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Voltage modeling of a PEM electrolyzer based on the input current for the design and construction of an electronic emulator

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RECONOCIMIENTO

Por medio de la presente, hago constar que el trabajo de tesis de Ángel Mauricio Hernández Gómez titulado "Voltage modeling of a PEM electrolyzer based on the input current for the design and construction of an electronic emulator", fue realizado en la unidad de Energía Renovable, sistemas híbridos de energía, sistemas híbridos del Centro de Investigación Científica de Yucatán, A.C. bajo la dirección del Dr. Víctor Manuel Ramírez Rivera y Dr. Damien Guilbert (GREEN, Universidad de Lorraine, Nancy, Francia), perteneciente al Programa de Posgrado en Ciencias en Energía Renovable de este Centro.

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"All great things are simple, and many can be expressed in single words: freedom, justice, honor, duty, mercy, and hope".

Winston Churchill

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RESUMEN

El electrolizador de membrana de intercambio de protones (PEM, por sus siglas en inglés) es un dispositivo considerado como una alternativa viable para la generación de hidrógeno basada en fuentes de energía renovable (RES, por sus siglas en inglés). Su modelado es fundamental para estudiar su interacción con las RES y la electrónica de potencia. En la literatura actual, los modelos para el dominio eléctrico se basan principalmente en ecuaciones empíricas y semi-empíricas. Sin embargo, las operaciones dinámicas generalmente no son tomadas en cuenta. Por este motivo, esta tesis se ha centrado en el modelado estático-dinámico para el voltaje de un electrolizador PEM. Así, se desarrolla un modelo de alta precisión para el desarrollo de emuladores. En esta tesis, se presenta una breve introducción del electrolizador PEM. El propósito principal del Capítulo 1 es resumir y analizar los modelos reportados para describir el dominio eléctrico. En el capítulo 3 se propone y valida experimentalmente un modelo eléctrico estático-dinámico para la pila y cada celda en un electrolizador PEM. Por lo tanto, es posible replicar con precisión el comportamiento dinámico del electrolizador PEM sujeto a cambios rápidos de corriente. En el capítulo 4 se presenta un estudio del fenómeno de voltaje de autodescarga en un electrolizador PEM. Aunque el fenómeno de autodescarga ha sido ampliamente investigado para dispositivos de almacenamiento de energía como baterías y supercapacitores, no se han reportado trabajos previos en la literatura sobre este fenómeno para electrolizadores. Por esta razón, el capítulo 4 se centra principalmente en investigar el voltaje de auto descarga que se produce en un electrolizador PEM. Se ha desarrollado un modelo con base en diferentes pruebas realizadas para el voltaje de autodescarga. Así, teniendo en cuenta esta caída de voltaje en el modelado, se obtienen simulaciones con un mayor grado de fiabilidad a la hora de predecir el comportamiento de los electrolizadores PEM.

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 modelingis 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. For this reason, this thesis has been focused on the static-dynamic modeling for the voltage of a PEM electrolyzer. Thus, a high accuracy model for the development of PEM electrolyzer emulators is developed. In this thesis, a brief introduction of the PEM electrolyzer is presented. The main purpose of Chapter 1 summarizes and analyzes the reported models to describe the electrical domain. Furthermore, dynamic operation issues are highlighted and recent works about modeling the dynamics are introduced. In Chapter 3 is proposed and experimentally validated a static-dynamic electrical model for the stack and each cell ina PEM electrolyzer. So, it is possible to replicate accurately the dynamic behavior of the PEM electrolyzer subject to fast current change. A study of the self-discharge voltage phenomenon in a PEM electrolyzer is presented in Chapter 4. Although the self-discharge phenomenon has widely been investigated for energy storage devices such as batteries and supercapacitors, no previous works have been reported in the literature about this phenomenon for electrolyzers. For this reason, Chapter 4 is mainly focused on investigating the self-discharge voltage that occurs in a PEM electrolyzer. One model has been developed based on different tests carried out for the self-discharge voltage. Thus, by taking into account this voltage drops in the modeling, simulations with a higher degree of reliability are obtained when predicting the behavior of PEM electrolyzers.

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, biomassenergy, wind energy, earth energy, sea energy, biological, and bacterial energy [3]. It is expected thatby 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 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. In this thesis, PEM electrolyzers were the only object of study.

PEM electrolyzer

It can be viewed as an incremental development of alkaline electrolyzers and it is considered a promising methodology for producing hydrogen thanks to its simplicity, high energy efficiency, compact system design, and specific production capacity [19, 20]. 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. Subsequently, the electrons and protons recombine at the cathode to produce hydrogen [21], see Figure 1.



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

CHAPTER 1

BACKGROUND

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 their efficient and reliable operation [21–24]. 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 [25].

