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Investigation of PEM electrolyzer modeling: Electrical domain, efficiency, and specific energy consumption

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Abstract

Proton exchange membrane (PEM) electrolyzer is an advanced technology considered a viable alternative for the generation of hydrogen-based on renewable energy sources (RES). Its modeling is essential to study its interaction with RES and power electronics. In the current literature, the models for the electrical domain are mainly based on semi-empirical and empirical equations. However, dynamic operations are generally neglected. Besides, a few works about electrolyzer efficiency have been reported, especially Faraday's efficiency, which is a key parameter to express the losses due to gas diffusion. The main purpose of this review is to summarize and analyze the reported models to describe the electrical domain. Furthermore, dynamic operation issues are highlighted and recent works about modeling the dynamics are introduced. Finally, a discussion is provided about the different efficiency (Faraday, voltage, energy) and the specific energy consumption, which are important indicators linked with the performance.

Keywords: PEM electrolyzer; Modeling; Faraday's efficiency; Voltage efficiency; Specific energy consumption; Dynamic operation.

1. Introduction

Over the last decade, the global demand for energy has been growing at a very high rate due to the increase of population and the depletion of fossil fuels [1]. These factors have prompted interest in developing at large scale renewable energy sources (RES) for electricity, clean fuel, and heat production [2].

The RES are the resources that have "the future inside" by definition because they can be reformed in the environment by natural processes. RES include solar energy, water energy, biomass energy, wind energy, earth energy, sea energy, biological, and bacterial energy [3]. It is stipulated for the year 2050 several countries (Australia, Denmark, Macedonia, Portugal, etc.) will depend only on RES [2, 4–7].

Hydrogen is an energy carrier since it is one of the most efficient, cleanest and lightest fuels. There is a vast experience of handling hydrogen in the industry, which reinforces the belief that it is a safe resource. It is as versatile as electricity, it can be stored and it can be produced by RES, which is important from the sustainability point of view [8–16]. Different processes for hydrogen production can be used: photodissociation of water, thermochemical cycles, microscopic organisms as algae, etc. These processes are still far from practical

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use. In comparison, a process already available for application is water electrolysis [17], which is the process of using electricity to split water into hydrogen and oxygen.

Commonly the electrolyzers are used to produce the water electrolysis, which are reliable devices that do not require continuous maintenance since they hardly include mobile elements. Also, they are silent and have a high degree of modularity, which makes them suitable for decentralized applications in residential, commercial, and industrial areas [18]. There are three main kinds of electrolyzers: Alkaline electrolyzer, Proton Exchange Membrane (PEM) electrolyzer, and Solid Oxid (SO) electrolyzer.

Water electrolyzer modeling is a powerful tool for simulation, exploring control strategies, prediction, and understanding of the behavior of hydrogen-generation systems. It is especially important when the electrolyzer is coupled directly with RES since it ensures efficient and reliable operation of them [19–22]. Besides, compared to alkaline technology, PEM technology is particularly suitable to be coupled with RES since it can absorb the energy from RES during transients. It is one of the most important features requested when coupling with dynamic sources such as RES [23].

In recent years, several reviews about modeling of the electrolyzers have been reported. In [24], the authors have presented a work where the fundamentals of the electrolysis are examined and the performance of various designs of alkaline electrolyzers is compared based on the thermodynamic and kinetic analysis. In [18], a review of electrolyzer technologies for hydrogen production and the state of the art of their integration with RES has been reported. In [25], a review of the areas of electrocatalysis, essential components, and modeling activities for PEM electrolyzers has been introduced. In [26], the authors have presented a work focused on modeling SO electrolyzers and remaining key issues. In [22], a state-of-the-art of the mass transport model for PEM electrolyzers based on analytical, semi-empirical and mechanistic methods has been presented. The work [27] has presented a review of the models of the low temperatures electrolysis system for alkaline and PEM electrolyzers. In [28], a review of multiphysics models provided experimental data needed to calculate thermos-physical properties and the correlations for the simulations of alkaline electrolyzers has been carried out. In [29], a review of different techniques to produce hydrogen in a focus on alkaline electrolysis has been reported. Finally, the work [30] has presented a review mainly focused on the recent development of PEM electrolyzer including the evolution reaction electrocatalysts of the hydrogen and the oxygen, and by highlighting the most efficient electrocatalysts among similar materials.

From this current state-of-the-art, it can be noted that five reviews have been reported for alkaline and PEM electrolyzers; while only one review for SO has been carried out since this technology is under research and development. Among PEM electrolyzer reviews, only in [22, 27], models of PEM electrolyzers are summarized and discussed from the mass transport and low-temperature electrolysis modeling point of view. Besides, static models of the electrical domain have been presented but the dynamics have not been discussed. Recently, a first work [31] has been reported about the dynamic operations of PEM electrolyzers. The authors have demonstrated that the electrolyzer takes some time to reach its steady-state operation as a result of a dynamic current profile. This is mainly due to the move of charge inside the electrolyzer. The response time strongly depends on the input energy, and consequently, the response may be more or less fast. To model the dynamics

of the electrolyzer, an equivalent electrical circuit has been developed and validated experimentally. The results demonstrate the effectiveness of the model in modeling accurately the dynamic behavior of PEM electrolyzers compared to classical static models.

It has to be noted also that a few works have been reported about Faraday's efficiency, which is the key parameter modeling the losses due to the gas diffusion. Based on the previously reported reviews, the objective of this work is to summarize and analyze the static models based on semi-empirical and empirical equations for the electrical domain. Besides, dynamic issues of PEM electrolyzers are discussed and recent models are presented. Finally, a discussion is provided about the different efficiency (Faraday, voltage, energy), and the specific energy consumption which are linked with the performance of PEM electrolyzers.

This work is composed of five sections. After introducing the current state-of-the-art about the previously reported reviews focused on electrolyzers and the remaining key issues, Section 2 introduces the basic principles, advantages, and disadvantages of the PEM electrolyzer. Besides, dynamic issues are discussed to emphasize their importance in modeling accurately dynamic operations of PEM electrolyzers. Then, in Section 3, a summary and an analysis of the electrical domain modeling is reported from the static and dynamic point of view. After that, in Section 4, an investigation of the efficiency, the specific energy consumption, and its relation with the performance of PEM electrolyzers is made. Besides, a discussion is provided to emphasize the two important issues which require further investigation in the future. Finally, in Section 5, the conclusion is drawn out.

