

Numerical Assessment of a High-Pressure Polymer Electrolyte Membrane (PEM) Water Electrolyser

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Abstract:

In this paper, a simplified mathematical model of a high-pressure Polymer Electrolyte Membrane (PEM) water electrolyser was developed and the simulation code was conducted. The polarization curve was presented and the impact of operation parameters of the PEM electrolysis was investigated. It was found that the higher pressure and temperature are the least cell voltages are required for high current density and therefore the better performance of the electrolysis.

Keywords: *Polymer Electrolyte Membrane (PEM), Mathematical model, Water electrolysis, High pressure.*

1. INTRODUCTION

Hydrogen-based energy systems are attractive with their benefits, which align well with public concern about pollutant emissions and climate change. Hydrogen fuel is efficient and seen as renewable and clean energy. But hydrogen is not a primary energy and therefore must first be produced. However, the production of hydrogen need to resolve its problems Shiva et al. (2019). Most of the current production is done by reforming fossil sources and releases as much CO₂ if not more than the direct use of these sources. Hydrogen can also be produced by electrolysis by integrating the system with any kind of renewable energies like, the solar energy, which allows the energy produced in natural cycles to be stored for use when needed Shiva et al. (2019). Finally, to know whether current and future hydrogen technologies have a chance to replace fossil energy agents, it is necessary to take into account the entire chain of production, storage.

Electrolysis of water with a polymer electrolyte membrane is considered by researchers to be a technology of the future for the production of hydrogen, as it can benefit from the developments in PEM fuel cells, and the associated cost reduction, Dutta et al. (2001). In this context, the work presented in this article is a study of a Proton Exchange Membrane Electrolyser (PEM) for the production of hydrogen.

Improving the performance of PEM electrolyzes to increase their efficiency (decrease gas diffusivity, membrane ohmic resistance and increase ionic conductivity) is the goal of many researchers Shiva et al. (2019).

Theoretical modeling has demonstrated the most attention in the literature Tekin et al. (2006). Numerical modeling to solve equations that are obtained based on the physics and electrochemistry of the phenomena taking place inside the electrolyser Haluk et al. (2006) proposed a dynamic model for a PEM electrolyser according to mole conservation at the cathode and anode, which studied phenomena related to electro-osmotic drag, water transport as well as the diffusion across the membrane. This model considers the PEM electrolyser with 4 auxiliaries: anode, cathode, membrane and voltage auxiliary. The author introduced this detailed dynamic model for use in fuel cell and PEM electrolyzer applications where membrane water transport and pressurized hydrogen storage are introduced. However, the effects of gas diffusion or heat transfer are ignored in this model. TimM. Brown et al. (2008) proposed a study based of a discrete reversible fuel cell system using dynamic model which was developed by the Matlab Simulink® software. This study combines models that illustrate the first dynamic principles of a proton exchange membrane (PEM) fuel cell, an electrolyzer, a cooling radiator and a hydrogen storage tank as well as empirical models of manufacturing components realized at equilibrium. Dynamic simulations show highlight factors and charge and discharge control issues contributing to overall efficiency of the

system. Jianhu Nie et al. (2009) have proposed a 3D model that studies the fluid flow through the bipolar plates of the electrolytic cell of PEM. In this model three-dimensional experimental measurements and numerical simulations of water flow were performed in order to examine velocity distributions and the pressure in the bipolar plates of a PEM electrolysis cell. The results show that the lower pressure at the inlet of tube comparing to the outlet tube. This model is also used to study the influences of temperature, pressure and the distribution of velocity and the influence of current densities on the hydrogen production rate. Millet et al. (1993-1996) proposed a research to study the development of water electrolyzers with a medium-sized solid polymer electrolyte. The model is used to measure anode overvoltage, cathodic overvoltage and ohmic drop, in a range of ambient temperature and a current density of 20 to 80 °C and 0 to 1 A.cm⁻², respectively.

