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STUDIES ON MEMBRANE ACID ELECTROLYSIS FOR HYDROGEN PRODUCTION

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ABSTRACT

Hydrogen represents great opportunity to be a substitute for fossil fuels in the future. Water as a renewable source of hydrogen is of great interest, since it is abundant and can decompose, producing only pure H_2 and O_2. This decomposition of water can be accomplished by processes such as electrolysis, thermal decomposition and thermochemical cycles. The electrolysis by membrane has been proposed as a viable process for hydrogen production using thermal and electrical energy derived from nuclear energy or any renewable source like solar energy. In this work, within the context of optimization of the electrolysis process, it is intended to develop a mathematical model that can simulate and assist in parameterization of the electrolysis performed by polymer membrane electrolytic cell. The experimental process to produce hydrogen via the cell membrane, aims to optimize the amount of gas produced using renewable energy with non-carbogenic causing no harm by producing gases deleterious to the environment.

KEY WORDS

Electrolysis; Non-Carbogenic Hydrogen; PEMFC.

1. INTRODUCTION

The technology of fuel cells with polymer electrolyte, the PEMFC (Proton Exchange Membrane Fuel Cell) is the subject of intense research in recent years due to its higher energy efficiency compared to fossil combustion machines and also enabling the use of renewable sources to generate hydrogen. Theoretically, when reversing a PEMFC, you get a PEM electrolyser, called PEMEC (Proton Exchange Membrane Cell Electrolysis). There are already relevant researches on fuel cells bifunctional called URFC (Unitized Regenerative Fuel Cell) [1]. These cells make both the work of a PEMFC as a PEMEC as well.

In electrolytic cells, the anode is the region where oxidation occurs. Due to the difficulty of oxygen evolution at the anode, it is necessary a catalyst layer to improve operational performance [2]. The overpotential is relatively high (circa -1.75 V) compared to the equilibrium potential (-1.23 V). So, it consumes relevant amount of energy to promote electrolysis. The exceeding energy amount generates simultaneously heat inside the cell respecting the thermodynamic entropic balance.

The principle of a PEM water electrolysis cell (PEMEC) [3] is shown in **Erro! Fonte de referência não encontrada.**. There are two electrocatalytic layers (platinum) platted on both side of a thin polymeric membrane material (perfluorosulfonic polymer). Nafion MEAs have been used, following the tradition of PEMFCs. The polymeric membrane is a proton-conducting

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media of high ionic conductivity and low electrical resistivity. The cell is polarized with a voltage of at least 1.4 V (and a maximum value of 2 V), which is applied to the cell when liquid water is supplied to the anode. The water electrolysis takes place according to the half-cell reactions presented in the Figure 1. Oxygen is produced at the anode and hydrogen at the cathode. PEM cells (including bipolar plates, current collectors and so-called membrane-electrode assemblies or MEAs) of various surfaces stacked in a filterpress configuration to adapt the productivity of the electrolyser both to the input power available and the production needs.