2. PEM electrolyzer technology

2.1. Operation and characteristics

As mentioned in the introduction, three main technologies of electrolyzers have been reported such as alkaline, PEM, and SO. However, only alkaline and PEM technologies are currently available in the market; while SO technology is still under research and development [26]. Among the two available technologies, alkaline technology is the most mature and widespread technology since its operation principles were introduced more than 100 years ago. Therefore, so many alkaline water electrolysis plants have been developing so far. On one hand, the main benefits of this technology are low-cost catalysts (i.e. cobalt, nickel, iron), high lifespan and gas purities [29]. On the other hand, this technology suffers from having a low current density (between $0.2-0.4 A \cdot cm^{-2}$) which slows down its development in emerging markets of great potential. Furthermore, in terms of flexibility, alkaline technology is not fit in load-following operation, which is requested by coupling it with RES. To overcome the above-mentioned issues for alkaline technology (i.e. current density, flexibility), PEM technology has been developing since the 1960s. Indeed, this technology can operate at high current densities (around $2 A \cdot cm^{-2}$) and is particularly suitable to be coupled with RES due to its fast response time. As a result, since RES are considered very dynamic sources, the energy flowing during transients can be absorbed by the PEM electrolyzer, enhancing the efficiency of the system. However, compared to alkaline electrolyzers, PEM electrolyzers use expensive catalysts such as platinum (at the cathode side) and iridium (at the anode side), increasing consequently the global price of the electrolyzer.

In [32], a survey of the most significant scientific and technological materials to build a PEM electrolyzer has been reported. The PEM electrolyzer cell is essentially a PEM as an electrolytic conductor between an anode and a cathode. The 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 converted into chemical energy. The electrons exit the cell through an external circuit. After, the electrons and protons recombine at the cathode to produce hydrogen [22], see Figure 1.

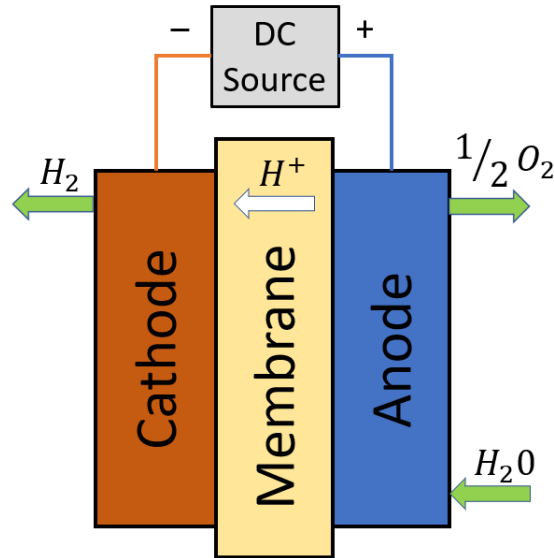
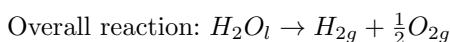
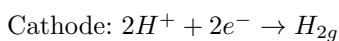
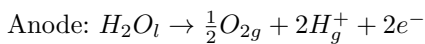


Figure 1: Schematic illustration of a basic water PEM electrolysis system.

The PEM is responsible for providing high proton conductivity, low gas crossover, compact system design, and high-pressure operation. The low membrane thickness is in part the reason for many of the advantages. The low gas crossover rate of the polymer electrolyte membrane allows for the PEM electrolyzer to work under a wide range of power input. The high-pressure operation of an electrolyzer brings the advantage of delivering hydrogen at high pressure for the end-user, thus requiring less energy to further compress and store the hydrogen [25]. Problems related to higher operational pressures in PEM electrolysis are also present, such as cross-permeation phenomenon which increases with pressure. The corrosive acidic regime provided by the PEM requires the use of distinct materials. These materials must not only resist the hard corrosive low pH (around 2) condition but also sustain the high applied over-potential (around 2 V), especially at high current densities. Corrosion resistance applies not only for the catalysts used but also for current collectors and separator plates. Only a few materials can be selected that would perform in this hard environment [25].

The reactions in the PEM electrolyzer are:



2.2. Dynamic issues

Over the last decades, so many contributions have been reported in the literature about the development of static models based on semi-empirical and empirical equations [22, 27]. However, the modeling of the dynamics is generally neglected due to a few studies developed on it. Like fuel cells, electrolyzers are electrochemical devices and their response time to reach a steady-state operation may be slow or fast depending on the operating conditions. Recently, a first investigation [31] has been provided on PEM electrolyzer responses based on dynamic current profiles. It has been demonstrated that the responses are linked with the operating conditions, and consequently, the modeling of these dynamics is crucial to make reliable and accurate the model.

In Figures 2 and 3, two dynamic operations are reported and have been carried out by using a commercial-400W PEM electrolyzer. The specifications of the studied PEM electrolyzer can be found in [31]. The first test has been performed with a step current from 0 to 10 A; while the second with a step current from 10 to 0 A. In both tests, it can be noted that the PEM electrolyzer responds immediately as a result of the step current. It is one of the most important features required for electrolyzers when coupling with RES since they are dynamic sources which their operation strongly depends on the weather conditions. The immediate response is followed by a slow voltage rise or fall before the electrolyzer reaches its steady-state operation. This slow response is linked with the dynamics of the reactions both at the anode and the cathode as reported in [31].

This emphasizes that the dynamics are currently important issues and must be taken into consideration in modeling the PEM electrolyzer by offering more accuracy. Besides, since the dynamics can be slower or faster according to the input energy, it is crucial to develop accurate and reliable models based on adaptive parameters.

