

POLARIZATION AND POWER CURVES OF AN ALKALINE FUEL CELL

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Abstract. *Development of new fuels as an alternative to oil based ones has raised in importance every day, due to the continuous growth of global energy demand and automotive vehicles utilization. Fuel cells are one of the cleanest and more efficient alternatives for energy generation. Main reason why fuel cells have not been extensively used is because they are still not economically competitive. An alternative for fuel cell operational cost minimization is developed in the present research. Total volume is adopted as project restriction, because maximum performance on a specific volume will allow smaller fuel cell packages for a desired power. Objective, on this research, was to perform a unitary fuel cell mathematic modeling to preview its performance as a function of operational and geometric parameters, on transient regime, for control and optimization. The results showed the influence of the size of the fuel cell and its gases entrance temperature. Unitary fuel cell mathematic modeling to preview fuel cell performance as a function of operational and geometric parameters, on transient regime, for control and optimization, was successfully performed. Although, there are still several points to be analyzed for improving AMFC performance, which will be done in future researches.*

Key words: *alkaline fuel cell, mathematic modeling.*

1. INTRODUCTION

Fuel cell is a technology which uses the chemical combination of the oxygen (O_2) and hydrogen (H_2) gases to generate electric energy, releasing as waste heat and water (NETO, 2005).

This energy generation technologic concept exists there are more than 150 years and, on the last 30 years, its development was accelerated. Recently, fuel cells have caught scientific community eyes, because non-polluting electric vehicles are fuel cells' main market (M. LINARD, 2000). Although, there are still many obstacles to be surpassed for that goal to be reached. Hydrogen storage tank capability and fuel cell modules durability and potency improvements are needed to turn feasible the commerce of cars with fuel cells. Also, a hydrogen production and distribution system will need to be built. On top of everything, general cost reduction is needed.

Fuel cells are a trustable source of high efficiency clean energy with large possibilities of use. As their pollution emission rates are about nulls, their use will allow air quality improvement. Other advantage on their use is heat cogeneration capability, which implies water vapour production. Fuel cell thermodynamic optimization turns feasible fuel cell usage by reducing its operational costs and maximizing its energy generation capability.

Alkaline fuel cell work can be shortly synthesized. Electrolyte is formed by an alkaline watery solution and transversed by hydroxide ions, which band together with $2H^+$ and electrons to generate a water molecule. When hydrogen is broken into $2H^+$, at electrode, these two released electrons round externally and generate energy.

Although PEMFC (polymeric membrane fuel cell) is the most used fuel cell type, to build a polymeric membrane whose efficiency can be compared to the commercial ones remains still a challenge to Brazilian researches. Also, possibility of working with electrodes different than platinum is considered. Platinum short availability and high prices, and also its unavailability on brazilian soils, determined the choice of a nyquil-cobalt electrode development. As a nyquil-cobalt electrode can not be used in acid environment, as in PEMFCs, alkaline environment was needed. Thus, to build a completely brazilian alkaline fuel cell, the modified alkaline fuel cell was chosen for this fuel cell development research.

Alkaline Membrane Fuel Cell relies on an especial difference: its alkaline electrode is not liquid, as on other cell types, but made out of cellulose lamellas soaked on a potassium hydroxide solution. Because of this membrane this new type of fuel cell was named AMFC – Alkaline Membrane Fuel Cell.

Mathematic model obtained on this research can be used on other fuel cell types, since reactions and electrolyte types are known. Therefore, chemical equations and energetic reactions can be substituted in this model.

Objective, on this research, was to perform a unitary fuel cell mathematic modeling to preview its performance as a function of operational and geometric parameters, on transient regime, for control and optimization.