Meng et al. (2008) proposed a detailed thermodynamic analysis to enhance the design performance of the PEM electrolyzer for producing hydrogen as well as identifying the main losses. In this study exergy and energy analyzes are used to investigate the hydrogen production characteristics using electrolysis of PEM water. Further, the authors stated that the invaluable specificity of electrochemical characteristics of the PEM electrolyzer are fully integrated into the thermodynamic analysis. In fact, parametric analyzes were performed to study the operating parameters and the effect of design on energy conversion efficiency. This model made a quantitative study to determine the percentage of energy efficiency in the case where the operating temperature is high, the current densities are low, the thickness of the electrolyte is reduced, and finally the catalytic activity of the electrodes is high. A synthesis of recent PEM models encountered in the literature was presented. The advantages and disadvantages were discussed. Although several phenomena occur in a PEM cell, only three have the greatest impact on the performance of the electrolysis type: (i) Electrochemical reactions in the catalyst layers, (ii) Proton transfer in the membrane, and (iii) Mass transport to all regions of the PEM cell. Given the importance of modeling mass and heat transfer phenomena in the PEM electrolyzer, in the next section we focused on developing a model and analyzing the different existing processes.

2. THEORETICAL MODEL

In this section a prototype of the electrolyze of the PEM type was developed. The particularity of this prototype is the imbalance of the pressure through the model: in fact, the anode chambers operate at a pressure close to atmospheric pressure, while it reaches 70 bar for the cathode chambers. Due to that some mechanically stressed is seen, and on the other hand ignore the need to bring high pressure water, consequently saving us energy.

The theoretical model developed aims to study the relevance between current and voltage of electrolytic cells. The ideal open circuit voltage is lower than the actual voltage which can be estimated as follows Haluk et al. (2006) :

$$V = E + \eta_{act} + \eta_{ohm} + \eta_{diff} \quad (1)$$

The irreversible losses in the electrolyzer are called polarizations or overvoltages which have three origins: activation overvoltage (η_{act}), Ohmic overvoltage (η_{ohm}) and diffusion or concentration overvoltage (η_{diff}).

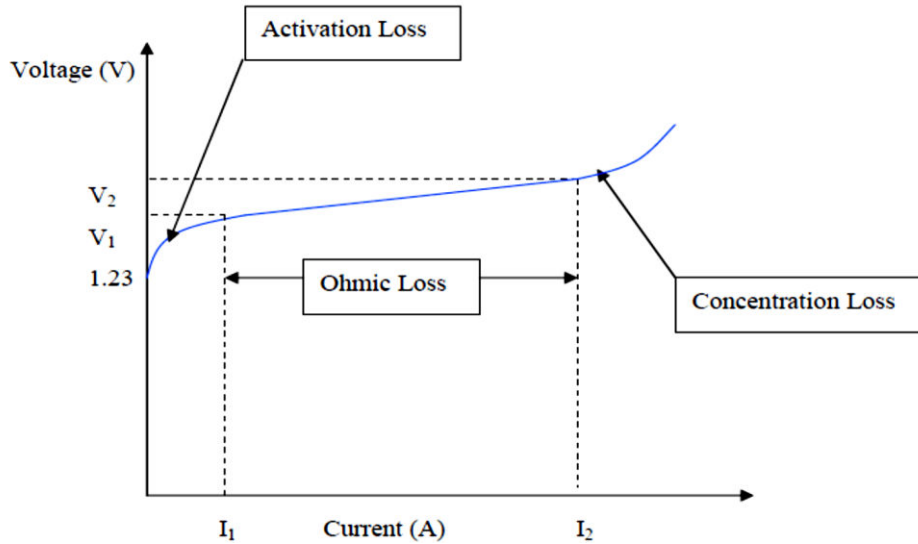


Figure 1. The origins of overvoltages in the PEM electrolyzer

Each terms of the Eq. (1) will be expressed in the following section:

Reversible conditions were considered for the electrochemical cell, i.e., open circuit conditions, the Open-circuit voltage is estimated using equation below Haluk et al. (2006):

$$E = -\frac{\Delta G}{2F} \quad (2)$$

The reaction is reached in the electrolyser: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

Under standard conditions, the Gibbs free energy variation can be expressed as:

$$\Delta G^\circ = G_{f, \text{produits}}^\circ - G_{f, \text{réactifs}}^\circ \quad (3)$$

The following relationship was used to apply the pressure correction since the non-standard conditions of temperature and pressure were considered.

$$\Delta G = \Delta G^* + RT_{cell} \times \ln \frac{P_{H_2} \cdot \sqrt{P_{O_2}}}{P_{H_2O}} \quad (4)$$