In recent years, several reviews about modeling of the electrolyzers have been reported. In [26], 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 [27], a review of the areas of electrocatalysis, essential components, and modeling strategies for PEM electrolyzers has been introduced. In [19], the authors have presented a work focused on modeling SO electrolyzers and remaining key issues. In [21], a state-of-theart of the mass transport model for PEM electrolyzers based on analytical, semi-empirical and mechanistic methods has been presented. The work [28] has presented a review of the models of the low temperatures electrolysis system for alkaline and PEM electrolyzers. In [29], a review of Multiphysics models provided experimental data needed to calculate thermosphysical properties and the correlations for the simulations of alkaline electrolyzers has been carried out. In [30], a review of different techniques to produce hydrogen in a focus on alkaline electrolysis has been reported. Finally, the work [31] has presented a review mainly focused on the recent development of PEM electrolyzer including the evolution reaction electrocatalysts of the hydrogen and the oxygen, 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 [21, 28], 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 [32] 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 charge movement 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 experimentally developed and validated. The results demonstrate the effectiveness of the model in accurately reproducing the dynamic behavior of PEM electrolyzers compared to classical static models.

It is also worth noting 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 chapter 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 parameters (Faraday, voltage, energy), and the specific energy consumption which are linked with the performance of PEM electrolyzers.

In recent years, the modeling of voltage for PEM electrolyzers has gained a growing interest from industrials and researchers to optimize, design and implement PEM electrolyzer, see Figure 1.1.



Figure 1. 1. Evolution of the number of works for PEM electrolyzer voltage through the years.

1.1 Static modeling

A polarization curve is an important tool not only for the study of PEM electrolyzers but, for allkinds of electrolyzers, describes the relationship between the cell voltage V_{cell} and the cell current I_{cell} , for alkaline electrolyzer see the works [33–52], and for SO electrolyzer, [53–78]. 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 [34, 79]. The polarization curve in one cell can be expressed like the product of V_{cell} and I_{cell} .

$$P_{cell} = V_{cell} \cdot I_{cell} \tag{1.1}$$

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 .

$$P_S = V_S \cdot I_S \tag{1.2}$$

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 series, and the stack current is the sum of currents flowing through the number of cells N branchesconnected in parallel [18], see Table 1.1.

Parameter	Parallel	Serie
V _s	V _{cell}	$\sum_{j=1}^{N} V_{cell,j}$
I _s	$\sum_{j=1}^{N} V_{cell,j}$	I _{cell}

Table 1.1. Stack parameters V_S and I_S depending on electrolyzer configuration.

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:

$$V_{cell} = V_{rev} + \eta_{act} + \eta_{ohm} + \eta_{con}$$
(1.3)

where Vrev is the reversible potential, nact, nohm, and ncon are the activation, ohmic and concentration over-potentials. Table 1.2 shows the number of references about the reversible voltage and over-potentials, and Figure 1.2 illustrates the number of works about these over-potentials for PEM electrolyzers.

	$V_{\text{cell}} =$	$V_{\text{cell}} =$
Electrical domain	$V_{\rm rev} + \eta_{\rm act} + \eta_{\rm ohm}$	V rev + η_{act} + η_{ohm} + η_{con}
PEM	[21, 22, 24, 28, 31, 32], [35, 80–105]	[18, 20, 23, 27, 79, 106–115]

Table 1.2. Works about the reversible potential and the over-potentials.



Figure 1. 2. Number of works about the different over-potentials for the PEM electrolyzer.

1.1.1 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's in 1998 [116] 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:

$$V_{cell} = V_{rev} + r \cdot I_{cell} + s \cdot \log[k \cdot I_{cell} + 1]$$
(1.4)

Equation (1.4) 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 Gibb's energy, pressure, and temperature (see Subsection 1.1.2). In comparison, the second term is linked with the ohmic over- potential nohm by its parameter r. Finally, the last term is related to the activation over-potential nact based on two parameters s and k.

As reported in [33], 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 (1.4). Among the parameters, only the parameter 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 [33]:

$$V_{\text{cell}} = V_{\text{rev}} + \left(\frac{r_1 + r_2 \cdot T}{A}\right) \cdot I_{\text{cell}} + s \cdot \log\left[\left(\frac{k_1 \cdot T^2 + k_2 \cdot T + k_3}{A \cdot T^2}\right) \cdot I_{\text{cell}} + 1\right]$$
(1.5)

In spite of Ulleberg's model is accurate to describe the current-voltage curve according to 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 [39]:

$$V_{\text{cell}} = V_{\text{rev}} + ((r_1 + d_1) + r_2 \cdot T + d_2 \cdot P) \cdot I_{\text{cell}} + s$$

$$\cdot \log \left[\left(k_1 + \frac{k_2}{T} + \frac{k_3}{T^2} \right) \cdot I_{\text{cell}} + 1 \right]$$
(1.6)

To take into consideration the gas pressure P, additional parameters d1 and d2 can be found in equation (2.6). 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 1.1.

1.1.2 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 (1.3) (i.e., the reversible potential and its overpotentials) from an empirical perspective.

