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Estimation of temperature gradient method for a particular PEM electrolyser system

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Abstract: Behaviour of PEM electrolyser is frequently represented by some time dependent functions and other physical variables including temperature. The effect of temperature and current in this relationship is essential to regulate the potential and hydrogen output of electrolyser. Hence they are responsible to bring the dynamic to the non-linear system. The current can be considered constant, because it is supplied by a source. However, in this work we could express the current like a temperature function. On the other hand, the temperature is taken as a independet variable. Thereby, the problem turns to know the temperature value. Immersion and Invariance (gradient estimator) technique is proposed to solve this problem. Thus, the unknown temperature value will be found designing a temperature estimator avoiding temperature sensors to electrolysers.

Keywords: Electrolyser; Temperature estimation; Gradient estimator; Lyapunov application; Mathematical model.

1. INTRODUCTION

Energy production from the combustion of fossil fuels represents a serious negative impact on world economics and environment. Hydrogen has been identified as a promising fuel for viable energy supply provided that it is obtained from renewable energy. The future increase in the demand for hydrogen is a consequence of the increasing demand from the energy in a wide range in both transportation and stationary applications Belmokhtar (2013).

There are different methods to produce hydrogen: thermochemical cycles, microscopic organisms as algae, and photo-dissociation of water, etc.; which are still far from practical applications. Water electrolysis is a well-established technology and one of the most widely used methods for producing high purity hydrogen Belmokhtar (2013).

There are three main water electrolysis technologies available; 1) alkaline, 2) proton exchange membrane (PEM), and 3) solid oxide electrolyte (SOE) water electrolysis. Alkaline water electrolysis is the conventional and the most mature technology of the three and accounts for the majority of installed water electrolysis capacity worldwide. However, the PEM technology has been gaining interest owing to its compact system design, reportedly superior dynamic operation capability, high hydrogen purity, and high efficiency at higher current densities compared with alkaline electrolysis Ruuskanen (2017).

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The PEM electrolyser cell consists primarily of a PEM as an electrolytic conductor. The anode and cathode are fixed together and are known as the membrane electrode assembly. In the PEM electrolyser, water molecules and ionic particles are transferred across the membrane from the anode to the cathode, where it is decomposed into oxygen, protons, and electrons. In the reaction process, electrical energy is supplied to the system and transformed into chemical energy. The electrons cell exit through an external circuit. The electrons and protons recombine at the cathode to release hydrogen gas. A basic schematic of a PEM electrolyser is shown in Rahim (2016) Figure 1.

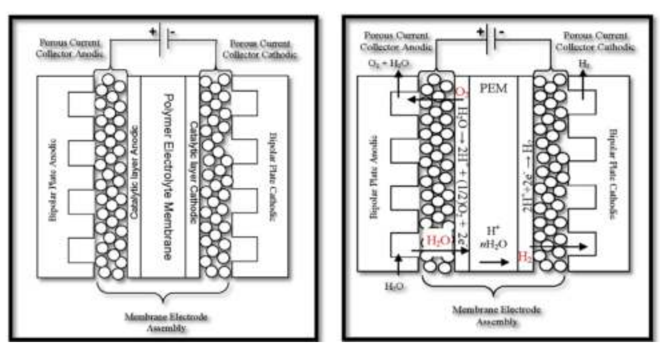

Fig. 1. Principle of operation of a single PEM electrolyser Rahim (2016).

The chemical reactions at the anode and the cathode are provided below Rahim (2016).

Anode: $H_2O_l \rightarrow \frac{1}{2}O_{2g} + 2H_g^+ + 2e^-$
Cathode: $2H^+ + 2e^- \rightarrow H_{2g}$
Overall reaction: $H_2O_l \rightarrow H_{2g} + \frac{1}{2}O_{2g}$

To maximize the electrolyser performance, it is necessary manipulate and regulate some physical variables as temperature and current to keep some optimal necessary work condition. So, the objective have been to obtain the maximum efficiency of PEM electrolyser. To carry out this objective is indispensable to have sensors and actuators for each physical parameter to feedback measure variables in particular for temperature and current.
A problem to be considered is the measurement of temerature; it is well known that sensors life is short, their cost is high and their distribution is limited. To cope with this, the design of an estimator through the Immersion and Invariance technique in Liu (2010) and Ortega (2012) is proposed to reconstruct temperature of a electrolyzer.
The work is presented as follow, Formulation of gradient estimator is described in section 2, electrolyser model development is discussed in section 3, application of temperature estimator to electrolyser system is presented in section 4, simulation results are introduced in section 5, finally, some concluding remarks are presented in section 6.

