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Thermodynamics aspect of high pressure hydrogen production by water electrolysis

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Abstract - *Hydrogen can be produced from water electrolysis which can operate at atmospheric pressure or high pressure. Today's industry including vehicle one, devotes efforts to produce high pressure hydrogen by using pressurized electrolyser. The purpose of this work is to estimate the ideal electrical energy needed for high pressure hydrogen under high pressure water electrolysis conditions. Calculations are based on the estimation of the enthalpy and free Gibbs energy of water electrolysis at various pressures and temperatures, referring to both the work of LeRoy & Onda.*

Résumé - *L'hydrogène peut-être produit à partir de l'électrolyse de l'eau fonctionnant sous pression atmosphérique ou à haute pression. Pour certaines industries, l'industrie chimique et surtout le secteur de l'automobile, beaucoup d'efforts sont canalisés vers la production de l'hydrogène pur à haute pression, en employant des électrolyseurs pressurisés. L'objet de cet article est d'estimer l'énergie électrique idéale requise pour la production de l'hydrogène dans les conditions de l'électrolyse de l'eau à haute pression. Les approximations, inspirées des travaux de LeRoy et Onda, sont basées sur l'évaluation de l'enthalpie et de l'énergie libre de Gibbs de l'électrolyse de l'eau à diverses pressions et températures.*

Keywords: Hydrogen production - High pressure hydrogen - Water electrolysis – Electrolyser - Enthalpy voltage - Electrolysis voltage – Power.

1. INTRODUCTION

One of the new emerging technologies having the world's clean energy choice is based on hydrogen. Flexible, affordable, safe, domestically produced, can be used in all sectors of the economy and in all regions of the country; hydrogen may play an important role as an energy carrier of the future [1].

Hydrogen like electricity can be produced from many different sources, including fossil fuels, renewable resources, and nuclear energy; a thorough review of the available literature on issues relevant to hydrogen production reveals that water electrolysis would be the easiest option and the only one currently practical [2]. As noticed by Prince-Richard [3] electrolysis can make use of the electrical and water infrastructure already available in many areas. It also provides access to nuclear and renewable energy sources, which have very low Greenhouse Gas emissions. Moreover, an interesting synergy between similar aspects of water electrolysis and fuel cell technologies could have a noticeable impact on the development and cost of the electrolytic hydrogen fuelling option.

The chemical process involved in the water electrolysis, split the water molecules to produce hydrogen and oxygen, can be viewed as the reverse process which the proton exchange membrane fuel cell (PEMFC) is based on. From this observation merge the idea to use a solid membrane, like perfluorosulfonic acid polymer (Nafion), as a membrane electrolyser.

Our objective is to present a thermodynamic model that describes the high pressure hydrogen production by means of a solid membrane (SPE), like perfluorosulfonic acid polymer (Nafion), rather than classic liquid electrolyte (alkaline electrolyte), at high pressure water electrolysis

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conditions. The thermodynamic model based on the work of LeRoy [4] and Onda [5] is implemented into a computer program to simulate the high pressure hydrogen production.

2. PRINCIPLE OF WATER ELECTROLYSIS

If an electrical potential is applied to the electrodes of a solid polymer electrolysis cell, Fig. 1, the following reaction occurs at the electrodes:

At the anode, water is introduced and dissociated into oxygen, hydroxonium ions H_3O^+ and electrons ⇒

$$6\,H_2O_{(liq)} \quad \rightarrow \quad 4\,H_3O^+ + 4\,e^- + O_2 \tag{1}$$

At the cathode, as the hydroxonium ions H_3O^+ migrate through the membrane it recombine with electrons, which pass via an external circuit, to form hydrogen gas and water ⇒

$$4\,H_3O^+ + 4e^- \quad \rightarrow \quad 4\,H_2O_{(liq)} + 2H_2 \tag{2}$$

The overall cell reaction is the sum of the reaction (1) and reaction (2) is written as follows ⇒

$$2\,H_2O_{(liq)} + \text{Electrical Energy} \quad \rightarrow \quad 2H_2 + O_2 \tag{3}$$