• Reversible potential. The reversible potential or open circuit voltage is the minimum required voltage that allows the electrolysis [18, 21]. The reversible potential at the cell has a relation with the Gibbs free energy:

$$\Delta G = \Delta H - T \cdot \Delta S \tag{1.7}$$

And the reversible voltage as:

$$V_{rev} = \frac{\Delta G}{n \cdot F} \tag{1.8}$$

where, at standard condition, the temperature is T = 298.15 K, the pressure in the electrolyzer is 1 atm, $\Delta S = 0.1631$ kJ mol-1K-1 is the entropy chance, $\Delta H = 285.84$ kJ mol-1 is the enthalpy change, n = 2 is the number of the electron moles transferred per hydrogen mole, and F = 96485 C mol-1 is the Faraday's constant. Based on these conditions and equations (1.7) and (1.8), many authors work with Vrev = 1.23 V [21].

Another important concept related with the reversible potential and voltage efficiency is the thermo-neutral potential Vth, which is obtained employing enthalpy ΔH instead of ΔG for the potential calculation [31].

$$V_{th} = \frac{\Delta H}{n \cdot F} = \frac{\Delta G + T \cdot \Delta S}{n \cdot F}$$
(1.9)

Where in standard condition Vth=1.48 V.

Activation over-potential. The activation over-potential represents the potential to initiate the proton transference 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, 21]. The activation energy required at both anode and cathode due to the activation overpotential can be modeled by relating the Butler-Volmer expression, as many authors have done:

$$\eta_{act} = \eta_{act,a} + \eta_{act,b} \tag{1.10}$$

Where

$$\eta_{act,a} = \frac{R \cdot T}{\alpha_a \cdot z \cdot F} \cdot \log\left[\frac{i_a}{i_{0,a}}\right]$$
(1.11)

$$\eta_{act,c} = \frac{R \cdot T}{\alpha_c \cdot z \cdot F} \cdot \log\left[\frac{i_c}{i_{0,c}}\right]$$
(1.12)

where R = 8.314 J K-1 mol-1 is the universal gas constant, z is the stoichiometric coefficient, which 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. αa and αc are the charge transference coefficients. The values of αa and αc are 0.5 on the symmetry reactions. However, in [102] has been demonstrated that αa and αc may vary, for example, in [111], the values for $\alpha a = 2$ and $\alpha c = 0.5$, are considered.

• 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, 21]. The membrane over- potential can be expressed as a function of the membrane thickness φ (cm), the conductivity of the membrane σ mem and i0.

$$\eta_{ohm,mem} = R_{ion} \cdot i_0 \tag{1.13}$$

where Rion = φ/σ mem is the ionic resistance. The local ionic conductivity with water content and temperature function can be written as:

$$\sigma_{mem} = (0.005139\lambda - 0.00326) \cdot exp\left[1268 \cdot \left(\frac{1}{303} - \frac{1}{T}\right)\right]$$
(1.14)

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

$$\lambda = 0.08533 \cdot T - 6.77632 \tag{1.15}$$

The electronic over-potential can be expressed as:

$$\eta_{ohm,ele} = R_{ele} \cdot i_0 \tag{1.16}$$

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

$$R_{ele} = \frac{\rho \cdot l}{A_c} \tag{1.17}$$

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

$$\eta_{ohm} = \eta_{ohm,mem} + \eta_{ohm,ele} \tag{1.18}$$

• 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, 111]. It has been reported that Vcon is much lower than Vohm and Vact, for this reason, many authors take Vcon = 0 in their studies. However, the concentration over-potential is widely estimated with the Nernst's equation given by:

$$\eta_{con} = \eta_{con,a} + \eta_{con,c} \tag{1.19}$$

Where

$$\eta_{con,a} = \left(\frac{R \cdot T}{z \cdot F}\right) \cdot In\left[\frac{C_{02,mem}}{C_{02,mem,0}}\right]$$
(1.20)

$$\eta_{con,c} = \left(\frac{R \cdot T}{z \cdot F}\right) \cdot In\left[\frac{C_{H2,mem}}{C_{H2,mem,0}}\right]$$
(1.21)

where CO2,mem and CH2,mem are the oxygen and hydrogen concentration at the membraneelectrode interface, respectively.

1.1.3 Dynamic modeling

In recent years, some authors have found a way to assimilate the electrolyzer like an electronic circuit, as shown in Figure 1.3, intending to study the present dynamics in the current-voltage curve. This circuit is composed of the following components [32]:

- 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 1. 3. Equivalent circuit for a PEM electrolyzer.

From Figure 1.3, the stack voltage of the electrolyzer is expressed as follows:

$$V_{cell} = E_{rev} + \eta_{act,c} + \eta_{act,a} + \eta_{ohm}$$
(1.22)

Furthermore, the dynamic equations for η act,c and η act,a are:

$$\frac{d\eta_{act,c}}{dt} = \frac{I_{cell}}{C_c} + \frac{\eta_{act,c}}{\tau_c}$$
(1.23)

$$\frac{d\eta_{act,a}}{dt} = \frac{I_{cell}}{C_a} + \frac{\eta_{act,a}}{\tau_a}$$
(1.24)

where *C*c and *C*a are the capacitors for anode and cathode, *R*c and *R*a are the resistances for anode and cathode. The time constants τc and τa governing the dynamics are variables according to the operating conditions at the input of the electrolyzer. The equivalent resistances *R*c and *R*a are determined based on the activation voltage and input current of the electrolyzer:

$$\tau_c = C_c \cdot R_c = C_c \cdot \left(\frac{\eta_{act,c}}{I_{cell}}\right)$$
(1.25)

$$\tau_a = C_a \cdot R_a = C_a \cdot \left(\frac{\eta_{act,a}}{I_{cell}}\right) \tag{1.26}$$

In [32], the authors have demonstrated that the dynamics in the PEM electrolyzer are slower compared to a PEM fuel cell [117]. 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 [32]. In the same way, it is possible to model the ohmic over-potential like an electronic circuit, see Figure 1.3, using Ohm's law.

$$\eta_{ohm} = R_{mem} \cdot I_{cell} \tag{1.27}$$

where Rmem represents the membrane resistance.