2. MATHEMATICAL MODEL

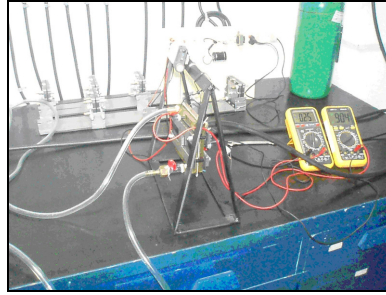


Figure 1. A Alkaline Membrane Fuel Cell

Vargas e Bejan, (2003) have developed an alkaline cell mathematic modeling, which was adapted on this research to represent the differentiated electrolyte of AMFC. Chosen method was Volume Elements Method (VARGAS et al., 2001).

General idea of Volume Elements Method is to subdivide, initially, problem dominion on finite dimensions sub dominions such as the whole sub dominions set is equal to the original dominion. Then, on every isolated sub dominion, electrochemistry and conservation (mass, energy and species) equations are applied, as well as analytic and empiric literature available correlations, to quantify existent fluxes. This model adopts for each volume element the Classic Thermodynamic basis hypothesis of uniform properties on control volume.

Generally, this local behave is descript with simple functions. Main characteristic on this proceeding, thus, consists on the use of local approximations on volume elements on which the original domain was divided, instead of using global character approximations. For obtaining responding results every time better, volume elements number should be increased, kept the same local behave adopted for each one of them, instead of adopting greater order functions on global character approximation.

Developed mathematic model might also be used for other fuel cell types, since type electrolyte and reactions are considered using pertinent chemical equations and energetic interactions.

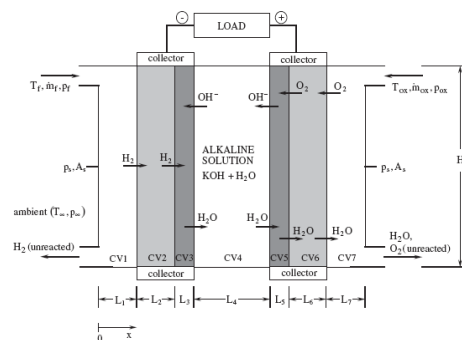
Fuel cell is divided onto seven control volumes, which correspond to the most important system parts. They interact energetically with each other and with the environment. These seven control volumes are:

- CV1 – fuel entrance chamber
- CV2 – anode diffusion layer
- CV3 – anode reaction layer
- CV4 – electrolytic solution and the support
- CV5 – cathode reaction layer
- CV6 – cathode diffusion layer
- CV7 – oxidant entrance chamber

Modeling considers all present flux phenomena, resulting on a time dependent unidirectional internal flux model with three-dimensional characteristics such as electrolyte wet area and thermal exchange between cell and neighbourhoods.

Model algebraic and differential equations solution result on temperature and pressure profile for each control volume on polarization and system potency curves.

Control volume chosen by Vargas and Bejan (2003) showed on figure 2 were used on this research.



For obtaining real electrochemical potential and consequentially the power, overpotential losses are subtracted from the reversible potential. Losses through kinetic reaction, ohmic losses through electronic and ionic resistance, and concentration losses due to diffusion (mass transportation) are considered as overpotential losses.

These losses are cell total current (I) dependent, which is required by external charge (or cell voltage). Galvanostatic technique was adopted to control cell total current, turning this variable into an independent one. Analysis was done for transient stage, considering real time control proposal.

Dimensionless variables were defined based on geometry and operational system parameters.

Vargas and Bejan (2003) developed the model whose resulted equations are presented below with brief explanation on the control volume they are related to, when alterations for adaptation to AMFC are needed. Variables were dimensioned.

2.1. Fuel and Oxidant entrance chamber (CV1 e CV7)

CV1 exchanges heat with the environment and with CV2. Same is applied to CV7, which exchanges heat with CV6 and with the environment.

Mass and energy balance for CV1, considering incompressible flux, lead to temperature on CV1,

$$\frac{d\theta_1}{d\tau} = \left\{ \frac{N_1}{\psi_f} (1 + \tilde{A}_L \xi_1) (1 - \theta_1) + (\theta_f - \theta_1) + \frac{\tilde{Q}_{12s}}{\psi_f} \right\} \frac{\theta_{1,0}}{P_f} \frac{\gamma_f}{\xi_1} \psi_f \quad (1)$$

Where θ is the dimensionless temperature, τ the dimensionless time, ξ the CV length, ψ is the dimensionless mass flow rate, ϕ the porosity, η are the overpotentials and γ the ratio of the species heats (cp/cv).