2. FORMULATION OF GRADIENT ESTIMATOR

The estimator design is formulated proposing one function where the system behaviour representation has been distinguishing measurable and not measurable signals show in Ortega (2012), there are a general kind of function depend of two variables T and i expressed by

$$F(T,i) = G(T) + H(T,i) \tag{1}$$

Where i and T are known and time dependent, such that measurable signals $F(T,i)$ is represented by

$$y(t) = F(T,i) \tag{2}$$

indeed, the representation in non-linear regression form will be

$$y(t) = \phi(T,i) \tag{3}$$

where

$$\phi(T,i) := G(T) + H(T,i) \tag{4}$$

after this formulation, the follow proposition is presented.
Proposition 1. Consider the function $\phi(T,i)$, where $F(T,i)$ is known and the corresponding to non-linear regression model with $\frac{\partial \phi(T,i)}{\partial T} > 0$, then, the gradient estimator is

$$\dot{\hat{T}} = \gamma(y(t) - \phi(\hat{T},i)) \tag{5}$$

with $\gamma > 0$ ensure that:

$$\lim_{t\rightarrow\infty} \hat{T} = T. \tag{6}$$

For all initial condition $\hat{T}_0$ such as $\frac{\partial \phi(\hat{T}_0,i)}{\partial T} > 0$.

Proof. To achieve the Immersion and Invariance estimator converges to desire value, it is necessary exploit monotonicity of map $T \mapsto \phi(T,i)$, then as

$$\frac{\partial \phi(T,i)}{\partial T} > 0. \tag{7}$$

which is define positive. Hence, the function is strictly monotonically increasing and satisfies

$$(\hat{T} - T)\left[\phi(\hat{T},i) - \phi(T,i)\right] > 0, \quad \forall \hat{T} \neq T \tag{8}$$

taking as Lyapunov function candidate

$$V(\hat{T}) = \frac{1}{2\gamma}(\hat{T} - T)^2 \tag{9}$$

its derivative, along the trajectories of 2, 3, 4 and 5 is given by

$$\dot{V} = -(\hat{T} - T)[\phi(\hat{T},i) - \phi(T,i)] < 0, \quad \forall \hat{T} \neq T \tag{10}$$

therefore, the boundary follow immediately from 8. Accordingly $V(\hat{T})$ is a *strict Lyapunov funtion* and the proof is completed calling upon Lyapunov's second stability theorem.

3. ELECTROLYSER MODEL

In this section is described the electrolyser mathematical model and its assumptions.

3.1 Hyphotesis

The following main assumptions are taken from García (2012).

1. Pressure effects are neglected.
2. The temperature is supposed to be uniform in the electrolyser stack.
3. The total stack working voltage can be obtained, multiplying the cell voltage by the number of series-connected cells.
4. The membrane is considered as being completely saturated of water.

3.2 Electrochemical model

The minimum voltage to start the water electrolysis reaction corresponds with the sum of the reversible potential for each semi reaction at both electrodes.
These minimum potentials are affected by pressure and temperature conditions of the reactions. Hence, when current is flowing through the electrodes, the operating voltage for a single cell (V_{cell}) is given by the reversible voltage and the sum of different overpotentials García (2012).

$$V_{\text{cell}} = V_{\text{rev}} + \eta_{\text{elec}} + \eta_{\Omega} \tag{11}$$

The reversible potential at the cell can be derived from the Nernst equation. The Nernst potential equation for water electrolysis at constant atmospheric pressure is empirically given by García (2012).

$$V_{\text{rev}} = 1.5184 - 1.5421 \times 10^{-3} T + 9.523 \times 10^{-5} T \log T + 9.84 \times 10^{-8} T^2 \tag{12}$$

Charge-transference and mass-transport phenomena at the electrodes must be considered when current flows through the electrolytic cell. These limitations (η_{elec}) on the semi-reactions are known as activation and diffusion over-potentials, respectively. On each electrode, one of the branches (oxidation at the anode and reduction at the cathode) will dominate during operation. Therefore, the anodic and cathodic activation overpotentials (η_a and η_c respectively) can be written as García (2012).

$$\eta_{\text{elec}} = \eta_a + \eta_c \tag{13}$$

Where

$$\eta_a = \frac{RT}{\alpha_a zF} \log\left(\frac{i_a}{i_{0,a}}\right), \tag{14}$$

$$\eta_c = \frac{RT}{\alpha_c zF} \log\left(\frac{i_c}{i_{0,c}}\right), \tag{15}$$

The value of the exchange current density at the anode electrode are typically much lower. So, the cathode contribution to the activation overpotential can be neglected, i.e. $\eta_c \approx 0$.