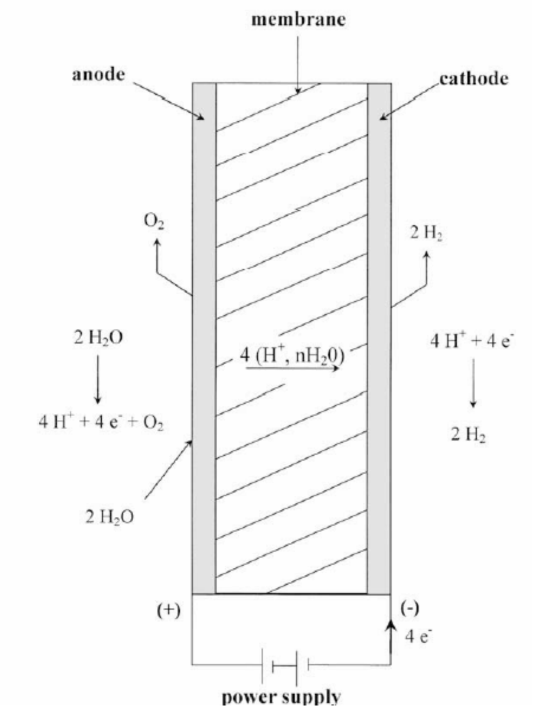
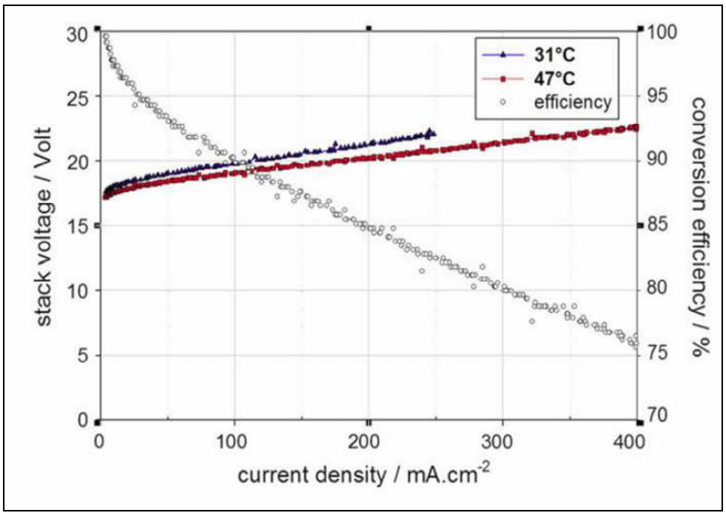


Figure 1: Conceptual model for PEMEC

Nowadays, there are commercial equipments of PEM water electrolyser which can produce hydrogen (and oxygen) up to 1 Nm^3H_2/h [4]. The literature [3] reveals that MEAs (250 cm^2) prepared with Nafion 117 as solid polymer electrolyte, with platinum (~0.5 mg/ cm^2) used as electrocatalyst at the cathode and the anode, with addition of iridium (1.2 mg/cm^2) at the anode. An assembling of 12 cells stack has aimed production results, in terms of developed current density, shown in **Erro! Fonte de referência não encontrada.**.

The result of current density of 0.4 A/cm^2 with a mean cell voltage of 1.88 V/cell is feasible to be obtained. The overall efficiency is close to 75% (calculated on the higher heating value). During operation, the temperature increases. As reported by the authors [3], this process at 90℃ with a typical cell voltage of 1.9 V obtained current density of 0.8 A/cm^2.



Graph 1: Cell voltage vs. current density curves measured at low temperature on the PEM water electrolyser. (12-cell stack, 250 cm^2 each, at atmospheric pressure)

Water electrolysis has been studied by several manners, focusing electrocatalysis, current collectors, even under different temperatures and pressures. Recently, by the GenHyPEM project, Millet et al [5] have made stacks with efficiency close to 80%. They have done experiments under 1-130 bar pressure range. Choi et al [6] studied a simple model of water electrolysis, incorporating electrode areas kinetics and transport in the membrane. The model examined resistance of each step of the electrolysis process using Pt and $PtIrO_2$ as electrocatalysts. Tin oxide added to the iridium oxide did not benefit Marshall [7] tests, since the cyclic voltammetry shows that active areas or quantity of active points decreases as the amount of tin increases. The best PEM cell performance was achieved with a pure IrO_2 anode giving 1.61 V at 1 Acm^{-2} and 90◦C. Tantalum was used in $Ir_xRu_yTa_zO_2$ powders synthesized and examined as anode electrocatalysts in PEM water electrolysis cells [8]. Very high performance was obtained for anode materials containing 20–40 mol% Ru and 0–20 mol% Ta and in total 7 of the 16 anode compositions resulted in cell voltages less than 1.6V at 1Acm^{-2} and 80 ◦C. The best result was obtained with an $Ir_{0.6}Ru_{0.4}O_2$ anode and 20 wt% Pt/C cathode (*E*cell=1.567V at 1Acm^{-2} and 80 ◦C) when using Nafion 115 as the electrolyte membrane. Grigoriev et al [9] studied the optimization of porous current collectors for PEM water electrolysis. Spherical powder size value of 50-75 µm is required in porous titanium plates to get overall cell efficiency. From the polarization curves measured at 90 ℃, it is shown that an inadequate pore structure of the current collectors can increase the cell voltage by up to 100 mV at 2 A cm^{-2}. Sawada et al [10] has used PEM prepared by the γ-ray-induced post-grafting of styrene into a crosslinked-polytetrafluoroethylene (PTFE) film and subsequent sulfonation with a similar system studied in this work.

