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INFLUENCE OF THE MODIFICATION OF ANODE A PEM TYPE FUEL CELL

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Abstract. *Currently a demand for electric energy consumption has reached alarming levels. This is due to the fact that, in proportion to the increase in energy consumption, there is a shortage of natural resources, thus making the development of renewable energy more and more necessary. Based on this fact, the present work was elaborated with the intention of studying one of the most recent technologies of the field of renewable energies: Proton Exchange Membrane Fuel Cell. In this way, a study was developed with the focus on improving the performance of a base model, modifying only the anode channels of the cell. As a starting point, three prototypes were made and carried out as analyzes using appropriate software, there are no results for the results of all the models and a prototype of better performance*.

Keywords: *Anode, Proton Exchange Membrane Fuel Cell, prototypes*

1. INTRODUCTION

The fuel cell is an electrochemical device that converts chemical energy into electrical energy to be fed by gaseous hydrogen and an oxidizing agent, which can be gas oxygen or atmospheric air. The quest for greater efficiency of fuel cells has led to studies of modified physical chemistry. Among the changes studied, the channels of supply of oxygen and hydrogen and their respective geometries are major influencers in the yield of the cell. The computational modeling will be performed with input parameters in the default channels of flow in the anode, aiming at a better performance in income.

2. PEM FUEL CELL

The fuel cell type polymeric membranes are so-called because it acts as an electrolyte a polymer that performs the ionic conduction of chemical species from the anode to the cathode when hydrated. This type of technology has several advantages such as high power density, operates at low temperature and has easy drive. With regard to the polymeric membrane, its constitution is amended by an organic polymer solid, usually the acid polytetrafluorethylene, which needs to be immersed in aqueous solution for conducting ions. It has a thickness varying between 12 and 210 µm. The membrane more currently used was developed by the company Dupont being called Nafion©. The operating mechanism of this type of cell to fuel - CaC is initiated by the injection of gaseous hydrogen by means of the plates enabling, aiming to reach the anode where this anchored the catalytic layer of platinum. At the moment the hydrogen undergoes oxidation and release electrons as the semi chemical in reaction 1.

$$2H_2 \rightarrow 4H^{+} + 4\overline{e} \tag{1}$$

The cations derived from the breaking of the gaseous hydrogen bond with water forming the ion hidroxônio (H_30), also called the proton. The ions hidroxônio influenced by the electric field move across the membrane moistened until it reaches the cathode. At the same time occurs the displacement of electrons in an external circuit providing the generation of electrical energy. On the other hand, in the cathode, gas oxygen or atmospheric air after passing through the diffuser plate comes into contact with the catalytic layer and undergoes a semi reaction of reduction as indicated by the following chemical in reaction 2.

$$O_2 + 4H^+ + 4\overline{e} \rightarrow 2H_2O \qquad (2)$$

It is observed through the semi reaction of reduction which one of the products generated is water vapor that serves to cool the cell or be reused to humidify the membrane. This water management is of utmost importance for the life of the cell and the generation of electrical energy, since the membrane with insufficient moisture can cause the loss of efficiency in the transportation of the group hidroxônio through your group or sulfonic even cause its dryness. The great challenge for this type of technology is to establish moisture in the membrane and in the electrode surface without water condensation which leads to obstruction of the cable broadcasters or even impede the mass transport within the cell membrane. Another point to consider is that the water serves as the refrigerant is preventing the cell operate above the temperature limit allowed.

2.1 Cell Thermodynamics

To understand the efficiency of a fuel cell it is necessary to understand some concepts as thermodynamic the energy content of the system - ΔH, the Gibbs free energy - ΔG and the entropy of the system - ΔS. The change of enthalpy is a state variable that shows the total energy of a system, in turn the Gibbs free energy shows the power available to be used, and finally the entropy indicates the degree of disorder in the system. These three variables are related as shown in equation 1.

$$\Delta G = \Delta H - T\,\Delta S \qquad (1)$$

According to the above equation The power available corresponds to the difference between the total energy released by the reaction and the energy released due to an increase in entropy of the system. It is related to irreversible processes. The theoretical efficiency of a fuel cell is calculated by the ratio between the available energy the total energy as in equation 2.