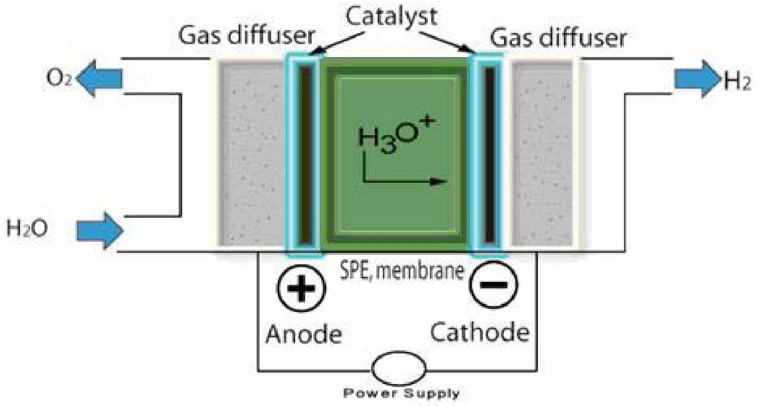

Fig. 1: Schematic representation of solid polymer electrolyte (SPE) water electrolysis

From (3), it is evident that the reverse reaction corresponds to the formation of water, so as we know the formation reaction is a reaction which forms a single compound from the elements which make it up [6]. This useful definition allows evaluating different thermodynamics relationships of water electrolysis by considering the thermodynamics of the formation reaction of water.

At Standard Temperature and Pressure conditions, (STP defined by the IUPAC, International Union of Pure and Applied Chemistry, is an absolute pressure of 1 bar and a temperature of 273.15 K), the splitting of water is a non-spontaneous reaction which means that the change in Gibbs energy is positive [5-7].

For an electrochemical process operating at constant pressure and temperature the maximum possible useful work (i.e., the reversible work) is equal to the change in Gibbs energy. Since work is viewed from the point of view of the chemical reaction system, the electrical work is positive for an electrolyser and negative for a fuel cell.

The change in enthalpy for the electrochemical decomposition of water is

$$\Delta H_{T,p} = \Delta G_{T,p} + T\,\Delta S_{T,p} \tag{4}$$

$\Delta H_{T,p}$ ($J.mol^{-1}$) is the enthalpy change at T and p, $\Delta G_{T,p}$ ($J.mol^{-1}$) is the Gibbs free energy, $\Delta S_{T,p}$ ($J.mol^{-1}K^{-1}$) entropy change, T temperature (K), p the pressure (atm).

According to LeRoy [4] and Onda [5], two essentials voltages, taking into account the energy needed for the hydrogen production, are defined:

The enthalpy voltage at T and p:

$$V_{T,p}(\text{volt}) = \Delta H_{T,p} / nF \tag{5}$$

The water electrolysis voltage at T and p:

$$E_{T,p}(\text{volt}) = \Delta G_{T,p} / nF \tag{6}$$

n : Number of electrons transferred per formula conversion, F : The Faraday constant equal to 96500 $Cmol^{-1}$.

The voltage associated with $\Delta H_{T,p}$ is commonly called the thermo neutral cell voltage; it is the voltage at which a perfectly efficient cell would operate if electricity provided the entire energy requirement. Under these conditions, the cell does not generate any waste heat, nor does it require any heat input; the cell has no net heat exchange, hence it is then said to be 'thermo neutral' [3].

Since the enthalpy voltage and the water electrolysis voltage depend on the enthalpy and the Gibbs energy of the formation reaction of water (5, 6), we can predict the temperature changes by means of a well known thermodynamics relationships [6]. The calculation approach is based on the fact that the enthalpy and Gibbs energy are properties that depend on the initial and final states of compounds (reactants and products); they may be calculated for any convenient path connecting theses two states [6]. The first part of our calculation is to propose a hypothetical path that leads from liquid water at 25 °C to gaseous hydrogen and oxygen at temperature above 100 °C and up, under atmospheric pressure. This path is illustrated on Fig. 2.