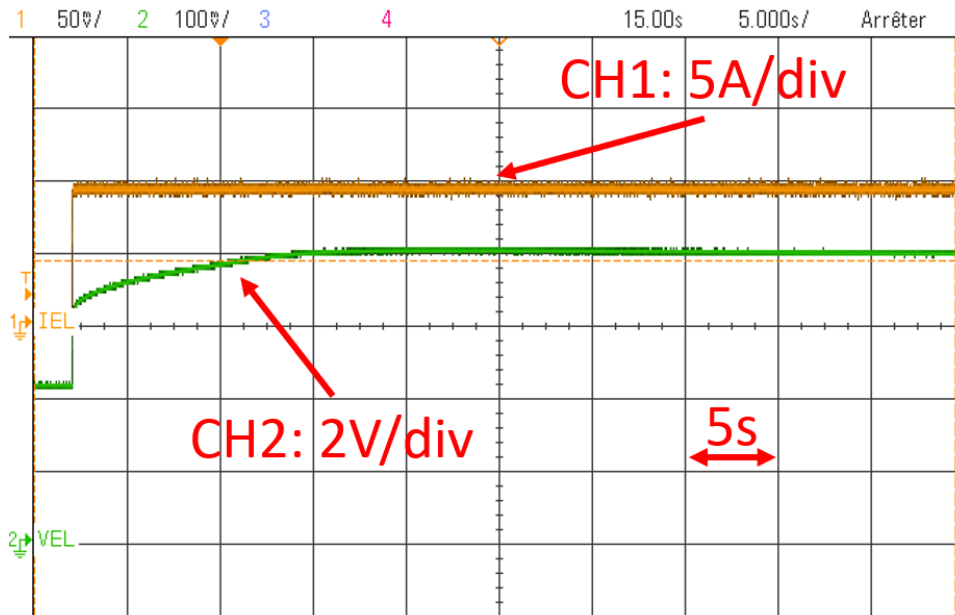


Figure 2: Response of the electrolyzer as a result of a rising electrical current from 0 to 10 A.

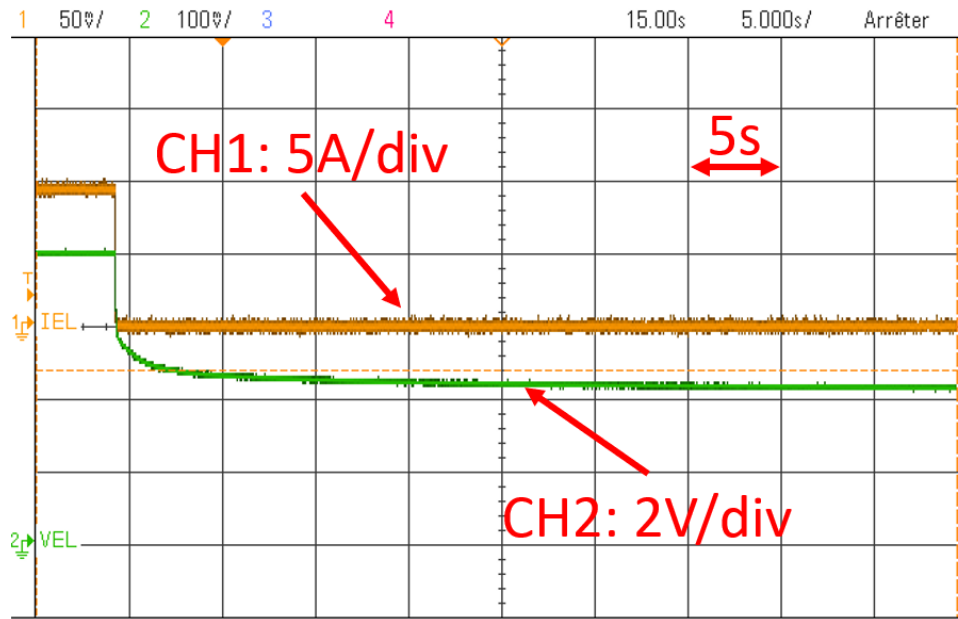


Figure 3: Response of the electrolyzer as a result of a falling electrical current from 10 to 0 A.

3. Electrical domain modeling

Several PEM fuel cell models have been reported, but so few PEM electrolyzers models have been [22, 33]. In recent years, the modeling of PEM electrolyzers has gained a growing interest from industrials and researchers to optimize, design and use the PEM electrolyzer in a good way, see Figure 4. In this section, static models based on semi-empirical and empirical equations are presented and analyzed. Besides, since the dynamics modeling has been neglected in previous reviews [22, 27], it is reported in this section based on recently published works. This enables to highlighting the remaining issues for dynamics modeling.

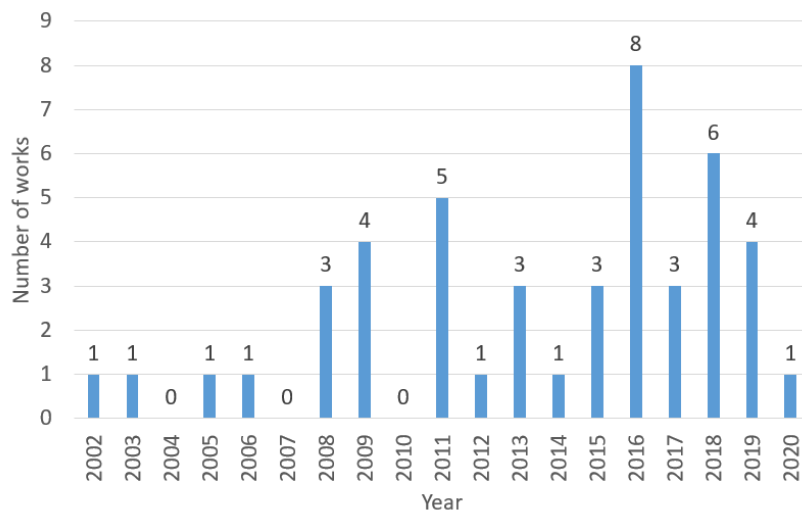


Figure 4: Evolution of the number of works about voltage to the year for the PEM electrolyzer.

3.1. Static modeling

3.1.1. Introduction

A polarization curve is an important tool not only for the study of PEM electrolyzers but, for all kinds of electrolyzers, describes the relationship between the cell voltage V_{cell} and the cell current I_{cell} , for alkaline electrolyzer see the works [34–53] and for SO electrolyzer [54–79]. Since the current directly corresponds to the production rate by Faraday’s law, the polarization curve gives a correlation between electric power and the production rate [35, 80]. The polarization curve in one cell can be expressed like the product of V_{cell} with and I_{cell} .

$$P_{\text{cell}} = V_{\text{cell}} \cdot I_{\text{cell}} \quad (1)$$

and the polarization curve in the stack can be expressed similarly like the product of the stack voltage V_S with the stack current I_S .

$$P_S = V_S \cdot I_S \quad (2)$$

As the current in the electrolyzer is direct from one source the study is focused on the voltage of the electrolyzer. The voltage at the stack terminals is the sum of the voltages of the number of cells N connected in serie, and the stack current is the sum of currents flowing through the number of cells N branches connected in parallel [18], see Table 1.