$$\eta = \Delta G / \Delta H \qquad (2)$$

The concept of the variation of energy live oligonucleotides can be understood as the energy available to perform external work. In the event of a cell to fuel the external work is the movement of electrons through the external circuto. In other words, in optimal condition, without loss in fuel cell, the whole Gibbs free energy is converted into electrical energy. Deepening the concept of free energy, it was discovered that the ΔG is related to the electrical potential of a battery fuel. The quantitative relation that establishes the value of the electric potential deducted from the energy of Gibbs was demonstrated by the chemist and German physicist Walter Nernst. Using the equation of Nernst that allowed to calculate the electromotive force of a cell with chemical species with different concentrations of a unit. In the case of fuel cells, the equation of Nersnt can be isncrita in terms of the partial pressures of gases reagents as in equation 3.

$$E = E^0 + RT/2F \ln(P_{H2}P_{O2}^{1/2}/P_{H2O}) \qquad (3)$$

Where the factor within the logarithm indicates the equilibrium constant in terms of pressure, F indicates the number of Faraday and E_0 indicates the electrical potential pattern 1atm and 25ºC. The equation shows that the potential of the battery basically depends on the temperature and partial pressures of the reactants. It is identified in the literature that the default condition of temperature and pressure, i.e., 25°C and 1 atm, the thermal energy released in the reaction of hydrogen and oxygen gases is of 285.6 Kj/mol and free energy available for the work of the electric charge is Kj/mol. Thus the theoretical efficiency ideal in the default condition is given by equation 4.

$$\eta = \Delta G / \Delta H = 0{,}83 \qquad (4)$$

2.2 Polarization curve

The characterization of a given CaC does by means of the polarization curve. This in turn aims to relate the potential of the cell and the current density provided by the cell, showing the points and effects that cause losses. Evaluating a typical polarization curve, we can highlight the main ranges with considerable losses, as we can see in Figure 1.

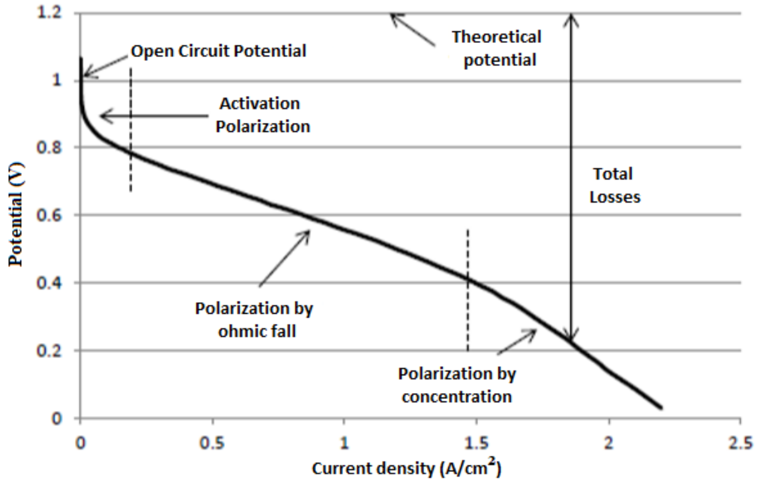


Figure 1: Polarization Curve

Given the proximity of the cell potential with activation polarization, we have the time of greater loss of fuel cell. This is due to the large amount of energy required for the reagent to overcome the impediment between the reagent and product states. The second stage of loss is the polarization by ohmic drop, which is due to the resistance between the reference electrode (cathode) and the working electrode (anode). Finally, we have the polarization by concentration, which is the last stage of losses. It consists of the consequence generated by the electrochemical reactions given by the diffusion of species in the electrolyte

2.3 Flow channels

According to Paulino (2014), the energy performance of Fuel Cell is determined by its maximum potential and polarization losses. The maximum potential of the Fuel Cell will be affected basically by the electrochemical reactions that occur in the electrodes and by the thermodynamic properties of the fuel and the oxidizer, while the polarization losses will occur by the activation (kinetic limitation of the electrode reaction), ohmic drop and limit by mass transport. These two factors will be influenced directly by the geometry and configuration of the electrode channels. Currently there are several studies of channels, with changes in their cross-sectional area, thickness, layout and length.

Among the most well-known models of channels are the channels with circular geometry that makes use of serpentine or parallel configurations, as shown in Figure 2.

