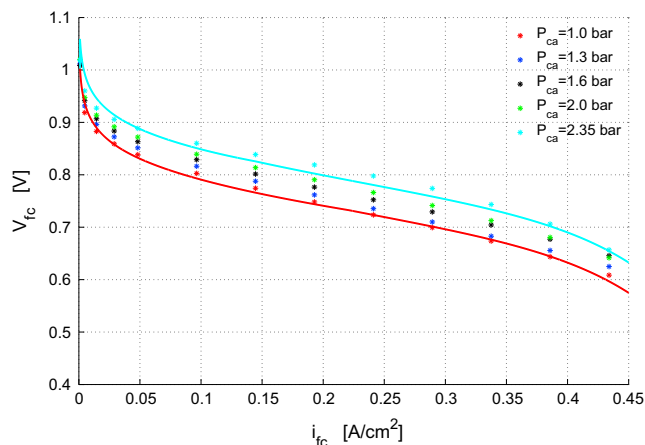[1] Amphlett JC, Baumert RM, Mann RF, Peppley BA, Roberge PR. Performance modelling of the ballard mark iv solid polymer electrolyte fuel cell. Journal of Electrochemical Society 1995; 142(1):9–15.
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