Based on the work reported in [32], a comparison between a static and dynamic modeling (taking into consideration the electrical circuit in Figure 1.3) is provided in Figure 1.4. It can be noted that the dynamic model offers more accuracy and reliability in describing 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 [32]. 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 1. 4. Comparison between static and dynamic modeling.

1.2 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 consideration this study for PEM electrolyzer, see Table 1.3 and Figure 1.5. The main efficiencies are the Faraday (η_f), voltage (η_V), and electrolyzer (η_{ele}).

Table 1.3. References addressing the different efficiencies in the PEM electrolyzer.

Electrolyzer	η_f	η_V	η_{ele}
	[18, 24, 28, 31, 35],	[31, 35],	[18, 32, 35, 80–82, 89]
PEM	[80–82, 106, 115, 118]	[80–82, 106]	[97, 101, 104, 105]
			[107–109, 115, 118]



Figure 1. 5. Number of references addressing efficiency for the PEM electrolyzer.

The efficiency parameters are linked by the following expression:

$$\eta_{ele} = \eta_f \cdot \eta_V \tag{1.28}$$

Among the three efficiency parameters, the Faraday's efficiency is a key parameter since it is related to the losses due to the gas diffusion [119–122]. This parameter which is linked to the operating conditions (i.e. current, temperature, pressure) has a great influence on the energy efficiency η_{ele} and also on the gas flow rates (i.e. oxygen and hydrogen) [24, 111]. Besides, the oxygen and hydrogen flow rates are given by the following equations:

$$f_{O2} = \frac{N \cdot I_{cell}}{4F} \cdot \eta_f \tag{1.29}$$

$$f_{H2} = \frac{N \cdot I_{cell}}{2F} \cdot \eta_f \tag{1.30}$$

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

1.2.1 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, 33, 36, 80]. A Faraday's efficiency lower than 1 is caused by current losses and by the hydrogen that is lost in the membrane [18, 34]. The Faraday's efficiency decreases significantly at low current densities [123].

$$\eta_f = \frac{Q_{id}}{Q_{re}} \tag{1.31}$$

First of all, based on second Faraday's law of electrolysis (1.32) and on the general gas equation (1.33), the expression of the theoretical hydrogen quantity can be determined (1.34) as:

$$Q_{rev} = I_{cell} \cdot T = n \cdot F \cdot z \tag{1.32}$$

$$P \cdot V_{H2} = n \cdot R \cdot T \tag{1.33}$$

$$V_{H2}(theoretical) = \frac{R \cdot I_{cell} \cdot t \cdot T}{F \cdot P \cdot z}$$
(1.34)

$$Q_{rev} = \frac{P \cdot V_{H2} \cdot F \cdot z}{R \cdot T}$$
(1.35)

where Qrev is the total electric charge passed through the gas [C]; t is the total time the constant PEM electrolyzer current was applied [s], V_{H2} 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 [33, 36, 52, 79, 80, 106, 116, 124]. 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 was proposed by Hug [52] in 1993; while the second one was developed by Ulleberg [116]. The first model [52] based on five-parameters provides the Faraday's efficiency at any temperature according to the current supplying the electrolyzer:

$$\eta_f = B_1 + B_2 \cdot exp\left[\frac{B_3 + B_4 \cdot T + B_5 \cdot T^2}{I_{cell}}\right]$$
(1.36)

This semi-empirical model can give a good agreement with the experimental data at any temperature. The five model parameters 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 [116] developed an empirical model to estimate the Faraday's efficiency according to the temperature and current. This model, based on four parameters, is described by:

$$\eta_f = \left(\frac{I_{cell}^2}{f_{11} + f_{12} \cdot T + I_{cell}^2}\right)(f_{21} + f_{22} \cdot T)$$
(1.37)

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 (1.37) is reported in several works focused on electrolyzer modeling [39, 124–126]. 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 [106], 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.