Due to corrosion of graphite, nickel is one of the less expansive possibilities of materials for water electrolysis. So, graphite plates covered with nickel will be done is this work.

Mathematical studies are made to compare with experimental results [10]. Assuming no mass transport limitation, Butler-Volmer expression is used throughout the electrochemical reaction. Then we have this expression in relation to the anode:

$$i = i_{A_0}\left[\exp\left(\frac{\alpha_A v_{e^-} F\eta_A}{RT}\right) - \exp\left(-\frac{(1-\alpha_A) v_{e^-} F\eta_A}{RT}\right)\right]$$

where i_{A_0} is the exchange current density at the anode (A/cm^2), α_A is the transfer coefficient, ν_{e}- is the stoichiometric coefficient of electrons in the anode reaction, F is the Faraday constant, η_A is the anode overpotential, R is the universal gas constant and T the temperature.

Assuming $\alpha_A = 0.5$ and $v_{e^-} = 2$ for anode, we have

$$\eta_A = \frac{RT}{F}\sinh^{-1}\left(\frac{i}{2\mathrm{i}_{A_0}}\right)$$

Similarly, if we assume $\alpha_A = 0.5$ and $v_{e^-} = -2$ for cathode, we have

$$\eta_C = -\frac{RT}{F}\sinh^{-1}\left(\frac{i}{2\mathrm{i}_{C_0}}\right)$$

where i_{C_0} is the exchange current density at the cathode. It should be noted that solutions in the chambers (anode and cathode) are assumed to be well mixed and thus the concentrations in the surface do not differ significantly from those inside the cell (between electrodes).

At steady state, the divergence of current density in the polymer electrolyte is zero, thus:

$$\frac{di}{dz} = 0 \qquad \text{and} \qquad i = -\sigma\frac{d\varphi}{dz}$$

where σ is the electrolyte conductivity (S/cm) and φ is the potential (V) in the membrane.

The potential applied in cell consists of the Nernst potential (V$_0$), anode (η_A) and cathode (η_C) overpotentials, membrane overpotential (η_M) and interface overpotential (η_I) as

$$V = V_0 + \eta_A - \eta_C + \eta_M + \eta_I$$

where the interface overpotential (η_I) must be written according to the R$_I$, membrane-electrode interfacial resistance, and the current density as $\eta_I = R_I i$

The Nernst potential or equilibrium open circuit potential (V$_0$) is empirically given as [11-12]

$$V_0 = \frac{\Delta G}{2F} + \frac{\Delta S}{2F}(T - T_{ref}) + \frac{RT}{2F}\left[\ln(P_{H_2}) + \frac{1}{2}\ln(P_{O_2})\right]$$

Based on the equation of electrochemical reaction, equilibrium potential can be expressed as [11-12]

$$V_0 = 1.23 - 0.9 * 10^{-3}(T - 298) + \frac{RT}{4F}\ln\left(P_{H_2}^2 P_{O_2}\right)$$