Table 1: Kind of V_S and I_S depending on electrolyzer configuration.

| Parameter | Parallel | Serie |
|-----------|----------------------------------|----------------------------------|
| V_S | V_{cell} | $\sum_{j=1}^N V_{\text{cell},j}$ |
| I_S | $\sum_{j=1}^N I_{\text{cell},j}$ | I_{cell} |

However, it is generally assumed that all the cells of a stack have the same voltage and current. As it is widely known the real cell voltage in a PEM electrolyzer cell can be expressed as the sum of the reversible potential and its over-potentials:

$$V_{\text{cell}} = V_{\text{rev}} + \eta_{\text{act}} + \eta_{\text{ohm}} + \eta_{\text{con}} \quad (3)$$

where V_{rev} is the reversible potential, η_{act} , η_{ohm} , and η_{con} are the activation, ohmic and concentration over-potentials. In Table 2 is summarized the papers about the reversible voltage and over-potentials and in Figure 5 is shown the number of works about these over-potentials for PEM electrolyzers.

Table 2: Works about the reversible potential and the over-potentials.

| Electrical domain | $V_{\text{cell}} = V_{\text{rev}} + \eta_{\text{act}} + \eta_{\text{ohm}}$ | $V_{\text{cell}} = V_{\text{rev}} + \eta_{\text{act}} + \eta_{\text{ohm}} + \eta_{\text{con}}$ |
|-------------------|--|--|
| PEM | [19, 21, 22, 27, 30, 31], [36, 81–106] | [18, 20, 25, 80, 107–117] |

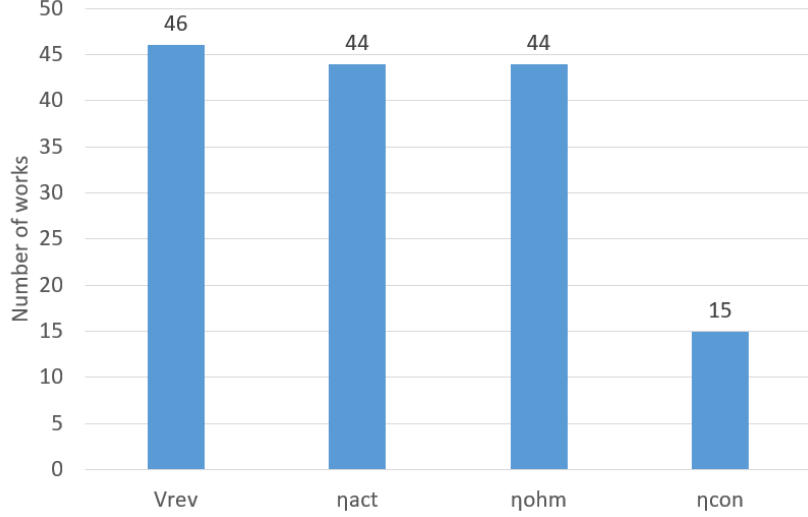


Figure 5: Number of works about the different over-potentials for the PEM electrolyzer.

3.1.2. Semi-empirical modeling

First of all, a simple way to model the current-voltage curve is to use a semi-empirical equation. The most known semi-empirical model has been developed by Ulleberg in 1998 [118] for alkaline electrolyzers but can be applied to PEM electrolyzers. It is based on thermodynamics basics and empirical electrochemical expressions. The semi-empirical model is described by the following expression:

$$V_{\text{cell}} = V_{\text{rev}} + r \cdot I_{\text{cell}} + s \cdot \log[k \cdot I_{\text{cell}} + 1] \quad (4)$$

The equation (4) can be determined by a static characterization (i.e. the parameter is considered as constant) or by using the empirical equation depending on the change in Gibbs energy, pressure, and temperature (see 3.1.3). In comparison, the second term is linked with the ohmic over-potential η_{ohm} by its parameter r . Finally, the last term is related to the activation over-potential η_{act} based on two parameters s and k .

As reported in [34], the temperature has a strong influence on the performance of the electrolyzer described by its current-voltage curve. For this reason, the effect of temperature has to be taken into account in the previous semi-empirical equation (4). Among the parameters, only the parameters r and k depend on the temperature T and the electrode area A ; while the parameter s is considered constant. Hence, the semi-empirical model based

on the temperature T and the electrode area A is given as follows [34]:

$$V_{\text{cell}} = V_{\text{rev}} + \left(\frac{r_1 + r_2 \cdot T}{A} \right) \cdot I_{\text{cell}} + s \cdot \log \left[\left(\frac{k_1 \cdot T^2 + k_2 \cdot T + k_3}{A \cdot T^2} \right) \cdot I_{\text{cell}} + 1 \right] \quad (5)$$

In spite of Ulleberg's model is accurate to describe the current-voltage curve according to the temperature, it does not include other parameters such as the pressure of the gas which has a great influence on the performance of the electrolyzer. Hence, some authors have modified Ulleberg's model by adding gas pressure to obtain a more reliable model. The modified Ulleberg's model taking into account the gas pressure is expressed by the following equation [40]:

$$V_{\text{cell}} = V_{\text{rev}} + [(r_1 + d_1) + r_2 \cdot T + d_2 \cdot P] \cdot I_{\text{cell}} + s \cdot \log \left[\left(k_1 + \frac{k_2}{T} + \frac{k_3}{T^2} \right) \cdot I_{\text{cell}} + 1 \right] \quad (6)$$

To take into consideration the gas pressure P , additional parameters d_1 and d_2 can be found in equation (6). These parameters are related to the linear change in the ohmic over-potential. The different parameters of the model can be determined by using the experimental data (according to the pressure and temperature) and the least-squares regression algorithm. Finally, the stack voltage of the electrolyzer can be deduced from Table 1.

3.1.3. Empirical modeling

To improve the accuracy of the current-voltage curve a lot of authors have studied and described each term that makes up the equation (3) (i.e. the reversible potential and its over-potentials) of an empirical way.

- Reversible potential

The reversible potential or open circuit voltage is the minimum required voltage for the electrolysis can be carried out in the electrolyzer [18, 22]. The reversible potential at the cell has a relation with the from Gibbs free energy:

$$\Delta G = \Delta H - T \cdot \Delta S \quad (7)$$

and the reversible potential is expressed:

$$V_{\text{rev}} = \frac{\Delta G}{n \cdot F} \quad (8)$$

where, at standard condition, the temperature is $T = 298.15 \text{ K}$, the pressure in the electrolyzer is 1 atm , $\Delta S = 0.1631 \text{ kJ mol}^{-1} \text{ K}^{-1}$ is the entropy change, $\Delta H = 285.84 \text{ kJ mol}^{-1}$ is the enthalpy change, $n = 2$ is the number of the electron moles transferred per hydrogen mole, and $F = 96485 \text{ C mol}^{-1}$ is the Faraday's constant. By these conditions and equations, (7) and (8) many authors work with $V_{\text{rev}} = 1.23 \text{ V}$ [22].