1.2.2 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 [80, 82]. 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 [33, 36, 80].

$$\eta_V = \left(\frac{V_{th}}{V_{cell}}\right) \tag{1.38}$$

1.2.3 Electrolyzer efficiency and specific energy consumption

Finally, the system efficiency is obtained by the ratio between the energy contained in the produced hydrogen and the energy needed to electrolyze the water consumed during the process [18]. Thus, the electrolyzer efficiency can be obtained by the equation (1.28) or by the ratio between the Higher Heating Value of hydrogen HHV_{*H*2}, which has a value of 3.54 *kWh/Nm*³, and the energy consumption *C*E [18, 34].

$$\eta_{ele} = \left(\frac{HHV_{H2}}{C_E}\right) \cdot 100 \tag{1.39}$$

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

$$C_E = \frac{\int_0^{\Delta t} N \cdot I_{cell} \cdot V_{cell} \cdot dt}{\int_0^{\Delta t} f_{H2} \cdot dt}$$
(1.40)

Figure 1.6 allows summarizing the electrical domain modeling (empirical and semi-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 chapter, 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 on 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 com- pared to alkaline electrolyzers, further investigations are required to better understand 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 is required to develop accurate models with adaptive parameters.



Figure 1. 6. Diagram of connection between the models to give the electrolyzer efficiency.

OBJECTIVES

General objective

Model the voltage of a PEM electrolyzer based on the input current for the design and construction of an electronic emulator.

Particular objectives

- Develop a comprehensive review of the different models reported in the literature for PEMelectrolyzers.
- Characterize several variables that can influence the PEM electrolyzer voltage based on the experimental data and input current.
- Develop a model for PEM electrolyzer voltage based on the previous characterization and validated it through experimental tests.
- Simulate the mathematical model using the software, Matlab.
- Schematize an electronic emulator based on the developed model.

CHAPTER 2

METHODOLOGY

Read different models reported in the literature to look at which physical variables influence the behavior of PEM electrolyzers and also learn different techniques for the development of mathematical models for PEM electrolyzers.

Collect data under different conditions of a PEM electrolyzer to characterize different variables that can influence the stack and cell voltages and their efficiency.

To develop the mathematical model, the previous review and the previous characterization are taken into account. The proposed model is compared with the experimental data for having a low error for the validation of the mathematical model.

Once the mathematical model had been done, it is proceeded to do the mathematical analysis and the simulation using Matlab® by means of an algorithm and different functions that the software already has. Finally, a scheme of an electronic emulator based on the developed model is proposed.

CHAPTER 3

ADAPTIVE STATIC-DYNAMIC ELECTRICAL MODEL FOR PEM WATER ELECTROLYSIS

Dynamic models for PEM electrolyzers have already been reported in the literature [127]. In [24], the authors have developed a model including four subsystems: anode, cathode, membrane, and an auxiliary component that models the relation between voltage and electric current. The work [23] has presented the development of a complete model based on modules describing the behaviors of the anode, cathode, membrane, and cell voltage. In [111], an electrochemical model of the electrolyzer stack to calculate the theoretical open-circuit using thermodynamic analysis has been developed. In [112], the authors have reported a model based on thermodynamics and electrochemical equations. This model has fitted a steady-state electric model with a dynamic thermal model. Following this approach, a recent review for alternative dynamic models has been presented in [28], this work covers systems for alkaline electrolyzer too. However, dynamic models for the electrolyzer voltage are very scarce; in [18] a static-dynamic model for voltage based on the thermodynamic, activation, double-layer, and ohmic effects has been developed, unfortunately, this model only applies for alkaline electrolyzer. The work [32] has introduced a dynamic model for the activation overpotential assimilating the PEM electrolyzer like an electronic circuit so, the authors have developed a static-dynamic model to describe the stack voltage. The authors have shown that dynamic behavior is strongly linked to the input current. However, the parameters used in the paper [32] have been adapted just for one specific electrical input current range. As a result, the developed model with constant parameters is less reliable for another input current. For this reason, based on this previous work [32], this chapter aims at developing a static-dynamic model for PEM electrolyzer voltage (stack and each cell) and proposing an algorithm to compute its parameters based on different electrical current inputs. Hence, the accuracy of the model in replicating the dynamic behavior of the electrolyzer can be improved.
3.1 Static-dynamic electrical model for PEM electrolyzer stack

To develop the adaptive model, experimental tests have been carried out on a commercial-400 W PEM electrolyzer. The tests consist of increasing and decreasing the current with a step of 1 A. This methodology allows a better modeling of the PEM electrolyzer stack dynamics.

3.1.1 Experimental test setup

To investigate the dynamics of a commercial PEM electrolyzer, an experimental test setup has been realized as shown in Figure 3.1. The test setup is composed of the following devices and components: (1) a laptop with a virtual control panel to control the DC power supply, (2) a DC power supply, (3) a 4-channel oscilloscope, (4) a pure water tank, (5) a commercial-400W PEM electrolyzer, (6) a current probe to acquire the current at the input of the electrolyzer, and finally (7) a voltage probe to acquire the stack voltage of the electrolyzer. The specifications of the studied commercial PEM electrolyzer NMH2 1000 from HELIOCENTRIS® Company are provided in Table 2.1. It has to be noted that the PEM electrolyzer NMH2 1000 system is combined with power electronics based on a single-phase diode rectifier and a DC/DC step-down converter. To investigate the dynamic behavior of this PEM electrolyzer, only the stack is used and is connected to an external DC power supply as depicted in Figure 3.1. Besides, the PEM electrolyzer uses a solid polymer electrolyte based on fluoropolymer Nafion material from DuPont® company. The thickness of the membrane is very thin, resulting in lower ohmic losses. To meet the pressure requirements of the storage tanks based on metal hydride material, the outlet pressure of the PEM electrolyzer is set to 10.5 bar.