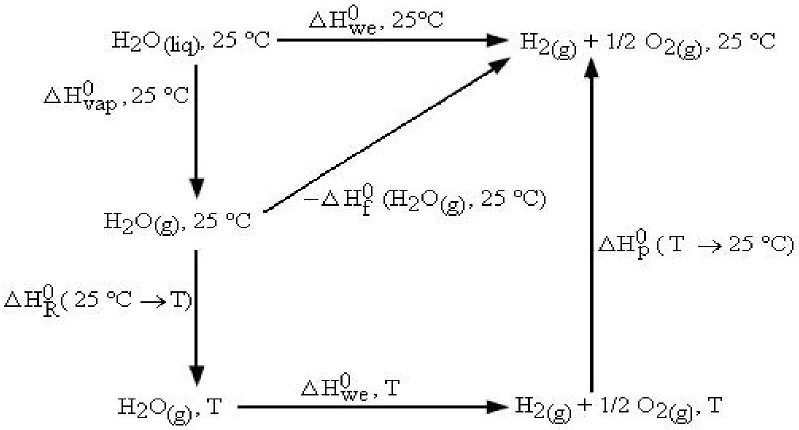

Fig. 2: Possible thermodynamic path leading to hydrogen at defined temperature from water at 25°C

The entities used are defined as follows:

$\Delta H^0_{vap.}$, 25°C	Heat of vaporization of water at 25 °C at constant pressure (1 atm)

$\Delta H_R^0, (25°C \rightarrow T)$	Total enthalpy change of reactants (water) at a constant pressure (1 atm) from 25 °C to *T*
$\Delta H_{we.}^0, T$	Enthalpy of water electrolysis at constant pressure (1 atm) at T
$\Delta H_{we.}^0, 25°C$	Enthalpy of water electrolysis at constant pressure (1 atm) at 25 °C
$\Delta H_p^0, (T \rightarrow 25°C)$	Total enthalpy change of products (hydrogen and oxygen) at a constant pressure (1 atm) from T to 25 °C
$\Delta H_f^0, (H_2O_{(g)}, 25°C)$	Standard heat formation of water at 25 °C

The reason for choosing this possible schematic is based on the fact that the entire entities (enthalpies) can be calculated, and data of water are available. According to Fig. 2 we can write the following equations:

The enthalpy of water electrolysis at any temperature and pressure is expressed as follows:

$$\Delta H_{T,p} - \Delta H_{25°C,1atm} = \left\lfloor \Delta H_{T,p} - \Delta H_{T,1atm} \right\rfloor - \left\lfloor \Delta H_{T,1atm} - \Delta H_{25°C,1atm} \right\rfloor \tag{7}$$

$$\begin{aligned} \Delta H_{T,p} - \Delta H_{T,1atm} = {} & \left\lfloor \Delta H_{T,p} - \Delta H_{T,1atm} \right\rfloor_{H_2} + 0.5 \left\lfloor \Delta H_{T,p} - \Delta H_{T,1atm} \right\rfloor_{O_2} \\ & - \left[\Delta H_{T,p} - \Delta H_{T,1atm} \right]_{H_2O} \end{aligned} \tag{8}$$

$$\begin{aligned} \Delta H_{T,1atm} - \Delta H_{25°C,1atm} = {} & \left\lfloor H_{T,1atm} - H_{25°C,1atm} \right\rfloor_{H_2} + 0.5 \left\lfloor H_{T,1atm} - H_{25°C,1atm} \right\rfloor_{O_2} \\ & - \left[H_{T,1atm} - H_{25°C,1atm} \right]_{H_2O} \end{aligned} \tag{9}$$

The same expression can be developed for the entropy and Gibbs free energy for water electrolysis. Here we present only equations for enthalpy.