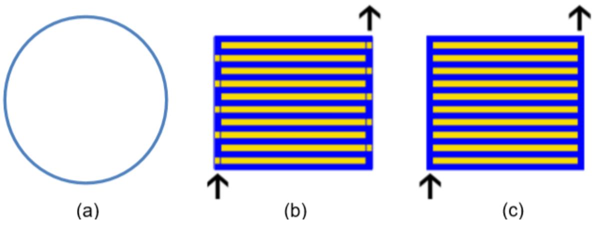


Figure 2 - Circular channel geometry (a), serpentine (b) and parallel (c) configurations

What is important to be highlighted is that in addition to the factors already mentioned this geometry and configuration will be directly responsible for the maintenance of water in the fuel cell. According to Taccani and Zuliani (2011), the geometry of a channel has an important influence on the transport of masses and the pressure drop in the CaC, which directly affects the performance and distribution of the cell. The serpentine configuration has been satisfactory over the years due to its water holding capacity and low pressure loss in the cell. However, a recent study has shown that channels with discontinuous geometries exhibit an increase in tension. According to Chang and Hung (2012), narrower channels increase current density, and in contrast, larger channels are favorable for low current densities. According to a study by Belchor et al (2012), a fuel cell operating at high current, pressure and humidity densities, but with low temperature and reagent flow, there will be a high concentration of water in the channels. This factor makes very narrow channels less likely to be recommended. However, if the cell conditions are of low current and pressure density, high temperatures and large reagent flow, there will be a lack of moisture in the channels, which will be highly detrimental to the yield of the fuel cell. Thus, a middle ground between the thermodynamic and electrochemical variables of the cell is necessary, seeking a better operational condition.

2.4 Prototypes

For the beginning of the study, a commercial PEMFC model was used, in which the geometry and arrangement of the anode channels served as a comparative basis for the development and analysis of the prototypes. In this way the anode model initially studied was that of Figure 3, which has a mixture of parallel channels with perpendicular channels.

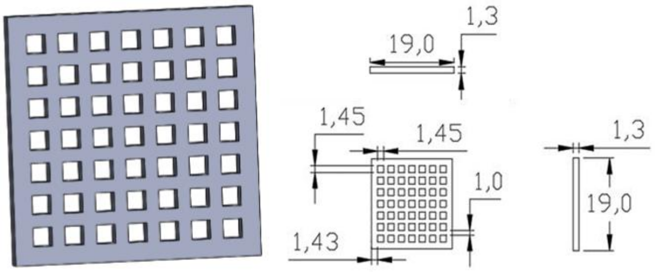


Figure 3 - Prototype base model

From this reference model, it was possible to elaborate three other prototypes with different geometry and arrangement, thus making a comparison and verifying a possible or not, an improvement in the performance of this PEMFC.