Another important effect is the overpotential due to ohmic losses η_{ohm}. These include the electronic losses due to the resistance of bipolar plates, electrode, current collector, etc. The dominant losses in η_Ω are the ionic losses caused by the resistance to the proton transport through the polymeric membrane. This ionic resistance can be expressed as a function of the thickness t_m and the conductivity σ of the membrane:

$$R_{ion} = \frac{t_m}{\sigma} \tag{16}$$

The temperature dependence of the membrane conductivity can be simply modelled, from a value at reference temperature, using an Arrhenius expression:

$$\sigma(T) = \sigma_{ref} \exp\left[-\frac{E_{pro}}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right] \tag{17}$$

Where E_{pro} is a temperature-independent parameter which represents the activation energy for proton transport in the membrane. The electronic resistance (R_{ele}) can be measured between the stack terminals at open circuit condition.

$$\eta_{ohm} = (R_{ele} + R_{ion})i \tag{18}$$

Parameter values of PEM electrolyser model are showed in table 1.

Table 1. Parameters of the mathematical model.

Symbol	Parameter	Value
E_{pro}	Activation energy	10456 eV
F	Faraday's constant	96485.3353 C/mol
$i_{0,a}$	Initial current density	1.2 A
$i_{0,c}$	Initial current density	1.2 A
R	Ideal gas constant	8.3144 $J/mol \cdot K$
R_{ele}	Electronic resistance	.8 Ω
t_m	Membrane Thickness	0.0125 cm
T_{ref}	Temperature of reference	298 K
σ_{ref}	Conductivity of reference	100 cm/Ω

4. APPLICATION OF TEMPERATURE ESTIMATOR TO A PEM ELECTROLYSER SYSTEM

Taken the example of compact form in 2, the measurable signals will be defined from the equation 11 as follow

$$y(t) = V_{cell}(T, i) \tag{19}$$

Where

$$\phi(T, i) := V_{\text{rev}}(T) + \eta_{\text{elec}}(T) + \eta_{ohm}(T, i) \tag{20}$$

Now a proposition to fuel cell system is presented.

Proposition 2. Consider the function $\phi(T, i)$ increasing with respect to T, and $T \geq 298.15$ then the low limit of i can be express in terms of T as

$$i_{\text{lim}} = \frac{RT^2\sigma(T)}{E_{pro}t_m}\left[1.44687 \times 10^{-3} - 9.523 \times 10^{-5} \log T - 19.68 \times 10^{-8} T - \frac{R}{\alpha_a ZF} \log\left(\frac{i_a}{i_{0,a}}\right)\right] \tag{21}$$

Remark: In this work the parameter 298 K is used as the lower limit because it is the minimum recorded temperature used to work with the electrolysers.

Proof. By hypothesis of $\phi(T, i)$

$$\frac{\partial\phi(T, i)}{\partial T} = \frac{\partial V_{\text{rev}}}{\partial T} + \frac{\partial\eta_{\text{elec}}}{\partial T} + \frac{\partial\eta_{ohm}}{\partial T} > 0$$

Developing the last ecuation

$$0 < -1.44687 \times 10^{-3} + 9.523 \times 10^{-5} \log T + 19.68 \times 10^{-8} T + \frac{R}{\alpha_a ZF} \log\left(\frac{i_a}{i_{0,a}}\right) + \frac{t_m}{\sigma(T)}\left(\frac{E_{pro}}{RT^2}\right) i$$

Clearing i. Then, the limit of i is

$$i_{\text{lim}} = \frac{RT^2\sigma(T)}{E_{pro}t_m}\left[1.44687 \times 10^{-3} - 9.523 \times 10^{-5} \log T - 19.68 \times 10^{-8} T - \frac{R}{\alpha_a ZF} \log\left(\frac{i_a}{i_{0,a}}\right)\right]$$

The behaviour of the derivative $\frac{\partial \phi(T,i)}{\partial T}$ is showed in the Figure 2 and Figure 3.