3. EFFECT OF TEMPERATURE ONLY ON $E_{T,p}$ AND $V_{T,p}$ AT STANDARD PRESSURE OF 1 ATM

Considering (8) and (9), the only limitation is that the species involved are considered at ideal gas state, thus the enthalpies of reactants and products are expressed as a function of temperature by equation of the form:

$$\Delta H^0 (T, \text{final}) = \Delta H^0 (T, \text{initial}) + \sum_{\text{species}} \int_{T,\ \text{initial}}^{T,\ \text{final}} C^0_{p,\ \text{species}} (T)\, dT \tag{10}$$

$(T, \text{initial})$: initial temperature, [K]; (T, final): final temperature, [K]; C_p^0: heat capacity of the species, function of temperature, [J.mol^{-1}K^{-1}].

The entropy change is expressed by considering the following thermodynamic relationship of ideal gas state [6, 8]:

$$\Delta S^0 (T, \text{final}) = \Delta S^0 (T, \text{initial}) + \sum_{\text{species}} \int_{T,\ \text{initial}}^{T,\ \text{final}} \frac{C^0_{p,\ \text{species}} (T)}{T}\, dT \tag{11}$$

Combining equations (5) and (10), we obtain the temperature effect of enthalpy voltage as follows:

$$V_{T,1atm} = 1.4850 - 1.490\,10^{-4} (T - 273.15) - 9.84\,10^{-8} (T - 273.15)^2 \tag{12}$$

Combining (6), (4) and (11) we obtain the Gibbs free energy for the corresponding temperature and then the reversible voltage as:

$$E_{T,1atm} = 1.5184 - 1.5421\,10^{-3}\ T - 9.523\,10^{-5}\ T\ln T + 9.84\,10^{-8}\ T^2 \qquad (13)$$

According to LeRoy [4] and Onda [5], since data have been extrapolated from steam table of water (12) and (13) are covering the temperature range from 25 °C to 327 °C.

4. THE EFFECT OF PRESSURE ON $E_{T,p}$ AND $V_{T,p}$

The effect of pressure on both E and V is given by (8) and the following well know thermodynamics relationship [6, 8]

$$H_{T,p_2} - H_{T,p_1} = \int_{p_1}^{p_2} \left(v - T\frac{\partial v}{\partial T} \right) dp \qquad (14)$$

$v\left(m^3\right)$ is the volume of the components and R is the universal gas constant, $R = 82.058$ (atm cm^3 mol^{-1} K^{-1}) [6, 8].

The integral can be handled under different consideration; we choose the virial equation of state [6, 8] to be performed with an eye to unifying the works of many authors into a comprehensive understanding of the method.

The remain calculation consists in the evaluation of the enthalpy departure for water; the task has been greatly simplified as the data for the thermodynamics properties of water are available and can be handled as data sheet or as embedded computer subroutine. We use the published computer program of steam table from The International Association for the Properties of Water and Steam [9]. The range of data is for temperatures and pressures:

$$273.15\ K < T < 1073.15\ K$$

$$0 < p < 1000\ \text{bars}$$

5. VISUALIZATION OF THE TEMPERATURE AND PRESSURE EFFECT ON THE ELECTROLYSIS VOLTAGE

The enthalpy voltage is calculated for the value from 1 bar to 1000 bars using the expression:

$$V_{T,p} = V_{T,1atm} + \Delta H_{T,p} - \Delta H_{T,1atm} \Big/ nF \qquad (15)$$

and the water electrolysis voltage:

$$E_{T,p} = E_{T,1atm} + \Delta G_{T,p} - \Delta G_{T,1atm} \Big/ nF \qquad (16)$$

The temperature change at 1 atm is shown on Figure 3 and the pressure change is shown on Figure 4.

We observe that $V(1atm)$ and $E(1atm)$ decreases as the temperature is rising, elevating temperature promote the splitting water significantly.

We observe as enthalpy voltage, V, decreases, reversible voltage, E, increases with rising pressure at 298 K. For E the curve increases rapidly from 1 atm to 50 atm then rise steadily. In fact according to Le Chatelier principle, the water electrolysis considered as an equilibrium equation, increasing pressure will lead to encourage water formation then more energy would be necessary to overcome the reverse reaction.