Mass and energy balance on oxidant entrance space (CV7), incompressible non-mixable flux consideration ($dm_7/dt = 0$) and space predominantly fulfilled with dried oxygen consideration lead to:

$$\frac{d\theta_7}{d\tau} = \left[\tilde{Q}_7 + \psi_{ox} \frac{c_{p,ox}}{c_{p,f}} (\theta_{ox} - \theta_7) + \tilde{H}(\theta_6)_{H_2O} - \tilde{H}(\theta_7)_{H_2O} \right] \frac{R_{ox} \theta_{7,0} \gamma_{ox}}{R_f P_{ox} \xi_7} \quad (2)$$

2.2 Anode and cathode diffusion layers (CV2 e CV6)

Reactions occur on anodic and cathodic diffusion layers. Both electrodes on a fuel cell are porous to proportionate a large wet superficial area to promote major possible contact between electrolytic solution and electrode and, consequently, great power density. Porous environment is constituted by one solid and one fluid sides. CV2 fluid mass is negligible if compared to the solid mass. Thus, on energy balance only the solid mass was considered. These control volumes exchange heat with the environment and with neighbour control volumes.

Wet areas on porous anodes and cathodes were estimated by dual-porosity synthesized metal electrodes consideration. Permeability was considered for obtaining each electrode wet area.

Energy balance resulted on the CV2 temperature below:

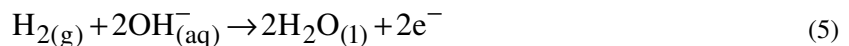
$$\frac{d\theta_2}{d\tau} = \left[(\theta_1 - \theta_2) + \frac{\tilde{Q}_2}{\psi_f} \right] \frac{\gamma_{s,a} \psi_{H_2}}{\tilde{p}_{s,a} (1 - \phi_2) \xi_2} \quad (3)$$

And for CV6:

$$\frac{d\theta_6}{d\tau} = \left[\tilde{Q}_6 + \psi_{O_2} \frac{c_{p,ox}}{c_{p,f}} (\theta_7 - \theta_6) + \tilde{H}(\theta_5)_{H_2O} - \tilde{H}(\theta_6)_{H_2O} \right] \frac{\gamma_{s,c}}{\tilde{p}_{s,c} (1 - \phi_6) \xi_6} \quad (4)$$

2.3 Anode and cathode reaction layer (CV3 and CV5)

Electric current is generated through reaction on the reactional anode layer (CV3),



were an alkaline solution was assumed on the electrolyte. Equation (10) shows that hydrogen and hydroxide are consumed on rates \dot{n}_{H_2} and \dot{n}_{OH^-} . Electrons are produced and water is generated on rate \dot{n}_{H_2O} .

CV3 is divided on 2 compartments, which form the anodic reactional layer: solid and liquid solution. However, on thermal analysis only solid is considered because CV3 fluid mass is negligible if compared to the solid mass. CV3 exchanges heat with neighbourhoods and generates heat through ohmic resistance.

CV3 temperature profile becomes:

$$\frac{d\theta_3}{d\tau} = [\tilde{Q}_3 - \Delta\tilde{H}_3 + \Delta\tilde{G}_3] \frac{\gamma_{s,a}}{\tilde{\rho}_{s,a}(1 - \phi_3)\xi_3} \quad (6)$$

Anode reversible electric potency as given by Nernst equation is showed below:

$$V_{e,a} = V_{e,a}^\circ - \frac{\bar{R}T_3}{nF} \ln Q_3 \quad (7)$$

where $V_{e,a} = \Delta G_3 / (-nF)$ and $V_{e,a}^\circ = \Delta G_3^\circ / (-nF)$.