Another important concept related whit the reversible potential and voltage efficiency is the thermo-neutral potential V_{th} , which is obtained employing enthalpy ΔH in its place of ΔG for the potential calculation [30].

$$V_{\text{th}} = \frac{\Delta H}{n \cdot F} = \frac{\Delta G}{n \cdot F} + \frac{T \cdot \Delta S}{n \cdot F} \quad (9)$$

where at standard condition, $V_{\text{th}} = 1.48 \text{ V}$.

- Activation over-potential

The activation over-potential represents the over-potential to initiate the proton transfer and the electrochemical kinetic behavior in the PEM electrolyzer. Some portion of the applied voltage is lost as a result of transferring the electrons to or from the electrodes during chemical reactions at the electrodes [18, 22]. The activation energy required at both the anode and the cathode due to the activation over-potential can be modeled by relating the Butler-Volmer expression as many authors have done:

$$\eta_{\text{act}} = \eta_{\text{act,a}} + \eta_{\text{act,c}} \quad (10)$$

where

$$\eta_{\text{act,a}} = \frac{R \cdot T}{\alpha_a \cdot z \cdot F} \cdot \log \left(\frac{i_a}{i_{0,a}} \right), \quad (11)$$

$$\eta_{\text{act,c}} = \frac{R \cdot T}{\alpha_c \cdot z \cdot F} \cdot \log \left(\frac{i_c}{i_{0,c}} \right) \quad (12)$$

where $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ is the universal gas constant, z is the stoichiometric coefficient refers to the number of electrons transferred in the global semi reactions defined by Faraday's law. The value of the stoichiometric coefficient in water electrolysis is 2. α_a and α_c are the charge transfer coefficients. The values of α_a and α_c are 0.5 on the symmetry reactions. However, in [103] has been demonstrated that α_a and α_c are variables, for example, it can be seen in [113] values for $\alpha_a = 2$ and $\alpha_c = 0.5$.

- Ohmic over-potential

The ohmic over-potential is the resistance caused by the flow of electrons and the electronic resistance of the PEM electrolyzer. This ohmic over-potential depends on the type of PEM, and electrode material. The ohmic over-potential due to membrane resistance, or ionic resistance, is the resistance to the proton transport through the PEM. Meanwhile, electronic resistance is caused by electronic materials such as bipolar plates, electrodes current collectors, etc. The ohmic over-potential is linearly proportional to the current [18, 22]. The membrane over-potential can be expressed as a function of the membrane thickness ϕ (cm), the conductivity of the membrane σ_{mem} and i_0 .

$$\eta_{\text{ohm,mem}} = R_{\text{ion}} \cdot i_0 \quad (13)$$

where $R_{\text{ion}} = \phi / \sigma_{\text{mem}}$ is the ionic resistance. The local ionic conductivity with water content and temperature function can be written as:

$$\sigma_{\text{mem}} = (0.005139\lambda - 0.00326) \cdot \exp \left[1268 \cdot \left(\frac{1}{303} - \frac{1}{T} \right) \right] \quad (14)$$

where λ is the degree of membrane humidification and it can be defined as:

$$\lambda = 0.08533 \cdot T - 6.77632 \quad (15)$$

The electronic over-potential can be expressed as:

$$\eta_{\text{ohm,ele}} = R_{\text{ele}} \cdot i_0 \quad (16)$$

The ohmic resistance of the electronic materials can be expressed as a function of the material resistivity ρ in (Ωm), the length of the path of the electrons l , and the conductor cross-sectional area A_c :

$$R_{\text{ele}} = \frac{\rho \cdot l}{A_c} \quad (17)$$

Therefore, as a result of the ionic resistance and electronic resistance, the ohmic over-potential can be expressed as:

$$\eta_{\text{ohm}} = \eta_{\text{ohm,mem}} + \eta_{\text{ohm,ele}} \quad (18)$$

- Concentration over-potential

The concentration over-potential or diffusion over-potential is caused by mass transport processes. In the case of water electrolysis, the biggest influence is likely due to the product transport limitations, if H_2 and O_2 are not removed as fast as they are produced their concentration in the reaction site increases slowing the reaction kinetics [18, 113]. It has been reported that V_{con} is much lower than V_{ohm} and V_{act} , for this reason, many authors take $V_{\text{con}} = 0$ in their studies. However, the concentration over-potential is widely estimated with the Nernst's equation.

$$\eta_{\text{con}} = \eta_{\text{con,a}} + \eta_{\text{con,c}} \quad (19)$$

where

$$\eta_{\text{con,a}} = \frac{R \cdot T}{z \cdot F} \cdot \ln \left[\frac{C_{O_2,\text{mem}}}{C_{O_2,\text{mem},0}} \right] \quad (20)$$

$$\eta_{\text{con,c}} = \frac{R \cdot T}{z \cdot F} \cdot \ln \left[\frac{C_{H_2,\text{mem}}}{C_{H_2,\text{mem},0}} \right] \quad (21)$$

where $C_{O_2,\text{mem}}$ and $C_{H_2,\text{mem}}$ are the oxygen and hydrogen concentration at the membrane-electrode interface, respectively.

3.2. Dynamic modeling

In recent years, some authors have found a way to assimilate the electrolyzer like an electronic circuit as is showed in Figure 6, intending to study the present dynamics in the current-voltage curve. This circuit is composed of the following components [31]:

- Two resistance-capacitor branches to model the dynamics both at the anode and cathode (activation over-potential).
- One resistance to model the membrane (ohmic over-potential).

- A DC voltage source (reversible potential).