ΔG^* : the Gibbs free energy variation can also be expressed as:

$$\Delta G^* = \Delta H^* - T_{cell} \Delta S^* \quad (5)$$

Water and oxygen are present at the anode electrode side while, the hydrogen is present at the cathode electrode Espinosa-López et al. (2018): . Therefore, the Gibbs free energy variation will be evaluated using equation below, Santarelli et al. (2009):

$$\Delta G^* = \left[H_{H_2}(T_{cat}) + \frac{1}{2}H_{O_2}(T_{an}) - H_{H_2O}(T_{an}) \right] - T_{cell} \left[S_{H_2}(T_{cat}, P_0) + \frac{1}{2}S_{O_2}(T_{an}, P_0) - S_{H_2O}(T_{an}, P_0) \right] \quad (6)$$

Enthalpy and entropy are evaluated by using the following correlations, Ulleberg et al. (2003): :

$$H_j(T) = a_j T + \frac{4}{5}b_j T^{6/4} + \frac{2}{3}c_j T^{3/2} + \frac{4}{7}d_j T^{7/4} \quad (7)$$

$$S_j(T, P) = a_j \ln T + 4b_j T^{1/4} + 2c_j T^{1/2} + \frac{4}{3} d_j T^{3/4} - R \ln P \quad (8)$$

The values of the coefficients (for 300K <T <4000K) are presented in the following Table 1:

Table 1. The values of the coefficients

	Substance	a_j	b_j	c_j	d_j
$j = 1$	Water	180	-85.4	15.6	-0.858
$j = 2$	Hydrogen	79.5	-26.3	4.23	-0.197
$j = 3$	Oxygen	10.3	5.4	-0.18	0

Part of the voltage produced is lost during the chemical reactions in both electrodes. This is due to the activation energy required at the cathode and anode and called the loss of activation Grigoriev et al. (2009). Therefore A big advantage of the proton exchange membrane (PEM) is that the loss of activation of oxygen is much larger than the loss of activation of hydrogen. Jianhu Nie et al. (2009).

The activation energy can be obtained using the Butler-Volmer (BV) equation Santarelli et al. (2009), in fact, the electrode /electrolyte interface can be estimated to study the current density for each electrode using these equations:

$$i = i_0 \left[\exp\left(\frac{\alpha_1 F}{RT} \eta_{act}\right) - \exp\left(-\frac{\alpha_2 F}{RT} \eta_{act}\right) \right] \quad (9)$$

If $\alpha_1 = \alpha_2$ then :

$$i = 2i_0 \left(\exp \sinh \frac{\alpha F}{RT} \eta_{act} \right) \quad (10)$$

The activation energy is expressed as:

$$\eta_{act} = \frac{RT}{\alpha F} \operatorname{arcsinh} h \left(\frac{i}{2i_0} \right) \quad (11)$$

Where, i , i_0 and α are the current density, the exchanged current density and the electronic transfer coefficient.

The activation overvoltage at the anode increases with the current density its expression is given by the Butler-Volmer equation Jun Chi et al. (2018):

$$\eta_{act,an} = \frac{RT_{an}}{\alpha_{an} F} \operatorname{arcsinh} h \frac{i}{2i_{0,an}} \quad (12)$$

Where, $i_{0,an}$ is the exchanged current density at the anode electrode.

On the other hand, the expression of the activation overvoltage is given for the cathode electrode as follows, Linkous et al. (1998)::

$$\eta_{act,cat} = \frac{RT_{cat}}{\alpha_{cat} F} \operatorname{arcsinh} h \frac{i}{2i_{0,cat}} \quad (13)$$

Where, $i_{0, cat}$ is the exchanged current density.

For the water electrolyser, oxygen and hydrogen must be removed, while in contrast water must be supplied to the reaction zone. It should be consider that all mass transfers take place in the porous electrode, water flowing through channels to the catalyst layers, hydrogen and oxygen are transported from reaction zones to canals since the reaction is present at the membrane-electrode interface, Lebbal et al. (2009).

The flow meets a resistance at the crossing of the electrode, and this resistance affected by the speed of the flow: this generates a loss of energy, and consequently a diffusion overvoltage: consequently the voltage value of the electrolytic cell at impose is high due to the limitations of mass transport. The Nernst equation then is set to study the diffusion overvoltage, Wang et al. (2005):

$$\eta_{diff} = V_1 - V_0 = (E^0 + \frac{RT}{zF} \ln C_1) - (E^0 + \frac{RT}{zF} \ln C_0) = \frac{RT}{zF} \ln \frac{C_1}{C_0} \quad (14)$$

The ohmic overvoltage can be calculated using equation as follows:

$$\eta_{ohm} = R_{cell} \cdot I \quad (15)$$

Where, R_{cell} : present the ohmic resistance.