Figure 3. 1. Experimental test setup.

Table 3. 1. Specifications of the PEM electrolyzer.

Parameters	Value	Unit
Rated electrical power	400	W
Rated stack voltage	8	V
Stack current range	0-50	A
Operating temperature range	288.15-	K
	313.15	
Hydrogen outlet pressure	10.5	bar
Cells number	3	-
Active area section	50	cm^2
Hydrogen flow rate range at STP (Standard Temperature and Pressure, 20°C and 1 bar)	0-1	SLPM (StandardLiter Per Minute)

The next subsection presents the responses of the PEM electrolyzer according to the input current.

Dynamic issues (PEM electrolyzer stack)

Based on the experimental test setup presented in the previous section, two dynamic tests have been carried out: one of the tests considers a current rise (from 0 to 10 A); whereas the second considers a current fall (from 10 to 0 A). The aim is to show the different dynamic behaviors, which are strongly linked with the input energy supplying the electrolyzer. The results are shown in Figures 3.2 and 3.3. Since the expected dynamics are relatively slow, a high time scale (i.e. 5 s) has been tuned to highlight the transient and steady-state operation.

From Figures 3.2 and 3.3, it can be noticed that the PEM electrolyzer is able to respond very quickly as a result of dynamic operations (i.e., rise or fall current). Fast dynamic response is one of the most important features requested for electrolyzers when coupling with RES. Indeed, since RES are very dynamic sources strongly depending on weather conditions, PEM electrolyzers have to offer a high flexibility to respond to dynamic operations so that it can absorb the energy during transients. The initial and final stack voltage, respectively in Figures 3.2 and 3.3, represent the reversible voltage of the PEM electrolyzer (i.e., for a given temperature and gas pressure) that is around 4.2 V. When a step current occurs, a sudden rise in PEM electrolyzer stack voltage followed by a slow rise can be observed before reaching the steady-state operation. The sudden voltage stack rise is related to the ohmic over-potentials due to the membrane since only the protons can go through it; while the slow rise emphasizes the dynamics both at the anode and the cathode (related to the activation over-potentials). The dynamics of the PEM electrolyzer are mainly governed by the input current supplying the electrolyzer. In other words, the speed of the dynamics strongly depends on the current. According to its value, the duration of the slow rise in PEM stack voltage may be faster or slower before reaching a steady-state value. These dynamics issues are particularly noticeable in the obtained experimental results. In the first test (i.e., Figure 3.2), the final steady state-value (around 8 V) is reached roughly in 23 s; while for the second test (Figure 3.3), it takes 30 s so that the PEM stack voltage reaches its steady-state operation (around 4.2 V). It has to be noted in Figure 3.2 a low voltage overshoot (around 8.3 V, namely 3.75% of the rated stack voltage), and a slow dynamic before reaching the steady-state stack voltage (around 8 V). This voltage overshoot can be explained since the rated stack voltage is reached for an input current equal to 7 A. If a step current is applied from an initial current lower than 7 A to a final current higher than 7 *A*, dynamics can be observed including a voltage overshoot. The voltage overshoot strongly depends on the input current. The higher the input current, the higher the voltage overshoots. The maximum voltage overshoot observed in experiments is equal to 9 *V* (around 12.5% of the rated stack voltage). For these tests, a current probe with a sensitivity ($10 \ mV.A^{-1}$) and a voltage probe with a sensitivity ($1/20 \ V$) have been used. As a result, given that the channel 1 (*i*el) and 2 (*V*el) scale are equal respectively to 50 *mV* and 100 *mV*, the real measured current and voltage (taking into consideration the sensitivity of the two probes) are equal to 5 A.div⁻¹ and 2 V.div⁻¹.



Figure 3. 2. Response of the electrolyzer as a result of a rising electrical current from 0 to 10 A.



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

In summary, since the dynamics of the PEM electrolyzer may change according to the operating conditions, the parameters of the model cannot be considered constant. To develop accurate models and minimize the errors, it is crucial to take into account these dynamic issues in the modeling of the electrolyzer. Therefore, the parameters of the model must be assessed in real-time according to the operating conditions. In this work, only the change in input current has been considered to develop an adaptive static-dynamic electrical model. Other parameters such as the gas pressure and temperature can also be taken into consideration as operating conditions, however, this complicates the development of an adaptive model. Based on experiments, a current range of up to 8 *A* has been considered to develop an adaptive static-dynamic electrical model. Indeed, over 8 *A*, no dynamics have been reported despite the rated current is equal to 50 *A*. Some explanations regarding this issue, from the author's perspective, are provided in Section 3.1.3.

In the next subsections, the dynamic model of the PEM electrolyzer is provided and the methodology to model the dynamics of the electrolyzer based on constant step current change as well. Besides, the algorithm to estimate the different parameters of the model is given. Finally, the obtained results with the developed model are compared with the experimental data to validate the

effectiveness of the model in replicating accurately the real static-dynamic behavior of the electrolyzer.