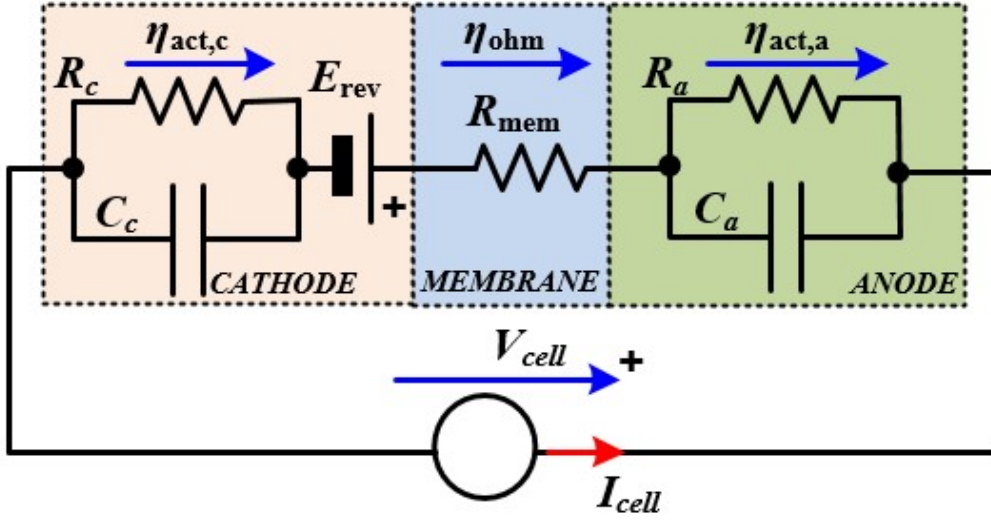


Figure 6: Equivalent circuit for a PEM electrolyzer.

From Figure 6, the stack voltage of the electrolyzer is expressed as follows:

$$V_{\text{cell}} = E_{\text{rev}} + \eta_{\text{act,a}} + \eta_{\text{act,c}} + \eta_{\text{ohm}} \quad (22)$$

Furthermore, the dynamic equations for $\eta_{\text{act,a}}$ and $\eta_{\text{act,c}}$ are:

$$\frac{d\eta_{\text{act,a}}}{dt} = \frac{1}{C_a} \cdot I_{\text{cell}} - \frac{1}{\tau_a} \cdot \eta_{\text{act,a}} \quad (23)$$

$$\frac{d\eta_{\text{act,c}}}{dt} = \frac{1}{C_c} \cdot I_{\text{cell}} - \frac{1}{\tau_c} \cdot \eta_{\text{act,c}} \quad (24)$$

where C_a and C_c are the capacitors for anode and cathode, R_a and R_c are the resistances for anode and cathode. The time constants τ_a and τ_c governing the dynamics are variables according to the operating conditions at the input of the electrolyzer. The equivalent resistances R_a and R_c are determined based on the activation voltage and input current of the electrolyzer:

$$\tau_a = C_a \cdot R_a = C_a \cdot \left(\frac{\eta_{\text{act,a}}}{I_{\text{cell}}} \right), \quad (25)$$

$$\tau_c = C_c \cdot R_c = C_c \cdot \left(\frac{\eta_{\text{act,c}}}{I_{\text{cell}}} \right) \quad (26)$$

In [31], the authors have demonstrated that the dynamics in the PEM electrolyzer are slower compared to a PEM fuel cell [119]. Indeed, the equivalent capacitor is equal to 37 F compared to 3 F obtained in PEM fuel cell.

Finally, the dynamics of the PEM electrolyzer are mainly governed by the anode reaction since its dynamic is slower compared to the cathode reaction [31]. In the same way, it is possible to model the ohmic over-potential like an electronic circuit, see Figure 6, using Ohm's law.

$$\eta_{\text{ohm}} = R_{\text{mem}} \cdot I_{\text{cell}} \quad (27)$$

where R_{mem} represents the membrane resistance.

Based on the work reported in [31], a comparison between a static and dynamic modeling (taking into consideration the electrical circuit in Figure 6) is provided in Figure 7. It can be noted that the dynamic model offers more accuracy and reliability in modeling the real behavior of a PEM electrolyzer supplied by dynamic current profiles. Indeed, the maximum error obtained with the dynamic model is around 4%; while the static model around 15%. The errors for the static model are particularly noticeable during the transients.

Finally, the parameters of the electrical circuit can be determined by using static and dynamic model identification as reported in [31]. However, the determined parameters are valid for a specific current range since the dynamics of the electrolyzer may change according to the operating conditions. For this reason, the development of models based on adaptive parameters is a challenging issue to make the model more reliable and precise.

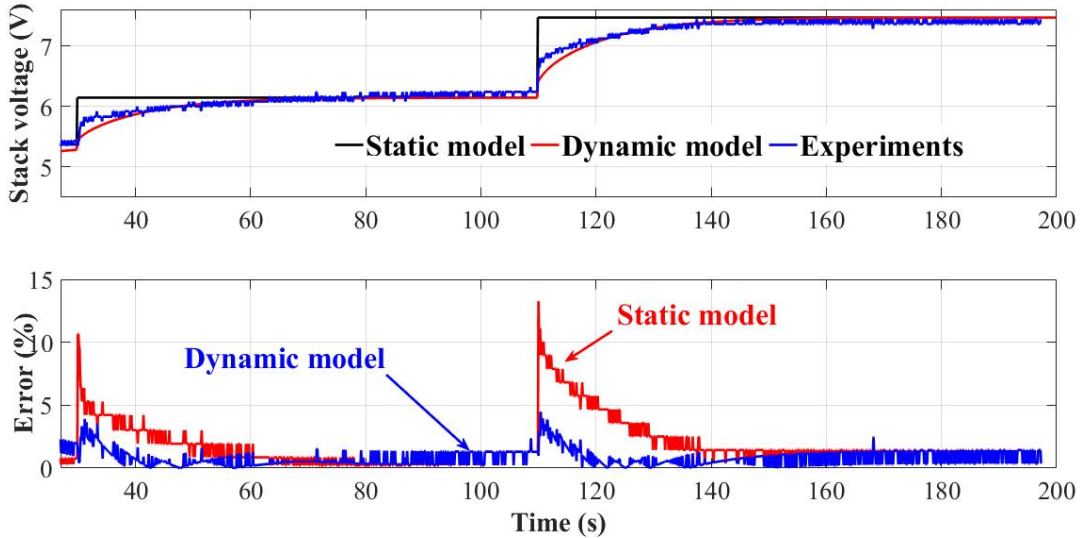


Figure 7: Comparison between static and dynamic modeling.

4. Analysis of the efficiency and specific energy consumption

The efficiency in an electrolyzer indicates the performance of the device if it has adequate energy and voltage consumption to the hydrogen production of the device. Few authors take into considerations this study for PEM electrolyzer, see Table 3 and Figure 8. The main efficiencies are the Faraday (η_f), voltage (η_V), and electrolyzer (η_{ele}).