The voltage drop at the diaphragm can calculated at the plates and electrodes separately as follows:

$$\begin{aligned} \eta_{ohm} &= R_{cell} \cdot I \\ &= R_{mem} I + (R_{eq,an} + R_{eq,cat}) I \\ &= \eta_{ohm,m} + \eta_{ohm,e} \end{aligned} \quad (16)$$

By referring to the model of Yigit et al. (2005), the ohmic overvoltage at the levels of the two electrodes is calculated as follows:

$$\eta_{ohm,e} = (R_{eq,an} + R_{eq,cat}) I \quad (17)$$

Where, $R_{eq,cat}$ and $R_{eq,an}$ are the equivalent resistance for both electrodes.

The ohmic overvoltage at the membrane is calculated as follows:

$$\eta_{ohm,m} = \frac{I}{A} \frac{\delta_m}{\sigma_m (1 + \frac{F^2 K_e C_{H^+}^2}{\sigma_m \mu_{H_2O}})} \quad (18)$$

Where, σ_m is the thermal conductivity of the membrane.

3. NUMERICAL METHOD AND MODEL VALIDATION

After having equated the various phenomena which govern the electrochemical process as well as the various overvoltages within a PEM electrolyser, a computational code is developed under FORTRAN and used to solve the mathematical model. The different simulation input parameters can be seen in following table.

Table 2. The values of the used parameters

Parameter	Value	Parameter	Value
α_{an}	2	μ_{H_2O}	$1.1 \cdot 10^{-3} \text{ Pa s}$
α_{cat}	0.5	A	160 cm^2
$i_{0,cat}$	10^{-3} A/cm^2	C_{H^+}	1000 mol/m^3
$i_{0,an}$	10^{-7} A/cm^2	F	96485 C/mol
n_d	$0.27 \text{ mol}_{H_2O}/\text{mol}_{H^+}$	K_e	$1.13 \cdot 10^{-19} \text{ m}^2$
D_w	$1.2810^{-10} \text{ m}^2/\text{s}$	\mathcal{E}	0.3
K_{darcy}	1.5810^{-18} m^2	\mathcal{E}_p	0.11
T°	25°C	ρ_{H_2O}	1000 kg/m^3
P°	1bar	F	96485 C/mol
R	$8.315\text{J}/(\text{mol K})$	δ_m	$254\mu\text{m}$
Λ	25		

To validate the mathematical model the polarization curves founded by Haluk Marangio et al. (2006) are used for different values of pressure and temperature. Figure 2 illustrates the results found for a pressure and a temperature respectively $P_{cat} = 10 \text{ bar}$ and $T_{an} = 55^\circ \text{C}$. The non-overlap between the found result and the reference one found by F. Marangio et al can be explained by the lack of precision of the data in the article Haluk Marangio et al. (2006).

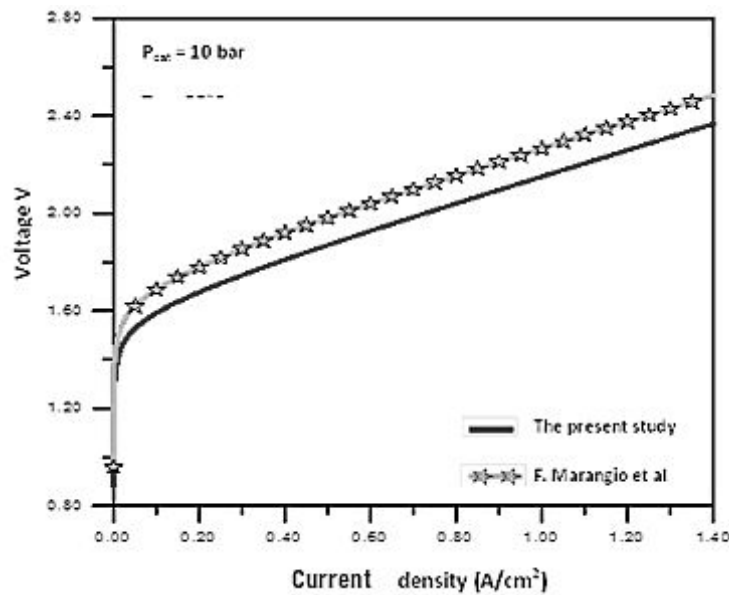


Figure 2. Model Validation

4. RESULTS AND DISCUSSION

4.1 Effect of the Pressure

The effect of the pressure is studied to see that effect on the polarization curve. The different values of voltage are compared at constant current density. From the Fig.3 and for $i = 1 \text{ A/cm}^2$, it is noted when the temperature increases, the cell voltage was decreases by 70 mV at low pressure electrolysis of (1 bar). On the other hand, a decrease in the voltage value of 235 mV is recorded at high pressure electrolysis of (70 bar). From this result, it can be demonstrated that pressure has a serious effect on the operation of the PEM electrolyser at high temperatures. This was not verified in the reverse case. (Fig.3).