The membrane potential can be obtained by integration the equation [$\frac{di}{dz} = 0$]:

$$\eta_M = \left(\frac{L_M}{\sigma_M}\right)i$$

where L_M is the PEM thickness, and σ_M is the electrolyte conductivity. The membrane resistance depends mainly on temperature and moisture content in the membrane. Nafion conductivity can be described by the following relation [13]:

$$\sigma_M = \sigma_M^{ref} \exp\left[1268\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right]$$

Therefore, the general voltage-current relationship of the cell to the electrolysis cell can be obtained by combining the previous equations:

$$V = V_0 + \frac{RT}{F}\sinh^{-1}\left[\frac{1}{2}\left(\frac{i}{i_{A_0}}\right)\right] + \frac{RT}{F}\sinh^{-1}\left[\frac{1}{2}\left(\frac{i}{i_{C_0}}\right)\right] + \left(\frac{L_M}{\sigma_M}\right)i + R_I i$$

2. OBJECTIVES

The present experimental studies aim to present the first results on PEMEC assembling using basically the same materials of a normal fuel cell and reversing the polarity. The water, kept at room temperature, is pumped into the plates channels, as raw material for the reaction and to help carrying the gases away from the cell. To study the gas evolution, a transparent acrylic cell was employed to show the bubble formation during electrolysis. Cell made with graphite plates, as in a normal fuel cell, was also used aiming at controlling the ability to produce hydrogen. Some experiences were also carried out to protect the surface of graphite against corrosion [6]. Due to this corrosion on graphite plates, an experiment utilized a coated plate with nickel electroless plating.

These experiments are compared with a theoretical simple model. Principles of electrochemical equations and parameters are used.

3. METHODOLOGY

3.1 Acrylic system assembling

As shown in **Erro! Fonte de referência não encontrada.**2, the system has two power connectors, two feeding tubes, two catalyst layers and a Membrane electrode assembly (MEA).

This arrangement and experiments were also assisted by two water pumps, two volumetric tubes for gases production, voltmeter, ammeter, power supply with current, potential controllers, temperature controllers and thermostats.

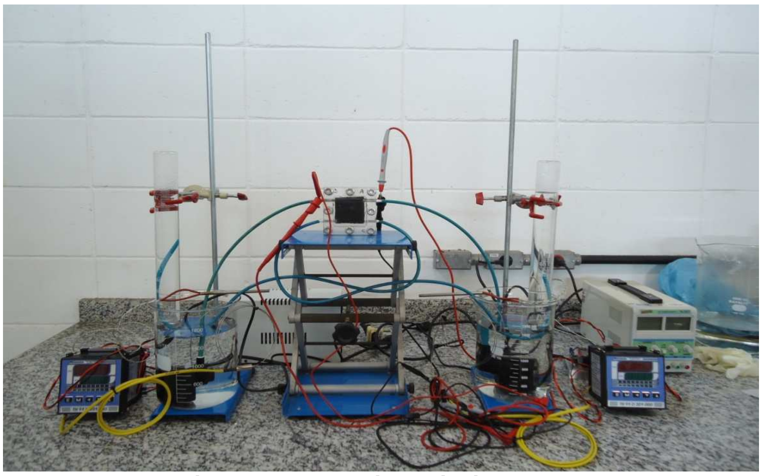


Figure 2: Water electrolysis system

The MEA (**Figure 3**) preparation (membrane electrode assembly) and the electrodes were made by IPEN method [15-16]. The specific contents were: (A) for cathode, it was used 1.1 mg/cm^2 of Nafion and 0.4 mg/cm^2 Pt, (B) for anode, it was used 1.1 mg/cm^2 of Nafion and 0.4 mg/cm^2 of Pt-Ru (1:1). The membrane was Nafion 115.