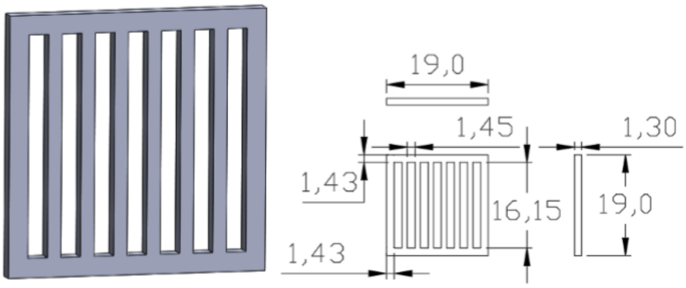


Figure 4 – Prototype 1

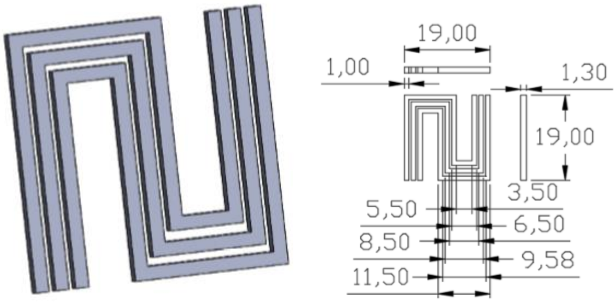


Figure 5 – Prototype 2

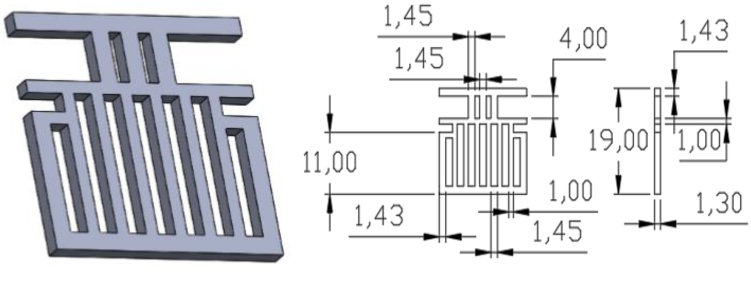
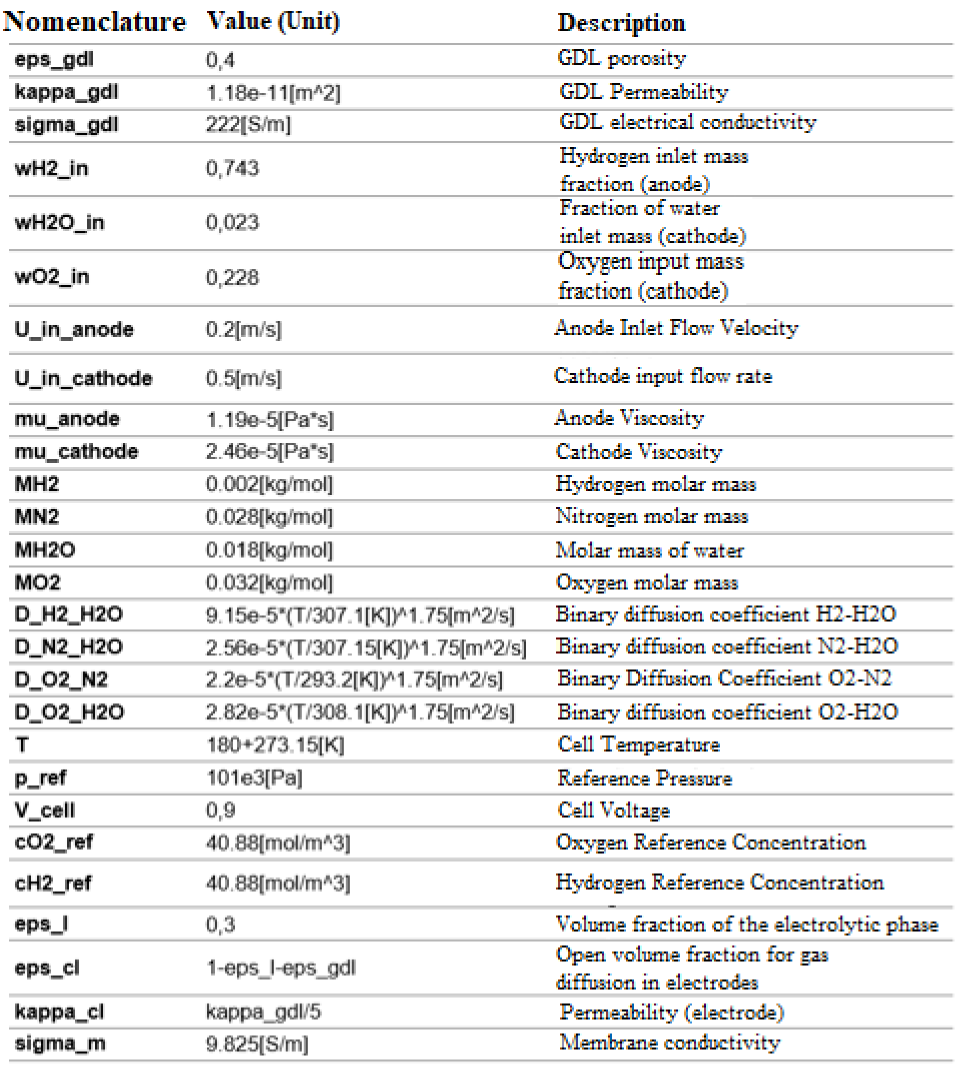


Figure 6 – Prototype 3

2.5 Simulation Conditions

In order to perform the simulation it was necessary to establish parameters that would satisfy the conditions of the software governance equations. In addition, a range of overpotential variation has been designated for the calculation of the polarization curve, which consists of the graphical form of the current density as a function of the overpotency applied in the set. Thus, we can observe the parameters used in Table 1, and the range determined for the calculation of the polarization curve was (1.0, -0.05, 0.3).