There are two mechanisms for potency losses at the anode: (i) charge transfer, and (ii) mass diffusion. Charge transfer potency loss is obtained from the Butler-Volmer equation for a given current I (Bockris and Drazic, 1972),

$$\frac{I}{A_{3,wet}} = i_{o,a} \left[e^{\frac{(1-\alpha_a)\eta_a F}{RT_3}} - e^{-\frac{\alpha_a \eta_a F}{RT_3}} \right] \quad (8)$$

Cathode reaction layer (CV5) analysis is analogous to the one presented for the anode reaction layer (CV3). CV5 is divided into two compartments, fluid and solid, and for thermal analysis only the solid compartment is taken into account.

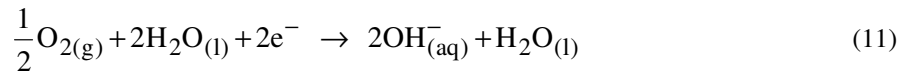
$$\frac{d\theta_5}{d\tau} = [\tilde{Q}_5 - \Delta\tilde{H}_5 + \Delta\tilde{G}_5] \frac{\gamma_{s,c}}{\tilde{\rho}_{s,c}(1 - \phi_5)\xi_5} \quad (9)$$

2.3 Electrolyte (CV4)

Present model adopts as alkaline solution a potassium hydroxide aqueous solution, which is represented by the chemical equation:



Alkaline solution (CV4) interacts with CV3, CV5 and the ambient. Alkaline solution analysis at the cathode reaction layer (CV5), is determined by/ Cathode reaction layer (CV5) alkaline solution analysis is:



Equation (11) shows that oxygen and water are consumed at the rates \dot{n}_{O_2} and $2\dot{n}_{H_2O}$, while water is produced at the rate \dot{n}_{H_2O} .

CV4 temperature is obtained through:

$$\frac{d\theta_4}{d\tau} = \left[\tilde{Q}_4 + \tilde{H}(\theta_3)_{H_2O} - \tilde{H}(\theta_4)_{H_2O} + \tilde{H}(\theta_5)_{OH_{aq}^-} - \tilde{H}(\theta_4)_{OH_{aq}^-} \right] \frac{\gamma_{sol}}{\tilde{\rho}_{sol}\xi_4} \quad (12)$$

where $\gamma_{sol} = c_{p,f}/c_{sol}$, and c_{sol} is the solution specific heat; i.e., $c_{sol} = 0.01yc_{KOH} + (1 - 0.01y)c_{H_2O}$.

Alkaline solution electrical resistance is given by $R_4 = L_4/(\sigma A_s)$. Hence, there is an ohmic loss in the alkaline solution (CV4). Additionally, potential loss occurs due to electrical resistance of the solution, which penetrates the porous reaction layers in CV3 and CV5. Therefore, the total dimensionless ohmic loss from CV3 to CV5 is

$$\tilde{\eta}_{sol} = \frac{I L_T}{\sigma A_s V_{ref}} \sum_{i=3}^5 \frac{\xi_i}{\phi_i}, \quad (\phi_4 = 1) \quad (13)$$

3. RESULTS AND DISCUSSION

On this research was studied the influence of temperature of the gases and the dimensions of the AMFC. The porosity of the electrolyte membrane was also obtained. It is important to consider the porosity effect on results, which interferes on thermal conductivity and control volume diffusibility thus, this effects will be studied on future researches.

AMFC simulation was adapted to Vargas and Bejan (2003) model concerning to the dimension of the AMFC prototype that has been studied at the Mechanical Engineer Department of the Universidade Federal do Paraná,

Porosity value for CV4 obtainment was 35% and will be used in the future to get the CV4 wetted area.

Pre results for AMFC will be shown and compared as the results obtained by Vargas and Bejan (2003), named as S1 or first test.

On the tests were availed the influences of the fuel cell dimensions (in the aim to approximate to the one developed) and the temperature of gases entrance, from the environmental and inside the fuel cell.

Table 1. Values used on the tests.