3.1.2 Mathematical modeling

Equation (1.3) represents a static model of the electrolyzer voltage. This static model has been used by many authors as reported in the literature [79, 80]. However, in [32], the authors have assimilated the electrolyzer like an electronic circuit to develop a static-dynamic model, see Figure 1.3. The equivalent circuit model is described in Subsection 1.1.3.

To have the complete solution of the electrolyzer voltage model, equation (1.22), it is needed to solve the equations (1.23) and (1.24). So, the solution is calculated for equation (1.23) and the solution of the equation (1.24) is analogous. Then, applying the Laplace's transform to the equation (1.23), it yields:

$$z \cdot L[\eta_{act,c}] - \eta_{act,c}(0) = \frac{\int_0^\infty exp[-zt] \cdot I_{cell} \cdot dt}{C_c} - \frac{L[\eta_{act,c}]}{\tau_c}$$
(3.1)

where $\eta \operatorname{act}, c(0)$ is the initial value of $\eta \operatorname{act}, c$. Clearing $L[\eta \operatorname{act}, c]$:

$$L[\eta_{act,c}] = \left(\frac{\tau_c}{z \cdot \tau_c + 1}\right) \cdot \left(\frac{\int_0^\infty exp[-zt] \cdot I_{cell} \cdot dt}{C_c} + \eta_{act,c}(0)\right)$$
(3.2)

Therefore, applying Laplace's inverse transform:

$$\eta_{\text{act,c}} = \left(\frac{\tau_c}{C_c}\right) \cdot L^{-1} \left[\frac{\int_0^\infty exp[-zt] \cdot I_{cell} \cdot dt}{z \cdot \tau_c + 1}\right] + \eta_{\text{act,c}}(0) \cdot exp\left[\frac{-t}{\tau_c}\right]$$
(3.3)

In this work, the current function *I*cell is determined by the step function:

$$I_{cell} = \begin{cases} A_1 & \text{si } t_1 < t_c \\ A_2 & \text{si } t_2 \ge t_c \end{cases}$$
(3.4)

where both A_1 and A_2 are constants in [A] and t_c is the time when the input A_1 changes to the input A_2 expressed in [s].

Thus, since equation (3.4) is a function of *I*cell and by applying the second Theorem of translation [128] to the equation (3.3), η act,c becomes:

$$\eta_{act,c} = \begin{cases} \left(\frac{\tau_c}{C_c}\right) \cdot f_1(t) + g_1(t) & \text{si } t_1 < t_c \\ \left(\frac{\tau_c}{C_c}\right) \cdot \left[(A_2 - A_1) \cdot \left(1 - exp\left[\frac{t_c - t}{\tau_c}\right]\right) + f_1(t)\right] + g_1(t) & \text{si } t_2 \ge t_c \end{cases}$$
(3.5)

and for η act,a:

$$\eta_{act,c} = \begin{cases} \left(\frac{\tau_a}{C_a}\right) \cdot f_2(t) + g_2(t) & \text{si } t_1 < t_c \\ \left(\frac{\tau_a}{C_a}\right) \cdot \left[(A_2 - A_1) \cdot \left(1 - exp\left[\frac{t_c - t}{\tau_a}\right]\right) + f_2(t)\right] + g_2(t) & \text{si } t_2 \ge t_c \end{cases}$$
(3.6)

Where

$$f_1(t) = A_1 \cdot \left(1 - exp\left[\frac{-t}{\tau_c}\right]\right), \quad f_2(t) = A_1 \cdot \left(1 - exp\left[\frac{-t}{\tau_a}\right]\right)$$
(3.7)

And

$$g_1(t) = \eta_{\text{act},c}(0) \cdot exp\left[\frac{-t}{\tau_c}\right], \qquad g_2(t) = \eta_{\text{act},a}(0) \cdot exp\left[\frac{-t}{\tau_a}\right]$$
(3.8)

So, the equivalent static-dynamic model for the electrolyzer voltage can be expressed as the equation:

$$V_{el} = E_{rev} + \eta_{act,c} + \eta_{act,a} + \eta_{ohm}$$
(3.9)

3.1.3 Parameter estimation

In this section, the parameters of equation (3.9) are estimated. These parameters are: *Erev*, *R*mem, η act,c(0), η act,a(0), *C*c, *C*a, *R*c, *R*a, τ c, and τ a. Using the Ohm's law, η act,c(0) and η act,a(0) are obtained as:

$$\eta_{\text{act,c}}(0) = R_c \cdot I_{cell}, \quad \eta_{\text{act,a}}(0) = R_a \cdot I_{cell} \tag{3.10}$$

The parameters *R*c and *R*a can be determined in terms of *C*c, *C*a, τ c, and τ a by the equations (1.25) and (1.26). To make easier the construction of an electrical circuit, the capacitors must be equal, so it is assumed that *C*c = *C*a. Indeed, this assumption is motivated by previous works reported in the literature regarding this important issue [129, 130].