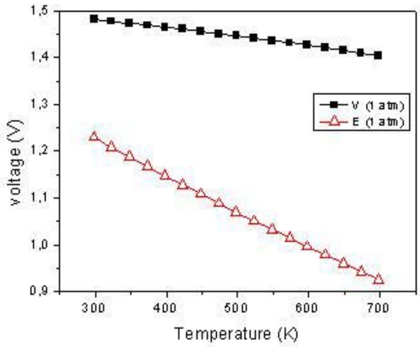

Fig. 3: Variation of electrolysis and enthalpy voltage with temperature at 1 atm

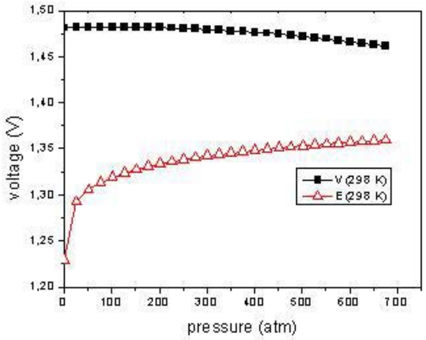

Fig. 4: Variation of electrolysis and enthalpy voltage with pressure at 298 K

In the next section we present the variation of enthalpy and electrolysis voltage versus the variation of temperature and pressure in Figs. 5 and 6, the numerical values are given in **Table 1**.

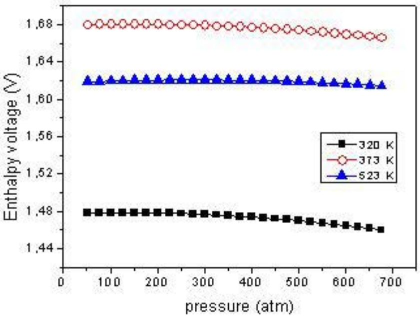

Fig. 5: Enthalpy voltage against pressure and temperature variations

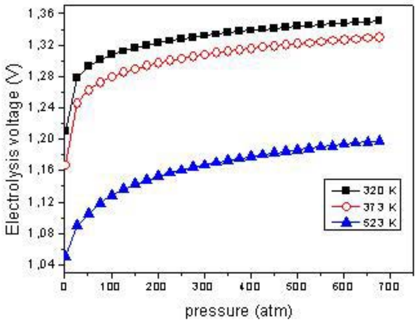

Fig. 6: Electrolysis voltage against pressure and temperature variations

First of all, the variation of both enthalpy and electrolysis voltage is somehow different from the presented data of LeRoy [4] and Onda [5], because the preceding authors uses data of steam table as interpolated values, the data used here seems to be more accurate and represents the variations of water behavior more precisely. Even though, the result obtained in this work with the different formulation of water properties, published by Spang [9], is quite similar to those given by LeRoy [4] and Onda [5], we compare the results in **Table 2**.

Table 1: Enthalpy and Electrolysis voltages versus pressure and temperature

	V (volt), This work			**E** (volt), This work		
Pressure (atm)	320 K	373 K	523 K	320 K	373 K	523 K
1	1.47783	1.46916	1.44165	1.21081	1.16725	1.05058
100	1.47860	1.68063	1.61967	1.30742	1.27952	1.12852
500	1.46984	1.67428	1.61895	1.34374	1.32170	1.18621
676	1.46005	1.66636	1.61473	1.35059	1.32994	1.19766

As shown in Fig. 5 and Fig. 6, it is clear that increasing pressure will increase the energy consummation and then more energy is required to perform hydrogen production.

We observe, that temperature play an advantageous factor for reducing the enthalpy and electrolysis voltage, since the energy of molecules agitation (water) introduced by temperature, tends to promote electrolysis, thus reducing electrical potential.