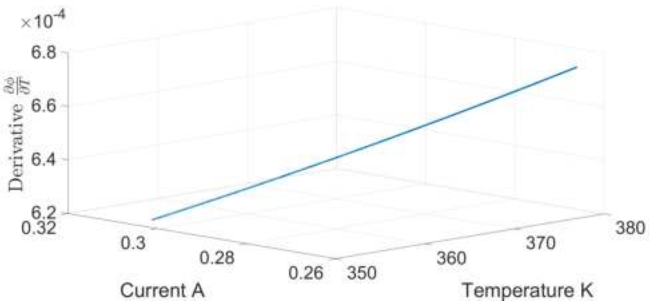

Fig. 2. Constrain of $\frac{\partial \phi}{\partial T}$ like function of T and i .

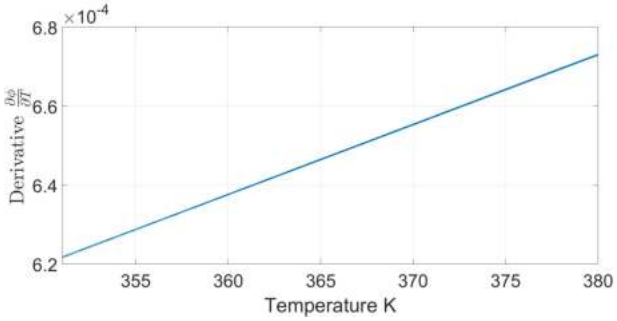

Fig. 3. Behavior of $\frac{\partial \phi}{\partial T}$ in function of T and i.

Proposition 3. Consider the function $\phi(T, i)$ increasing with respect to T, $T \geq 298.15$ and i such that must satisfy inequality

$$i > \frac{RT^2\sigma(T)}{E_{pro}t_m}\Big[1.44687 \times 10^{-3} - 9.523 \times 10^{-5}\log T$$

$$-19.68 \times 10^{-8}T - \frac{R}{\alpha_a ZF}\log\left(\frac{i_a}{i_{0,a}}\right)\Big]$$

Then the gradient estimator of temperature is

$$\dot{\hat{T}} = \gamma(y(t) - \phi(\hat{T}, i)) \tag{22}$$

With $\gamma > 0$ ensure that:

$$\lim_{t\to\infty}\hat{T} = T \tag{23}$$

Proof. For the values of T and i in the hypothesis by proposition 2, $\dfrac{\partial\phi(T,i)}{\partial T} > 0$ then, by proposition 1.

The gradient estimator of temperature is

$$\dot{\hat{T}} = \gamma(y(t) - \phi(\hat{T}, i))$$

With $\gamma > 0$ ensure that:

$$\lim_{t\to\infty}\hat{T} = T$$

5. RESULTS

We have developed an estimator for the oxygen pressure, the stability conditions for the estimator are derived by using Lyapunov functions and, under some conditions the electrical current has been characterized in terms of temperature.
We started working with parameters found in the literature García (2012) with the goal of determining the stability region for our estimator under of the constrains stated for the electrical current and temperature.

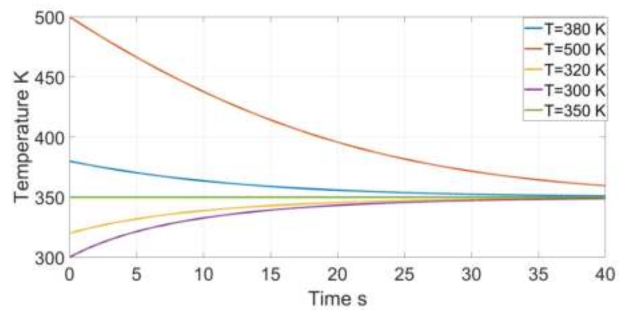

Fig. 4. Estimator with different initial values for T

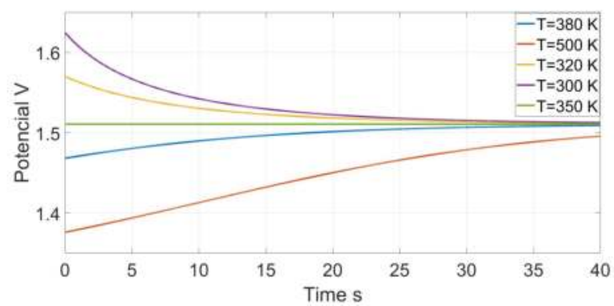

Fig. 5. Behaviour of the potential in the cell.