Table 3: Works about the different efficiencies in the PEM electrolyzer.

| Electrolyzer | η_f | η_V | η_{ele} |
|--------------|---|----------------------|---|
| PEM | [18, 21, 27, 30, 36], [81–83, 108, 117, 120] | [30, 36, 81–83, 108] | [18, 31, 36, 81–83, 90, 98, 102] [105, 106, 109–111, 117, 120] |

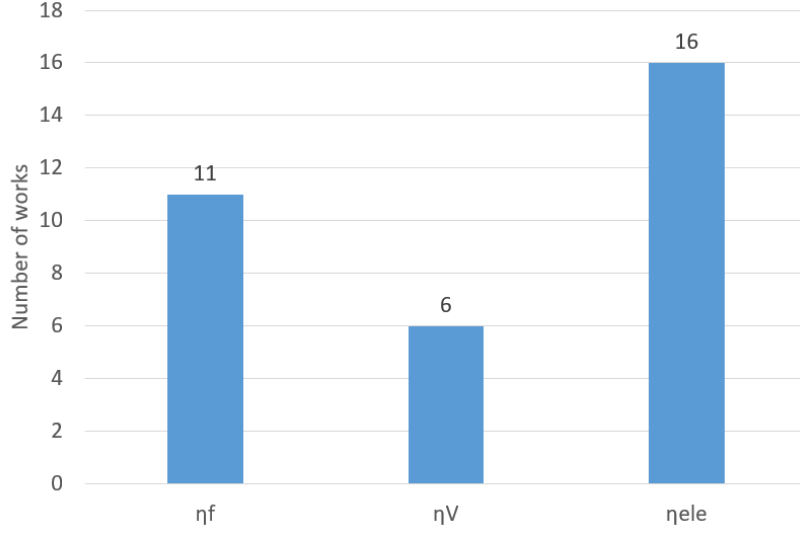


Figure 8: Number of works about efficiency for the PEM electrolyzer.

The three efficiency are linked by the following expression:

$$\eta_{ele} = \eta_f \cdot \eta_V \quad (28)$$

Among the three efficiency, the Faraday's efficiency is a key parameter since it is related to the losses due to the gas diffusion [121–124]. This parameter which is linked with the operating conditions (i.e. current, temperature, pressure) has a great influence on the energy efficiency η_{ele} and the gas flow rates (i.e. oxygen and hydrogen) as well [21, 113]. Besides, the oxygen and hydrogen flow rates are given by the following equations:

$$f_{O_2} = \frac{N \cdot I_{cell}}{4F} \cdot \eta_f \quad (29)$$

$$f_{H_2} = \frac{N \cdot I_{cell}}{2F} \cdot \eta_f \quad (30)$$

The Faraday's efficiency is investigated in the next subsection to highlight its role in the electrolysis process.

4.1. Faraday's efficiency

The Faraday's efficiency or current efficiency is relevant to model the production of hydrogen and oxygen in the electrolyzer. Usually is expressed as the ratio of the ideal electric charge Q_{id} over the real electric charge Q_{re} required for the production of a given amount of hydrogen or as the ratio of the hydrogen calculated over the real hydrogen produced [18, 34, 37, 81]. A Faraday's efficiency lower than 1 is caused by current losses and by the hydrogen that is lost in the membrane [18, 35]. The Faraday's efficiency decreases significantly at low current densities [125].

$$\eta_f = \frac{Q_{id}}{Q_{re}} \quad (31)$$

First of all, based on second Faraday's law of electrolysis (32) and on the general gas equation (33), the expression of the theoretical hydrogen quantity can be determined (34):

$$Q_{rev} = I_{cell} \cdot t = n \cdot F \cdot z \quad (32)$$

$$P \cdot V_{H_2} = n \cdot R \cdot T \quad (33)$$

$$V_{H_2}(\text{theoretical}) = \frac{R \cdot I_{cell} \cdot t \cdot T}{F \cdot P \cdot z} \quad (34)$$

$$Q_{rev} = \frac{P \cdot V_{H_2} \cdot F \cdot z}{R \cdot T} \quad (35)$$

where Q_{rev} is the total electric charge passed through the gas [C]; t is the total time the constant PEM electrolyzer current was applied [s], V_{H_2} is the gas volume [m^3].

Over the last decades, a few works have been reported in the literature regarding the investigation of Faraday's efficiency [34, 37, 53, 80, 81, 108, 118, 126]. The major part of the reported works is focused on the alkaline electrolyzer. In the literature, two empirical models have been developed to express the Faraday's efficiency according to the current for alkaline electrolyzers. The first model has been proposed by Hug [53] in 1993; while the second one has been developed by Ulleberg [118]. The first model [53] based on five-parameters provides the Faraday's efficiency at any temperature according to the current supplying the electrolyzer:

$$\eta_f = B_1 + B_2 \cdot \exp \left[\frac{B_3 + B_4 \cdot T + B_5 \cdot T^2}{I_{cell}} \right] \quad (36)$$

This semi-empirical model can give a good agreement with the experimental data at any temperature. Since the model is based on five parameters, they can be determined by performing tests at different temperatures

and using a least-square regression algorithm. However, the model does not take into account the effect of other variables, such as the pressure of the gas.

In comparison, Ulleberg [118] has developed an empirical model to estimate the Faraday's efficiency according to the temperature and current. It is based on four parameters described by:

$$\eta_f = \left(\frac{I_{\text{cell}}^2}{f_{11} + f_{12} \cdot T + I_{\text{cell}}^2} \right) \cdot (f_{21} + f_{22} \cdot T) \quad (37)$$

Compared to Hug's model, Ulleberg's model includes fewer parameters, only four against five. The four parameters can be determined in the same way. However, the effect of pressure is neglected in the model; while the pressure has an impact on Faraday's efficiency.

The equation (37) is reported in several works focused on electrolyzer modeling [40, 126–128]. However, this semi-empirical equation is only valid for the alkaline electrolyzer and cannot be applied to PEM electrolyzer due to the different materials used for their manufacturing. In [108], Tijani and Abdol Rahim have investigated the influence of operating temperature and membrane thickness on the Faraday's efficiency for a PEM electrolyzer. However, the authors have not proposed a model to express the Faraday's efficiency.