Table 2: Enthalpy and Electrolysis voltages variation according to different authors

T = 25°C	**V** (volt)			**E** (volt)	
Pressure (atm)	LeRoy [4]	Onda [5]	This work	Onda [5]	This work
1	1.481	1.481	1.481	1.229	1.2293
25	1.481	1.481	1.481	1.290	1.2916
50	1.480	1.480	1.481	1.304	1.3052
100	1.479	1.479	1.481	1.317	1.3191

6. ESTIMATION OF HYDROGEN PRODUCTION RATE AND POWER CONSUMPTION

High pressure hydrogen can be produced by using compressor and deliver hydrogen from 1 atm to higher pressure, or using pump to deliver pressurized water. According to Onda [5], using pump need less power than using compressor, in fact, the present industry trend is to highly pressurized electrolysers to eliminate conventional mechanical compressors for efficiency improvement.

We perform calculation accounting for the two ways to produce high pressure hydrogen and then we compare the power needed for water flow of 1 mol s^{-1} under electrolysis conditions(Wcomp power from compressor kW, Wpump power from water pump kW, Welect electrical power from electrolyser kW). The results are giving on **Table 3** and sketch on Fig. 7.

Table 3: Hydrogen production power versus pressure, comparison between Wpump and Wcomp

Pressure (atm)	$[\ \mathrm{Welect}(25°\mathrm{C}, \mathrm{p}) + \mathrm{Wpump}\ ]$ (kW)	$[\ \mathrm{Welect}(25°\mathrm{C}, 1\mathrm{atm}) + \mathrm{Wcomp}\ ]$ (kW)
100	259.55	283.57
200	262.32	297.43
300	263.98	306.90
400	265.18	314.32
500	266.10	320.52
600	266.84	325.88
700	267.44	330.63

The efficiency of the compressor and the pump are set to 50 %. We noticed that hydrogen produced by using pressurized water require less power than using hydrogen compressor, the difference is about 15 % kW, which is very significantly. We demonstrate the advantage of using pressurized water via pump instead of power consuming compressor.

Also, we evaluate the electrical water power, taking into consideration the temperature and pressure changes. The results are shown on Fig. 8 and giving in **Table 4**.

Hydrogen rate production estimation is based on scrutinizing the behavior of voltage versus electrical current inherent of the solid polymer electrolyser build as stack (like a fuel cell). But, facing a lack of information about SPE stack, we perform an evaluation of hydrogen rate production on a single cell of SPE with some assumptions:

- We consider a single cell of a SPE

- The current efficiency, the ratio of the number of electrons theoretically required to produce a given amount of hydrogen over the actual number of electrons supplied by the electrical current in producing this amount of hydrogen, is set at two levels 75 % and 95 % [3]
- The overall energy use of the SPE is used as hydrogen rate production instead of as straightforward evaluation of flow rate. The dimension unit of the overall energy use of SPE in kWh/Nm^3 H_2 or kWh/kg H_2 (Nm^3 means that volume is converted at STP conditions).

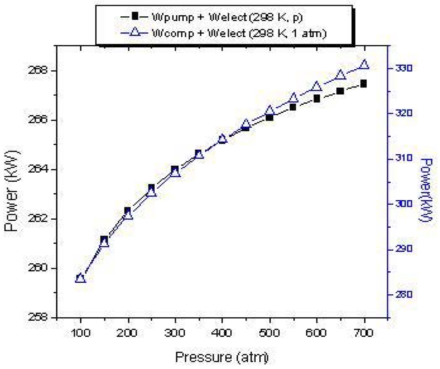

Fig. 7: Comparison between electrical power delivered by compressor and water pump for water electrolysis

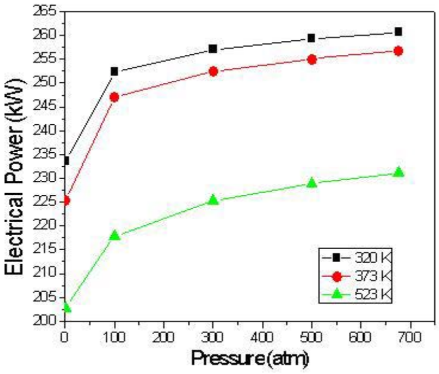

Fig. 8: Electrical power needed for hydrogen production versus temperature and pressure

Table 4: Electrical power needed for hydrogen production versus temperature and pressure

	Welect (kW)	This work	
Pressure (atm)	320 K	373 K	523 K
1	233.69	225.28	202.76
100	252.33	246.95	217.80
300	257.06	252.41	225.29
500	259.34	255.09	228.94
676	260.66	256.68	231.15

We summarize the results obtained on Figs. 9, 10 and **Table 5**. We plot only values for 95 % efficiency.