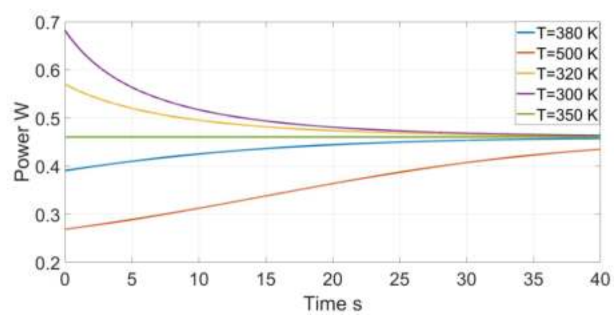

Fig. 6. Behaviour of the power in the cell.

Using the stability region simulations of the estimator were made with temperature to stimate equal to 350 K and different initial values for the estimator T. The estimator behaviour how can you conclude converge to

350 K with different initial values for T Figure 4 and different values γ Figure 7.

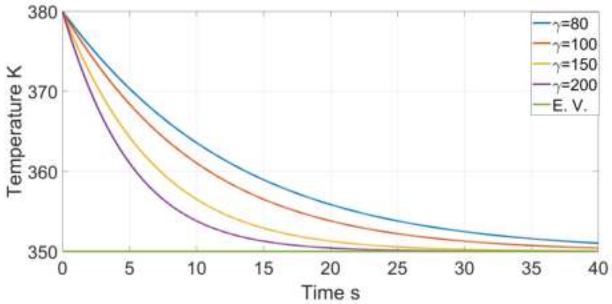

Fig. 7. Estimator with different initial values for γ

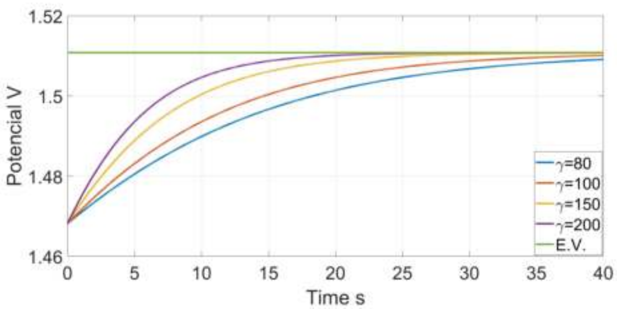

Fig. 8. Behaviour of the potential in the cell.

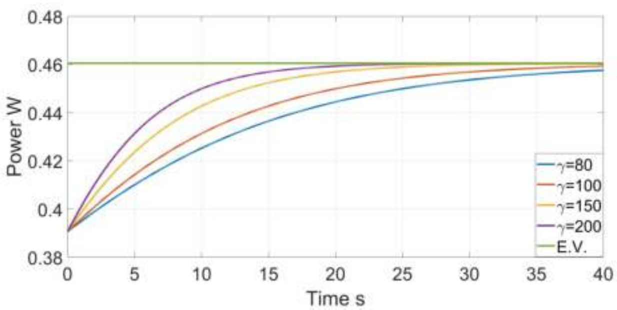

Fig. 9. Behaviour of the power in the cell.

We can see the cell potential behaviour with different initial values for T Figure 5 and different values γ Figure 8, in both cases we have stability and desired approach. Finally, the power behaviour with different initial values for T Figure 6 and different values γ Figure 9 shows stability with respect to time $t \to \infty$.

6. DISCUSSION

The gradient estimation technique using Immersion and Invariance approach, presented in this work is aim one parameter (temperature). The estimator works with the electrolyser potential and its stability is supported by monotonically increasing mathematically behaviour of $\phi(T, i)$ and conclude find a global stability by second Lyapunov's theorem, the stability region found was for $T > 298$ in unit K and $i > 0$ in unit A. The temperature estimator present absolute convergence within of this constraint, however corresponding working condition can be different because are directly related to laboratory environmental conditions. So, the next step will be to test this estimator with data of real temperature in a PEM electrolyser.
This way is useful to estimate other physical variables into the PEM electrolyser to avoid the use of any sensors.

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