4.2. Voltage efficiency

The voltage efficiency is the efficiency regarding the voltage used for the electrolyzer. Generally, the Faraday's efficiency is higher than the voltage efficiency, since it only takes into consideration the losses due to the gas diffusion [81, 83]. By comparison, voltage efficiency takes into account additional losses such as membrane losses and heat losses both in the anode and cathode. Voltage efficiency is defined as the ratio of the thermo-neutral potential over the cell voltage [34, 37, 81].

$$\eta_V = \frac{V_{\text{th}}}{V_{\text{cell}}} \quad (38)$$

4.3. Electrolyzer efficiency and specific energy consumption

Finally, the system efficiency is obtained by the ratio between the energy contained in the hydrogen produced and the energy needed to electrolyze the water consumed during the process [18]. Thus, the electrolyzer efficiency can be obtained by the equation (28) or by the ratio between the Higher Heating Value of hydrogen HHV_{H_2} , which has a value of $3.54 \text{ kWh}/\text{Nm}^3$, and the energy consumption C_E [18, 35].

$$\eta_{\text{ele}} = \frac{\text{HHV}_{H_2}}{C_E} \cdot 100 \quad (39)$$

where C_E relates the energy consumed to the hydrogen produced and can be calculated, for a given time interval Δt .

$$C_E = \frac{\int_0^{\Delta t} N \cdot I_{\text{cell}} \cdot V_{\text{cell}} \cdot dt}{\int_0^{\Delta t} f_{H_2} \cdot dt} \quad (40)$$

4.4. Discussion

First of all, Figure 9 allows summarizing the electrical domain modeling (semi-empirical and empirical) and its link with Faraday's efficiency, voltage efficiency, energy efficiency, and specific energy consumption. It can be noted that the voltage efficiency is linked with the electrical domain modeling (i.e. V_{cell}) but the Faraday's efficiency remains a key parameter for hydrogen production and the specific energy consumption, providing valuable information about the performance of the electrolyzer. As highlighted in this section, the investigation of the Faraday's efficiency has received less attention compared to the electrical domain modeling; whereas it has a great influence on the performance of the electrolyzer. Indeed, Faraday's efficiency related to the gas diffusion losses strongly depends on the operating conditions (i.e. pressure, temperature) and also the features of the electrolyzer (i.e. membrane thickness). Currently, Faraday's efficiency is based on two main empirical equations for alkaline electrolyzers developed in the 1990s. Since that period, no additional work has been reported in the literature on Faraday's efficiency modeling, especially for PEM electrolyzers. For this reason, since the membrane thickness of PEM electrolyzers is smaller compared to alkaline electrolyzers, further investigations are required to understand better the effects of operating conditions and thickness of the membrane on Faraday's efficiency. Besides, the dynamics of PEM electrolyzers are very important issues and have to be taken into consideration in modeling accurately the behavior of electrolyzers when coupling with RES. Furthermore, since the behavior of the electrolyzer is linked with the operating conditions, further analysis of the different behaviors are requested to develop accurate models with adaptive parameters.

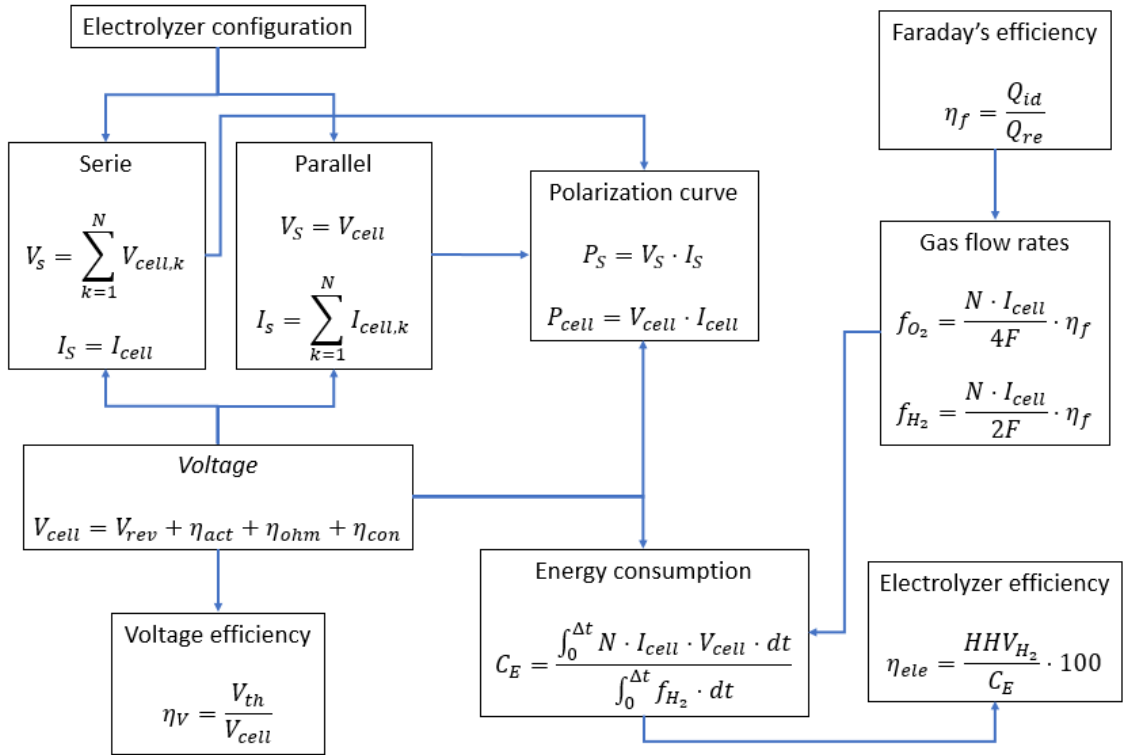


Figure 9: Diagram of connection between the models to give the electrolyzer efficiency.

5. Conclusion

The PEM electrolyzers, independently for industrial, household, etc. needs, can produce hydrogen highly pure. Besides, they can be coupled with RES, carried out a 100% renewable system due to their fast response time. It is one of the most important requirements for electrolyzer when coupling with dynamic sources.

Over the last decade, there has been an increase in works focused on electrical domain modeling. Generally, it is based on semi-empirical and empirical equations. However, the investigation on the dynamics and the Faraday's efficiency have received less attention while they are important issues to take into consideration when modeling the electrolyzer. Indeed, on one hand, the study of the dynamics allows developing models more accurate and reliable compared to static models. On the other hand, since the dynamics are strongly linked with the operating conditions, the development of accurate models based on adaptive parameters is required.

On the other side, further investigations are required regarding the effects of operating conditions on Faraday's efficiency. Hence, new empirical models could be developed to estimate the performance of the electrolyzer according to the operating conditions.

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