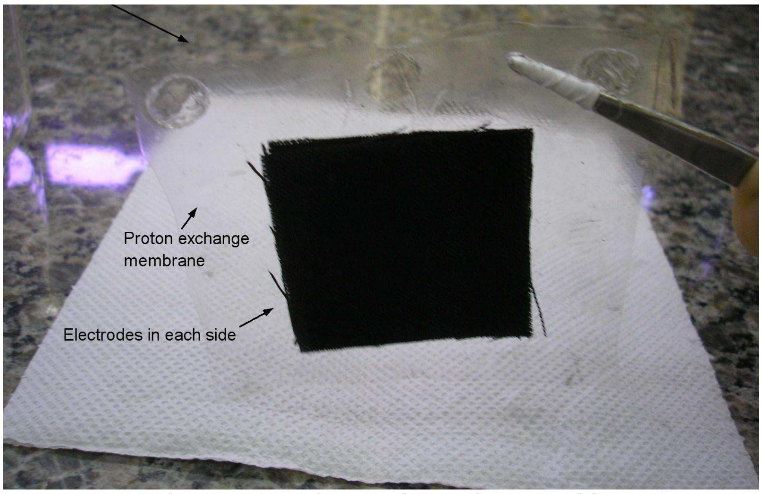


Figure 3: Membrane electrode assembly

The temperature of water circulating in system was 25℃. The gas pressure was kept at 1 atm. It was performed a potential scanning of DC power supply from 1.2 to 2.2 V to get the current density (A/cm^2). There were three repetitions after a stabilization period of at least 1 h.

Measurements of gases were made for three times to check the produced volume of hydrogen and oxygen in intervals of 30 minutes. Acrylic cell has electrodes with 25 cm^2.

3.2 Coated graphite cell assembling

Both plates were coated by electroless method with nickel. Before the treatment, it was necessary to clean it with water and soap and tricoethylene and acetone.

Figure 4: Graphite plate coated with nickel

The assembling for this experimental set was the same as used for acrylic cell. Nevertheless, the graphite cell has electrodes with 5 cm^2 and the potential scanning varied from 1.2 to 1.9V.

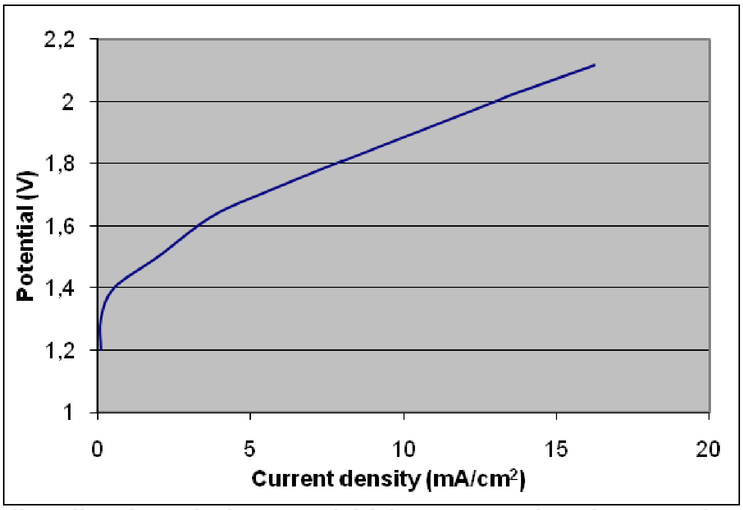
4. RESULTS

4.1 Experimental

The volume production of hydrogen and oxygen has the ratio of 2:1, either in acrylic assembling as in the graphite one. This confirms the stoichiometric balance equation of the electrochemical reaction, as presented in **Erro! Fonte de referência não encontrada.**.