	Temperatures (K)	Fuel Cell Dimensions (m)
1 st Test – S1	298.15	1.e-2 x 1.5e-1 x 1.5e-1
2 nd Test – S2	298.15	0.5e-1 x 1.e-1 x 1.e-1
3 rd Test – S3	288.15	1.e-2 x 1.5e-1 x 1.5e-1

The following pictures are grouped by the curve that demonstrate and the tests order.

Temperature's study is shown in Fig. 3. CV1's temperature were the lower in all simulations. S2 resulted in lower temperatures for CV2 and CV3's temperatures were lower than in the other tests, that is a consequence of the fuel cell size. CV5 and CV6 present the higher temperatures what can be explained by the higher value of the cathode's enthalpy.

Curves for S1 and S3 looked like the same. In S3 the temperatures were higher. That was expected since the environmental and the fuel oxidant's temperature was reduced.

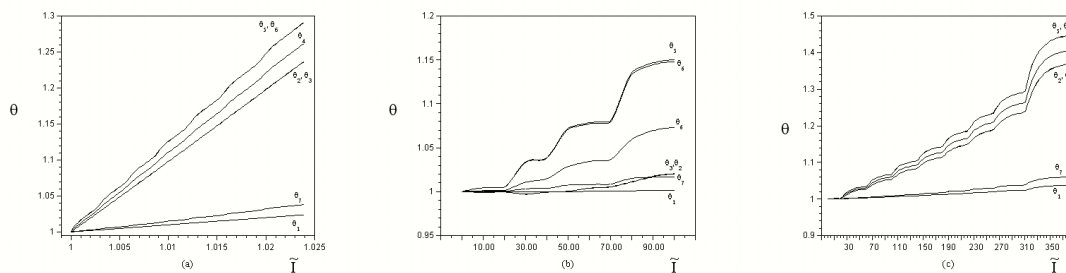


Figure 3. Temperatures of the Control Volumes for the three tests realized.

Figure 4 illustrates the total power and the polarization curve. The open circuit voltage on the three tests was equal to the reversible cell potential. S2 was the one with larger activation polarization dominated region. Even with the lower temperature S3 presented the same region dominated by activation polarization as in S1.

Since S2 presented the higher concentration polarization dominated region it can be concluded that the higher dimension difficult the mass transport what wasn't observed in S1.

S2's resulted in a lower current density and maximum power values; also its curve's form was very different from the others. The higher power was obtained in S3, what can be explained by the higher temperature that the fuel and the oxidant entered in the fuel cell.

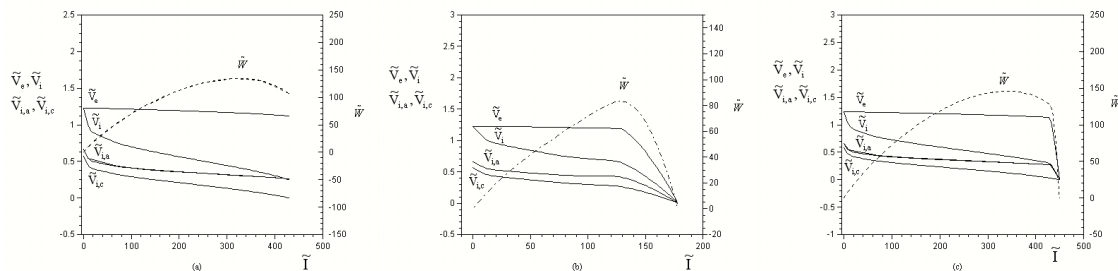


Figure 4. Power and Polarization Curves for the three tests realized.

4. CONCLUSION

Unitary fuel cell mathematic modeling to preview fuel cell performance as a function of operational and geometric parameters was successfully performed. The change made in temperature in S3 wasn't high enough to impact some alteration in the curves of temperature, power and polarization. In S2 we can conclude that as we change the size of the fuel cell the control volumes' length increases too. Although the cross section area doesn't change. Also it caused a higher lose for polarization. Furthermore there are still several points to be analyzed for improving AMFC performance, which will be done in future researches.

5. ACKNOWLEDGEMENTS

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