MODELLING LIQUID WATER EFFECT ON PROTON-EXCHANGE MEMBRANE FUEL CELLS

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Abstract - **This work introduces our ongoing research in developing accurate models for predicting and analyzing Proton-Exchange Membrane Fuel Cells performance. An initial model, whose response is compared with experimental data is first implemented. The simulated (and theoretically expected) cell voltage deviates from real behavior when the operating conditions change. Then an improved model, aimed to better approximate instantaneous voltage response to changing operating conditions by including liquid water dynamics, is developed. The results show that the new model achieves a better approximation of the voltage profile. The model is validated through experiments on a real fuel cell test-bench.**

Index Terms - **ECSA, fuel cell modelling, liquid water dynamics, proton-exchange membrane fuel cells**

I. NOMENCLATURE

V	Voltage
R	Universal gas constant
T	Temperature
T_{REF}	Reference temperature
α	Charge transfer coefficient
F	Faraday constant
P_c	Cathode gas pressure
P_{cREF}	Cathode gas reference pressure
i	Current
A	Catalyst layer geometric area
ΔG	Gibbs free energy change
J	Water flux

II. INTRODUCTION

Many variables affect the performance of a fuel cell, specifically, water, among them is an important and hard to model one. Liquid water is produced in the cathode catalyst layer during fuel cell operation and it is also removed through evaporation, diffusion and transport.

Electrical power generation in Proton-Exchange Fuel Cells (PMFC) is based on two electrochemical half reactions, that produce a potential difference between the anode and cathode electrodes, the main resultant specie is liquid water [1].

Starting with the Butler-Volmer equation, fuel cell voltage can be modeled as a function of operating conditions and cell parameters (1):

$$V = E_N - \frac{RT}{\alpha 2F}\ln\left(\frac{i}{i_0}\right) - \frac{RT}{\alpha 2F}\ln\left(\frac{P_c}{P_{cREF}}\right) \qquad (1)$$

The cell output voltage is usually modeled as the result of subtracting three sources of voltage losses from an ideal Nernst potential (E_N).

The first subtracted term represents the so called activation voltage losses (2). These losses are a function of two operating conditions temperature(T) and load current (i) and an internal cell parameter, exchange current density (i_0).

$$V_{act} = \frac{RT}{\alpha 2F}\ln\left(\frac{i}{i_0}\right) \qquad (2)$$

III. INITIAL MODEL

The initial model has been created in Simulink® following a modular architecture with differentiated parts for each of the main components of the fuel cell. As part of the INN-BALANCE project, a series of experiments have been carried out to characterize cell dynamic. Figure (1) shows the results of a stoichiometry sweep experiment: oxygen (cathode) stoichiometry is stepped down through time while all other operating conditions (including anode stoichiometry) are held constant.

It can be noted in the experimental curve that, when input oxygen stoichiometry changes to a lower level, the cell voltage decreases following that dynamic at first, however, after some time and even though every other cell input variable remains constant (temperature, current, pressure) the voltage recovers to a close value of the initial higher value in the step. This behavior is not accurately reproduced by the simulated curve, this one follows the decrease in oxygen flow and steps down to a lower voltage level remaining in it through the full step time.
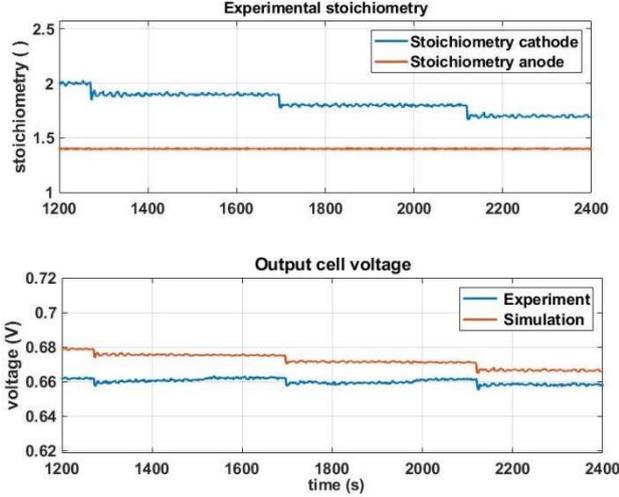
Fig. 1. Stoichiometry sweep experiment at cathode (anode constant) and comparison between real and simulated voltage

IV. IMPROVED MODEL

A. Liquid Water Dynamics

As stated before, activation losses depend on, among others, the exchange current density, furthermore, i_0 is related with the catalytic efficiency of the Cathode Catalyst Layer (CCL) [2]:

$$i_0 = i_{0REF} \frac{ECSA}{A} \left(\frac{P_c}{P_{cREF}} \right)^{0.5} e^{\left[\left(-\frac{\Delta G}{RT} \right) \left(1 - \frac{T}{T_{REF}} \right) \right]} \quad (3)$$

Electrochemical Active Surface Area (ECSA) defines the capacity of the cell catalyst to fulfill its function as an accelerator in the Oxygen Reduction Reaction (ORR), thus defining the efficiency in converting chemical energy into electrical energy. There is a relation between the water in the porous structure of the CCL and the instantaneous value of ECSA. The porous model of the CCL, proposed by Strahl et. al. establishes that removing larger amounts of water from the porous structure of the CCL, either by evaporation (changes in cell temperature) or by displacement (changes in the flow of oxygen), results in instantaneous variations of effective ECSA. Finding the optimal amount of water, the optimum effective ECSA (thus performance) could be achieved [3].

There is a relation to approximate ECSA as a function of fractional water contained in the CCL:

$$ECSA = ECSA_{REF} \left(e^{K_{act} s_{CCL}} - 1 \right) \quad (4)$$

Where s_{CCL} is the fractional amount of liquid water in the catalyst layer. The mass flux balance in the CCL completes the required relations to model liquid water dynamic [4].

$$K \frac{ds_{CCL}}{dt} = J_{gen} - J_{evap} - J_{diff} \quad (5)$$

B. Validation

This liquid water dynamic is now included in the model.

The updated model now achieves to better proximate the behavior presented in the experimental data. When the stoichiometry levels of the inlet oxygen step down, the amount of water being displaced from the CCL porous structure decreases, favoring an optimal hydration of the CCL and therefore improving cell voltage response, which recovers to a near constant value, even though oxygen supply is diminishing, figure 2.
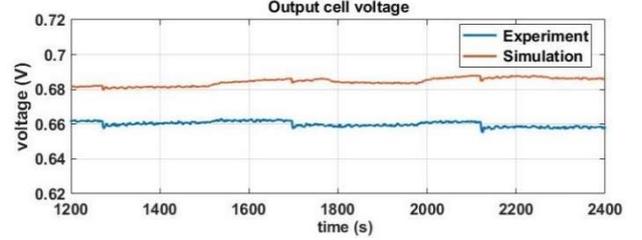
Fig. 2. Comparison between real and simulated voltage for the updated model.

V. CONCLUSION

We have developed, implemented and experimentally validated an accurate model of a Proton-Exchange Fuel Cell, in which the dynamic of liquid water in the catalyst layer has been successfully included. This model allows to better explain and predict the cell output voltage behavior. It is shown that variations in the fractional content of water located in the CCL has a relative immediate effect in the instantaneous output voltage profile of the fuel cell. Our on-going research effort is in applying accurate models for designing advanced high level model-based controllers to set optimal fuel cell operating conditions in order to improve performance and extend durability.

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