Table 1 - Parameters used in the simulation



Nomenclature	Value (Unit)	Description
eps_gdl	0,4	GDL porosity
kappa_gdl	1.18e-11[m^2]	GDL Permeability
sigma_gdl	222[S/m]	GDL electrical conductivity
wH2_in	0,743	Hydrogen inlet mass fraction (anode)
wH2O_in	0,023	Fraction of water inlet mass (cathode)
wO2_in	0,228	Oxygen input mass fraction (cathode)
U_in_anode	0.2[m/s]	Anode Inlet Flow Velocity
U_in_cathode	0.5[m/s]	Cathode input flow rate
mu_anode	1.19e-5[Pa*s]	Anode Viscosity
mu_cathode	2.46e-5[Pa*s]	Cathode Viscosity
MH2	0.002[kg/mol]	Hydrogen molar mass
MN2	0.028[kg/mol]	Nitrogen molar mass
MH2O	0.018[kg/mol]	Molar mass of water
MO2	0.032[kg/mol]	Oxygen molar mass
D_H2_H2O	9.15e-5*(T/307.1[K])^1.75[m^2/s]	Binary diffusion coefficient H2-H2O
D_N2_H2O	2.56e-5*(T/307.15[K])^1.75[m^2/s]	Binary diffusion coefficient N2-H2O
D_O2_N2	2.2e-5*(T/293.2[K])^1.75[m^2/s]	Binary Diffusion Coefficient O2-N2
D_O2_H2O	2.82e-5*(T/308.1[K])^1.75[m^2/s]	Binary diffusion coefficient O2-H2O
T	180+273.15[K]	Cell Temperature
p_ref	101e3[Pa]	Reference Pressure
V_cell	0,9	Cell Voltage
cO2_ref	40.88[mol/m^3]	Oxygen Reference Concentration
cH2_ref	40.88[mol/m^3]	Hydrogen Reference Concentration
eps_l	0,3	Volume fraction of the electrolytic phase
eps_cl	1-eps_l-eps_gdl	Open volume fraction for gas diffusion in electrodes
kappa_cl	kappa_gdl/5	Permeability (electrode)
sigma_m	9.825[S/m]	Membrane conductivity

3 RESULT AND DISCUSION

Making a comparative between the three prototypes of the work as the base model created, we have the behavior below for the different models regarding the curve of polarization and the concentration of hidrogenio in the anode.

3.1 Polarization curve

It is observed through the charts that the polarization of activation begins at 0,9V since, except for the configuration of the anode, the remaining parts of the whole fuel cell remained the same and the parameters of the range of study remained the same in all simulations. Already from 0.7V it is possible to observe a small change in the curve, caused by the polarisation of the fall ohmic. This occurs due to the reference electrode having different resistance of the electrode of work. Evaluating the performance of the cell through the curve of polarisation, it is observed in the three prototypes analyzed feature superior performance in relation to the base model. The highlight is the prototype 3, with the best current density (8.739 x10-1A/m^2) followed by the prototype 2 (8.723 x 10-1 A/m^2), both at 0.3V.