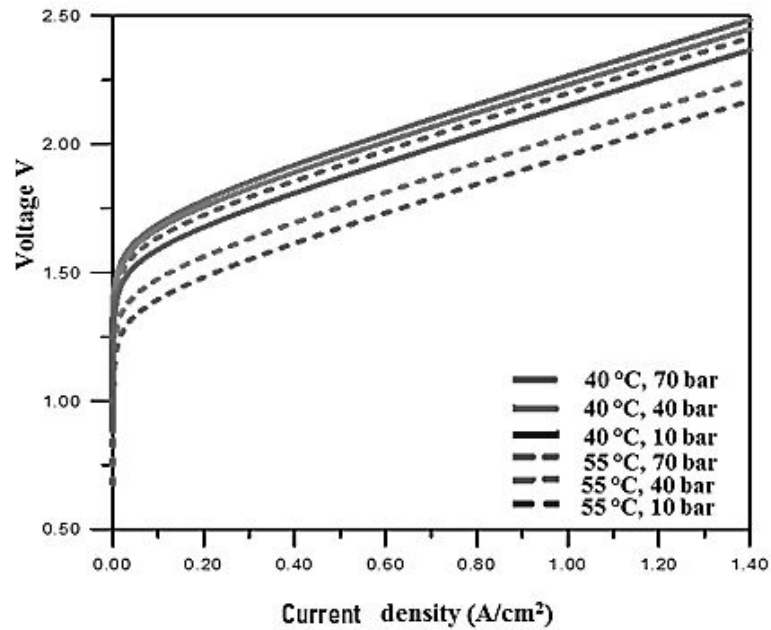


Figure 3. The effect of pressure on the polarization curve for high and low temperatures

4.2 Temperature Effect

The temperature effect on the polarization curve during the electrolysis process is studied for both cases of high and low pressure. The results are presented in Fig. 4 and Fig. 5. From the Fig. 4 it is noticed that the pressure was increased from 10 bar to 20 bar at constant temperature (40 °C) causing a slight decrease in tension. This decrease became more important following a slight increase in temperature (from 40 °C to 55 °C).

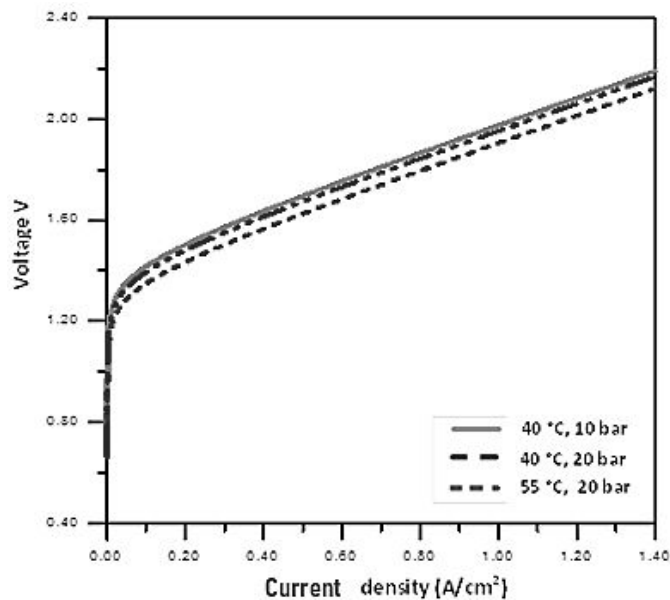


Figure 4. Influence of temperature at low pressures

For high pressure values, the effect of temperature is more pronounced than for low pressure values. Indeed, the Fig. 5 shows that the increase in temperature to 55 °C generates a decrease in the cell voltage showing greater values in the latter case compared to that where the temperature was constant.