4.1.1 Acrylic cell

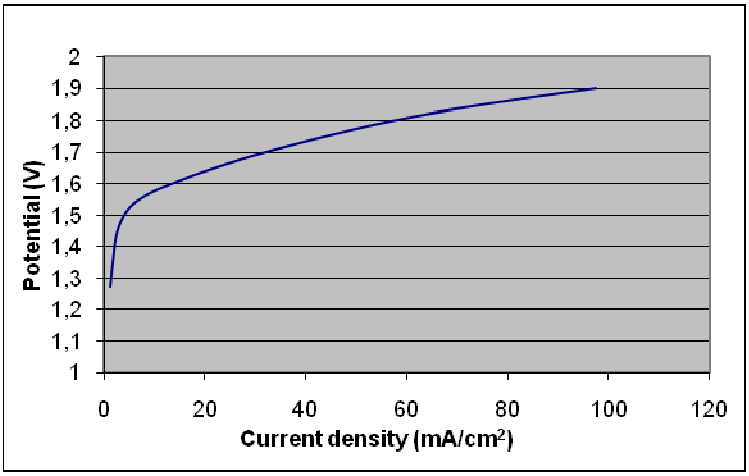
The results of H_2 production in the acrylic cell electrolysis was 0.03 mL/s when the system had a current density of 7.59 mA/cm^2 at 1.81 V. The **Graph 2: Acrylic cell** shows the relation of current with the potential between 1.2 and 1.9 V. As could be seen there is a high inclination in the ohmic region, showing that the resistance of the system was very high. The overall result of this cell was accounted on 37% of efficiency.



Graph 2: Acrylic cell's Electrolysis potencial (V) versus produced current density (mA/cm^2)

4.1.2 The graphite cell coated with nickel

The graphite cell coated with nickel had the results at **Graph 3: Potential (V) versus current density of a graphite electrolysis cell coated by nickel**, which shows the relation of current with the potential between 1.2 and 1.9 V. At 78 mA/cm^2, 1.84 V, the production of hydrogen had an average production of 0.05 mL/s. The overall efficiency of this coated nickel PEMEC was accounted as 52%.



Graph 3: Potential (V) versus current density of a graphite electrolysis cell coated by nickel

4.2 Mathematical Model Simulation

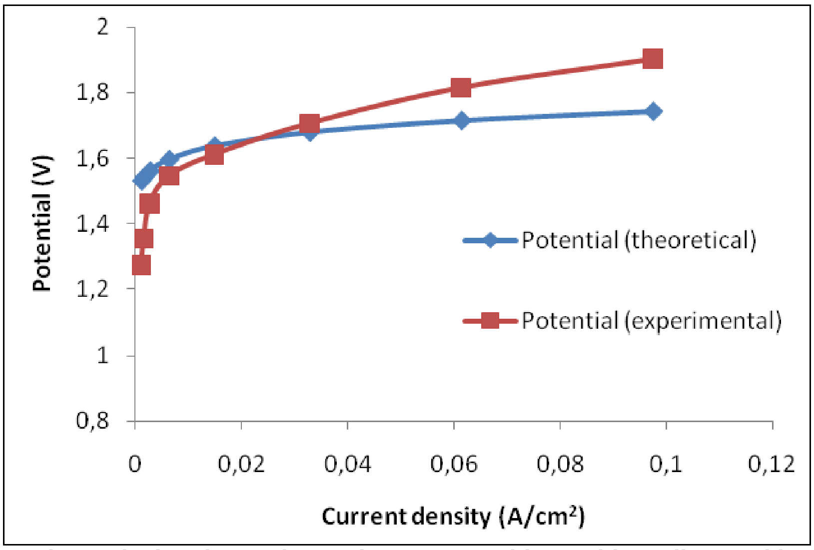
Some parameters, collected from the literature, and from data obtained experimentally at IPEN, it was simulated the potential results to acquaint the feasibility of literature suggested modeling. The data presented in the literature is shown in

Table 1.