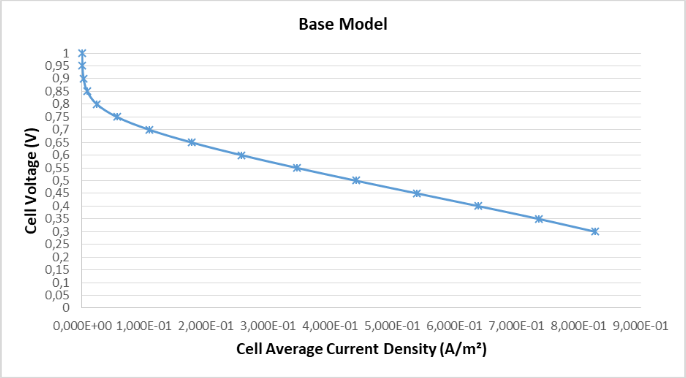


Figure 7 – Polarization curve of base model

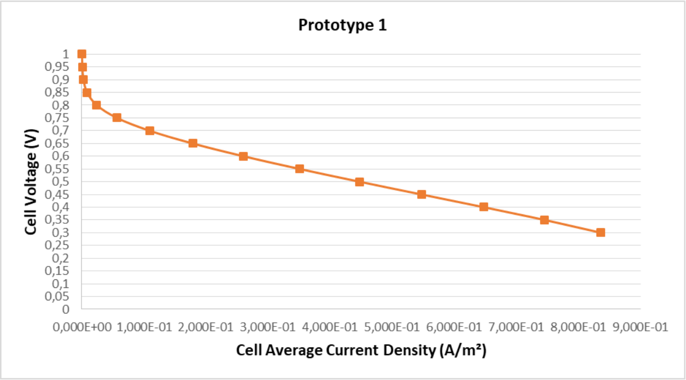


Figure 8 – Polarization curve of Prototype 1

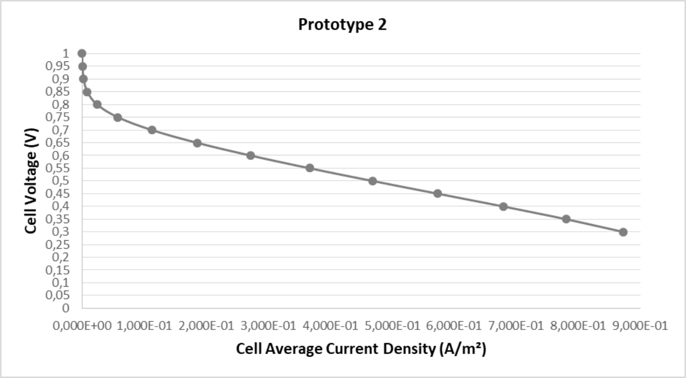


Figure 9 – Polarization curve of Prototype 2

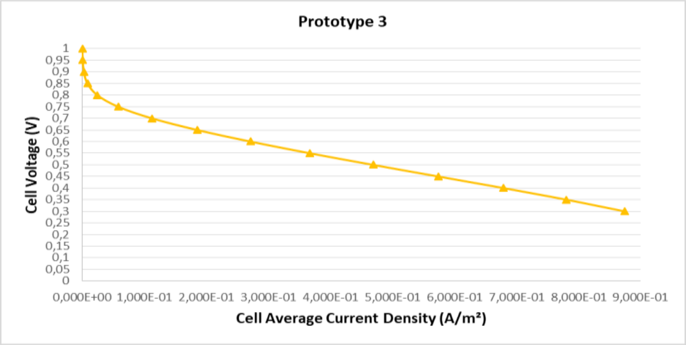


Figure 10 – Polarization curve of Prototype 3

3.2 Concentration of hydrogen in the anode

The concentration of hydrogen in the anode is one of the concerns when it makes changes in geometry and arrangement of the channels of the anode. The low hydrogen concentration will make the completion of active sites in the catalytic layer, and, in turn, the high concentration of hydrogen may compromise the ability of dissociation of hydrogen in catalytic layer. It was considered the same mass fraction of hydrogen in all models. Analyzing the maps of the gas concentration, it can be observed in the base model the largest hydrogen concentration at the bottom of the channels where the entrance of the hydrogen. It has low concentrations also in the middle part of the channels and on the sides of the upper part. The prototype 1 presents behavior near the base model, but with a difference noted on the sides of the prototype. The prototype 2 presents a distribution of hydrogen that virtually divides the cell in half. Finally, the prototype 3 was presented the best hydrogen concentration in the channels of the anode. This fact is given due to entry into the gas have been performed at three different points and the output performed only at a single point.