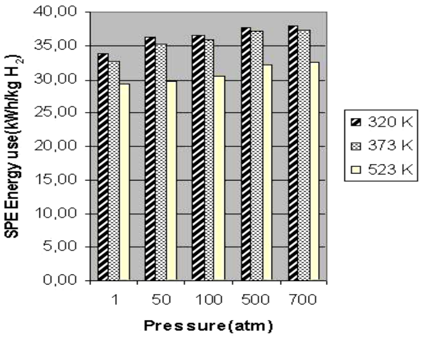

Fig. 9: Energy use of solid polymer electrolyser with 95 % efficiency (kWh/kg H_2)

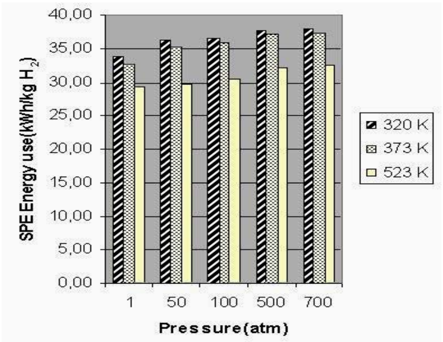

Fig. 10: Energy use of solid polymer electrolyser with 95 % efficiency (kWh/Nm^3 H_2)

Table 5: Energy use of a solid polymer electrolyser at different temperature and pressure kWh/kg H_2

	95 % efficiency			75 % efficiency		
Pressure (atm)	320 K	373 K	523 K	320 K	373 K	523 K
1	33.89	32.67	29.40	42.93	41.38	37.25
50	36.18	35.34	29.72	45.83	44.76	37.64
100	36.61	35.83	30.40	46.38	45.39	38.50
500	37.74	37.12	32.09	47.80	47.02	40.65
700	38.00	37.43	32.49	48.13	47.41	41.16

Table 6: Energy use of a solid polymer electrolyser at different temperature and pressure kWh/Nm^3 H_2

	95 % efficiency			75 % efficiency		
Pressure (atm)	320 K	373 K	523 K	320 K	373 K	523 K
1	3.03	2.92	2.63	3.83	3.69	3.33
50	3.23	3.16	2.65	4.09	4.00	3.36
100	3.27	3.20	2.71	4.14	4.05	3.44
500	3.37	3.31	2.87	4.27	4.20	3.63
700	3.39	3.34	2.90	4.30	4.23	3.67

We noticed that risen temperature will promote hydrogen production, which in not when risen pressure. This is well understood by the fact that pressure act as a force attempting to reduce hydrogen molecules action, and risen temperature gives molecules more energy.

7. CONCLUSION

The primary objective of the research was to find a constructive and mathematical coherent model that describes the high pressure hydrogen production by solid polymer electrolyser, under water electrolysis conditions. This was achieved by considering prior works of LeRoy [4] and Onda [5] modified and suitable to the SPE. We have shown that electrical power required for producing high pressure hydrogen by water electrolysis, with Nafion as the electrolyser membrane, can be evaluated by using simple thermodynamics calculations based on enthalpy and Gibbs free energy balance.

The second objective was to test the adequacy of our proposal numerical formulation versus the published data (**Table 2**), a good accuracy was concluded.

Finally, the model was used to understand the effect of some parameters like temperature and pressure, on the water electrolysis voltage. The model simulation leads to numerical values that indicate the importance of temperature and pressure on the entire efficiency of water electrolysis. We have demonstrated that increasing pressure as decreasing temperature will lead to deliver more power for water electrolysis.

Results encourage our endeavor to develop a mathematical tool that serve as an expert system to optimize the different parts of SPE water electrolysis.

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