Table 1: Parameters for the electrochemical model

Parameters	Values	Dimensions	Names
R	8.314	J / mol K	universal constant of gases
T	298	K	Temperature
F	96485	C/mol	Faraday Constant
i_{A_0}	10^{-9}	A/cm^2	anode exchange current density [12]
i_{C_0}	3×10^{-3}	A/cm^2	cathode exchange current density [12]
L_M	148	µm	thickness of the proton exchange membrane
σ_M	0.125	S/cm	conductivity of the electrolyte [17]
R_I	0	Ω	interface differential resistance
P_H	1	atm	Hydrogen pressure
P_O	1	atm	Oxygen pressure

The interface resistance R_I is assumed to be negligible, hence it was set to zero in Choi's model [6]. Plotting from experimental and theoretical data, using the mathematical formulation of CHOI [6] and NIE [12], the Graph 4 shows the results. As can be seen in the plot, there are differences between the experimental data and the modeling. In the electrocatalysis region, the experimental data revealed a bigger inclination than the model and, in the ohmic region, this trend inverted.



Graph 4: Theoretical and experimental measures with graphite cell coated by nickel.

5. DISCUSSION

As first basic evidence, despite the initial interest to produce hydrogen for cell fuel, also pure oxygen is obtained as a stoichiometric proportion, able to be a subproduct of this PEMEC technology.

The production results as 37% and 52% for the experimental cells (acrylic and Ni-platted graphite plate) were quite bellow the experiment made in the literature as described in **Erro! Fonte de referência não encontrada.** that accounts 75% of efficiency based on equilibrium potential for water electrolysis (-1.23V). First of all, the room temperature carried out in the experiments lowered significantly the efficiency compared to the literature. The higher efficiency of graphite cell with nickel platting against acrylic cell was due to the lower efficiency of acrylic cell to graphite cell could be attributed to the electricity distribution throughout the electrodes area, since the electrical contact of the electrodes in the acrylic cell is made with a small lateral area limiting conductivity.

In terms of modeling, using the literature given parameters, it must be said that the results were poor, since the comparison in Graph 4 showed very different curves positioning to the experimental results in this work. The polarization at activation region of the graph was not sensible enough to reproduce the experimental polarization, probably for the inadequacy of literature parameters mainly the exchange current data. The ohmic drop area was much less below than the produced in the experiments. It should be considered that probably this discrepancy is due to experimental assembling not reproducing the already presented in the literature. Perhaps, all these experiments should be replicated using the same catalysts offered by the literature authors with higher temperature range. Another point to consider is to substitute the plate material for more resistant ones, such as titanium or stainless steel.

6. CONCLUSIONS

Graphite cell coated with nickel played presented reasonable efficiency (52%) in terms of hydrogen production, but well below the considered state of art (75%). New experimental data should be made on new assemblies using titanium and stainless steel for better corrosion resistivity at anode region. Acrylic cells are useful only for visual control of bubble formation, but they are inefficient as water electrolysis for H_2 production.

The modeling using literature parameters for PEM water electrolysis is inadequate, but gives the general trending for the curve revealing the main regions of activation and ohmic development. The mathematical model compared with the potential curve for the experimental assembling revealed that this assembling should be remade using suggested electrocatalysts and temperature levels, higher than room temperature.

7. ACKNOWLEDGEMENTS

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8. REFERENCES

[1] YIM, S. D.; PARK G. G.; SOHN Y. J.; et al. **Optimization of PtIr electrocatalyst for PEM URFC.** International Journal of Hydrogen Energy, v. 30, n. 12, p. 1345 – 1350, sep., 2005.

[2] LIRONG, M. A.; SUI, S.; ZHAI, Y. **Investigations on high performance proton exchange membrane water electrolyzer.** International Journal of Hydrogen Energy, v. 34, n. 2, p. 678 – 684, jan., 2009.

[3] DOUCET, G.; et al. **Hydrogen-based PEM auxiliary power unit.** Int. Journal of Hydrogen Energy; v. 34; p. 4983–4989; 2009.

[4] MILLET, P.; et al. **GenHyPEM: a research program on PEM water electrolysis.** Int. Journal of Hydrogen Energy; v. 34; n. 11; p. 4974 – 4982; 2009.