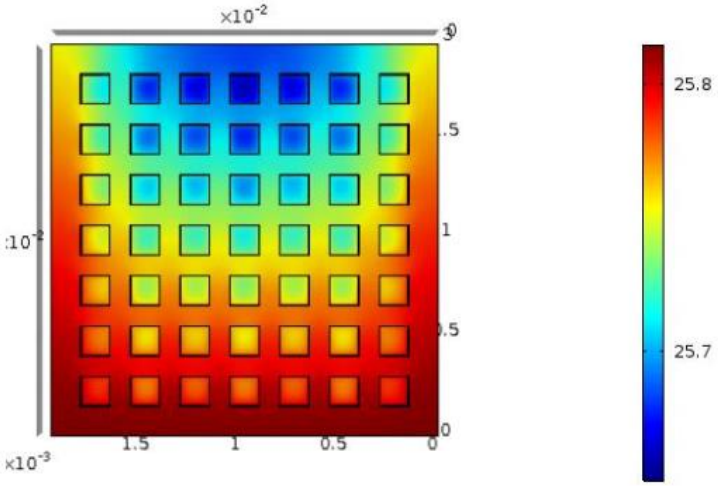


Figure 7 - Hydrogen concentration in the base model

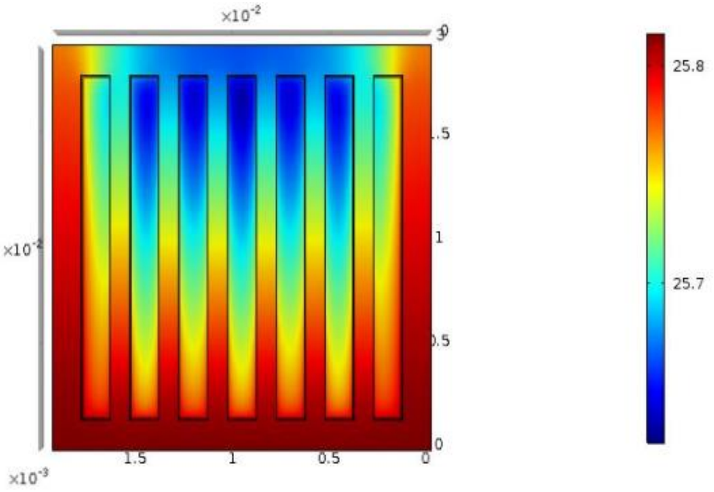


Figure 8 - Hydrogen concentration in prototype 1

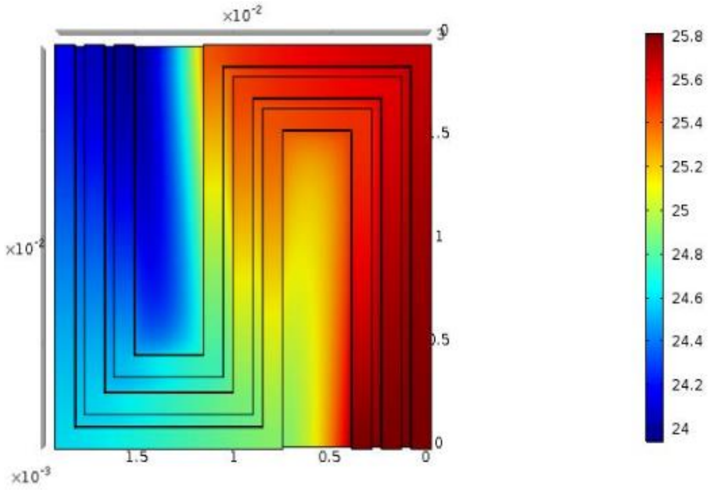


Figure 9 - Hydrogen concentration in prototype 2

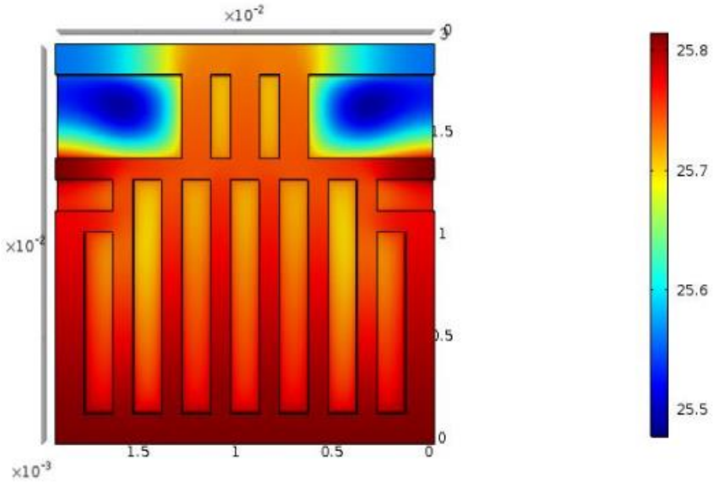


Figure 10 - Hydrogen concentration in prototype 3

4. CONCLUSION

A major milestone was the validation of mathematical models for this type of technology, which is still premature compared to other existing energy sources. Each applied equation has been efficiently proven, generating values that approximate reality.

The variations of the polarization curves were not so great among the prototypes due to the fact that in the present work only changes were made in the geometry of the anode channels, and the results also depend on the cathode channels, since the efficiency extracted from the CaC is Given by the reaction between hydrogen (anode) and oxygen (cathode).

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