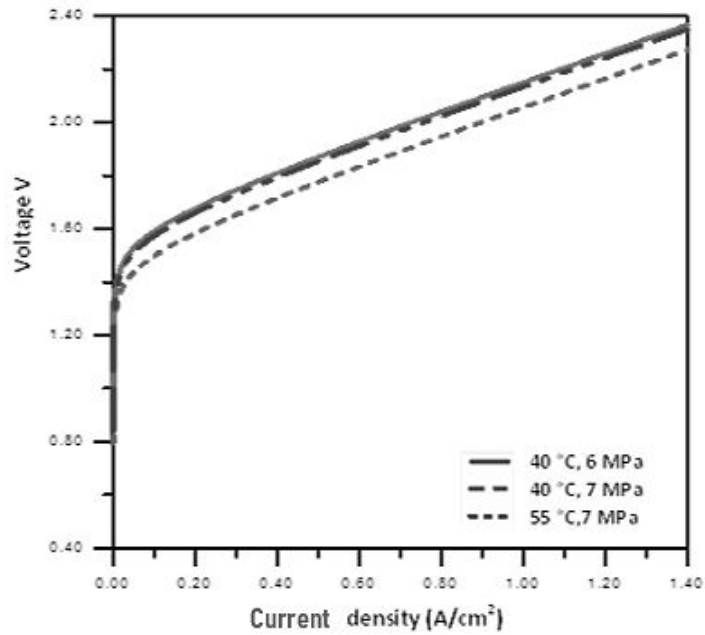


Figure 5. Influence of temperature in the case of high pressures

4.3 Effect of the Concentration of H⁺ Ions of the Nafion Membrane

The ionic conduction of the Nafion membrane is considered based on its H⁺ ion concentration. In addition, this concentration has a remarkable effect on the polarization curve of an electrolytic cell. The higher concentration of H⁺ ions yields lower the voltage of the cell.

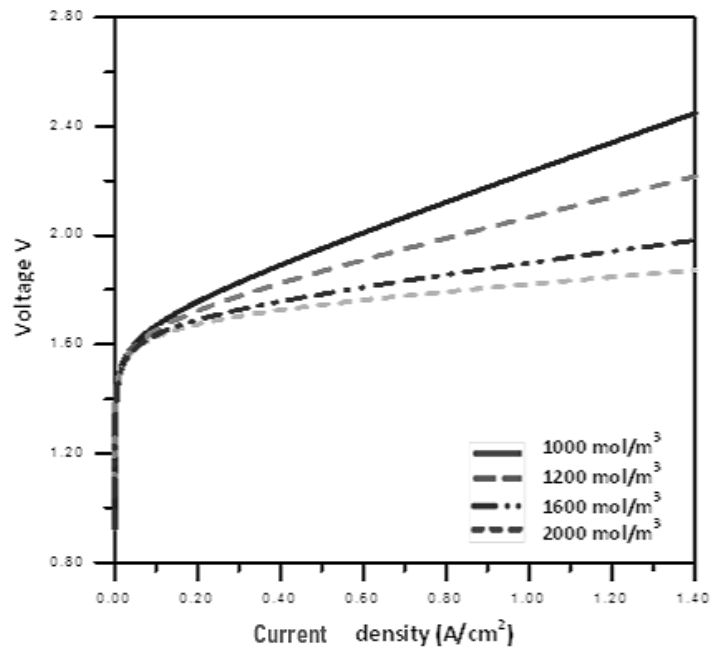


Figure 6. Influence of the concentration of H⁺ ions on the polarization curve

Conclusion

In this work, a simplified mathematical model of a high pressure (PEM) electrolysis was developed. The electrochemical process within the electrolyser has been numerically studied. The

calculation results have shown that the correct operation of the PEM electrolyser takes place when the model was ran at higher values of pressure and temperature and therefore the better performance of the PEM electrolyser. At high current density efficiency decreases as a result of the reduced performance and related heat dissipation.

Nomenclature

A	Current
E	Open-circuit voltage
ΔG	Gibbs free energy
H	Enthalpy
i	Current density
i_0	Exchanged current density
$i_{0,an}$	Exchanged current density for anode
$i_{0,cat}$	Exchanged current density for cathode
P	Pressure
$R_{eq,an}$	Equivalent resistance at the anode
$R_{eq,cat}$	Equivalent resistance at cathode
R_{cell}	Ohmic resistance
S	Entropy
T	Temperature
V	Voltage
α	Electronic transfer coefficient
σ_m	Thermal conductivity
η_{act}	Activation overvoltage
η_{ohm}	Ohmic overvoltage
η_{diff}	Diffusion or concentration overvoltage

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