[5] MILLET, P.; NGAMENI, R.; GRIGORIEV, S. A.; MBEMBA, N.; BRISSET, F.; RANJBARI, A.; ETIEVANT, C. **PEM water electrolyzers: From electrocatalysis to stack development.** Int. Journal of Hydrogen Energy; v. 35; p. 5043 – 5052; 2010

[6] CHOI, P.; BESSARABOV, D. G.; DATTA, R. **A simple model for solid polymer electrolyte (SPE) water electrolysis.** Solid State Ionics v. 175 p. 535–539; 2004

[7] MARSHALL, A.; BORRESEN, B.; HAGEN, G.; TSYPKIN, M.; TUNOLD, R. **Electrochemical characterisation of $Ir_xSn_{1-x}O_2$ powders as oxygen evolution electrocatalysts.** Electrochimica Acta v. 51 p. 3161–3167; 2006

[8] MARSHALL, A. T.; SUNDE, S.; TSYPKIN, M.; TUNOLD, R. **Performance of a PEMwater electrolysis cell using $Ir_xRu_yTa_zO_2$ electrocatalysts for the oxygen evolution electrode.** International Journal of Hydrogen Energy v. 32 p. 2320 – 2324; 2007

[9] GRIGORIEV, S. A.;MILLET, P.; VOLOBUEV, S. A.; FATEEV, V.N. **Optimization of porous current collectors for PEM water electrolysers.** International Journal of Hydrogen Energy. v. 34 p. 4968 – 4973; 2009

[10] SAWADA, S.; YAMAKI, T.; MAENO, T.; ASANO, M.; SUZUKI, A.; TERAI, T.; MAEKAWA, Y. **Solid polymer electrolyte water electrolysis systems for hydrogen production based on our newly developed membranes, Part I: Analysis of voltage - current characteristics**. Progress in Nuclear Energy; v. 50; p. 443-448; 2008

[11] BERNARDI, D. M.; VERBRUGGE, M. W. **Mathematical model of the Solid-Polymer-Electrolyte fuel cell.** Journal of the Electrochemical Society; v. 139; p. 2477-2491; 1992

[12] NIE, J.; CHEN, Y.; BOEHM, R. F.; KATUKOTA, S. **A photoelectrochemical model of proton exchange water electrolysis for hydrogen production.** Journal of Heat Transfer; v. 130; p. 1-6; 2008

[13] BEATTIE, P. D.; BASURA, V. I.; HOLDCROFT, S. **Temperature and pressure dependence of O_2 reduction at Pt | Nafion® 117 and Pt | BAM® 407 interfaces.** Journal of Electroanalytical Chemistry; v. 468; p. 180 – 192; 1999

[14] SILVA, M. A. O.; LINARDI, M.; SALIBA-SILVA, A. M. **Corrosão de grafite em eletrolisador tipo PEM.** 3rd International Corrosion Meeting; 2010

[15] BALDO, W. R. **Desenvolvimento de um método de preparação de conjuntos eletrodo – membrana – eletrodo para células a combustível a membrana trocadora de prótons (PEMFC)**. 2003. 71p. Dissertação (Mestrado em Ciências) – Instituto de Pesquisas Energéticas e Nucleares, Universidade de São Paulo, São Paulo; 2003.

[16] SANTOS, A. R.; CARMO, M.; OLIVEIRA-NETO, A.; SPINACÉ, E. V.; POÇO, J. G. R.; ROTH, C.; FUESS, H.; LINARDI, M. **Electrochemical and impedance spectroscopy studies in H2/O2 and methanol/O2 proton exchange membrane fuel cells.** Ionics; v. 14; p. 43-51; 2008.

[17] SANTIAGO, E.I.; ISIDORO, R. A.; DRESCH, M.A.; MATOS, B.R.; LINARDI, M.; FONSECA, F.C. **Nafion–TiO2 hybrid electrolytes for stable operation of PEM fuel cells at high temperature.** Electrochimica Acta; v. 54; p. 4111–4117; 2009.