To calculate the remaining five parameters, the behavior of the experimental data has been analyzed, both statically and dynamically. First of all, the static voltage-current curve is shown in Figure 3.4. From this figure, it can be noted that the PEM stack voltage increases and follows the increase in input current. However, from a current roughly equal to 7 A (i.e., a current density equal to 0.14 $A \cdot cm^{-2}$), the stack voltage remains constant near to 8 V. Even though this phenomenon has not yet been reported in the literature, some explanations can be provided from the author's point of view. Indeed, as mentioned in Section 1.1.2, the studied PEM electrolyzer system is composed of power electronics to meet the requirements (i.e., low DC voltage) to supply the electrolyzer from an AC source (i.e., power grid). For this reason, the power electronics part is based on a singlephase diode rectifier and a DC/DC step-down converter to supply the electrolyzer. On one hand, the use of these converters generates low and high-frequency current ripple. The low-frequency current ripple comes from the single-phase diode rectifier (i.e. around 100 Hz from an AC signal equal to 50 Hz); whereas the high-frequency current ripple comes from the DC-DC step-down converter (i.e. due to the high switching frequency of this type of converter; in our case, the frequency is equal to 20 kHz) [131]. On the other hand, many works have been reported regarding the effects of low and high-frequency current ripples on PEM fuel cell stack [131–134], and more recently, on alkaline electrolyzer from the energy efficiency point of view [34, 135]. In these previous works, it has been demonstrated that current ripple may impact the life span and performance of fuel cell and electrolyzer during their operation. For this reason, since the studied PEM electrolyzer has been supplied with high current ripple over a long time, some deteriorations have occurred, which can explain the obtained static curve in Figure 3.4.



Figure 3. 4. Static voltage-current curve.

The voltage dynamics have been analyzed by increasing the input current with a step of 1 A starting from 0 A up to 8 A and by decreasing it starting from 8 to 0 A (keeping the same current step). The obtained results are shown in Figures 3.5 and 3.6, respectively. On one hand, in Figure 3.5, it can be noted that the voltage dynamics are preponderant from 0 to 6 A; whereas the voltage dynamics are not significant from 6 to 8 A. On the other hand, in Figure 3.6, it can be observed a similar behavior, the voltage dynamics are not meaningful from 8 to 6 A; while the dynamics are more significant from 6 to 0 A. Hence, in both tests (increasing and decreasing the input current), the voltage dynamics are preponderant in a current range from 0 to 6 A, and are not particularly significant for a current range between 6 to 8 A. This observation supplements the results obtained with a static characterization (Figure 3.4).



Figure 3. 5. Behavior of the experimental data as a result of a rising electrical current.



Figure 3. 6. Behavior of the experimental data as a result of a falling electrical current.

After the analysis, a script has been developed by using MATLAB software to calculate the differential equations (1.23) and (1.24) to solve the equation (1.22). The script and the MATLAB command lsqcurvefit (based on the least-square regression algorithm) have been applied to adjust the parameters of the model to the data obtained experimentally for the different tests. The parameters adjustment has been performed three times to all different tests. In the first parameters adjustment of the parameters, the results have shown that the variations of *E*rev and *R*mem are not significant. For this reason, *E*rev and *R*mem have been considered with the constant value of 4.32 *V* and 0.329 Ω respectively, see Figures 3.7 and 3.8.



Figure 3. 7. Behavior and estimation of the parameter Erev.



Figure 3. 8. Behavior and estimation of the parameter Rmem.

In the second parameters adjustment, the estimated values found in the first adjusting have been used, Erev = 4.32 V and $Rmem = 0.329 \Omega$. The adjusting has shown the behavior of the parameters τc and τa as a Gaussian function, which is a result of the dynamics behavior of the voltages tests, Figures 3.9 and 3.10, and also emphasized a proportional relation between τc and τa . So, the parameter τc has been estimated as a current function:

$$\tau_c = 1.1562 \cdot exp\left[\frac{-(I_{cell} - 4.2672)^2}{0.09487}\right] + 0.606$$
(3.11)

and the parameter τ_2 has been estimated as $\tau a = 0.1 \cdot \tau c$. In Figures 3.9 and 3.10 can be appreciated the behaviors and estimations of τc and τa , respectively.



Figure 3. 9. Behavior and estimation of the parameter τc .



Figure 3. 10. Behavior and estimation of the parameter τa .

In the last adjusting, the estimated values obtained in the first and second adjusting Erev, *R*mem, τc and τa have been reused. In this adjusting, the behavior of the parameter *C*c has been studied,

which has shown a dependency of *I*cell and τc . For this reason, *C*c has been estimated as a function of *I*cell and τc .

$$C_1(I_{cell}, \tau_c) = F(I_{cell}, \tau_c) + H(I_{cell})$$
(3.12)

Where

$$F(I_{cell}, \tau_c) = 1.1 \cdot \tau_c \cdot (6.294 \times 10^{-6} \cdot exp[1.6943 \cdot I_{cell}] + 6.3204) - 0.002$$
(3.13)

And

$$H(I_{cell}) = 1.7 \cdot \arctan[I_{cell} - 2.5] - 0.07 \tag{3.14}$$





Figure 3. 11. Behavior and estimation of the parameter Cc.

3.2 Static-dynamic electrical model for each cell in a PEM electrolyzer

In continuity with the results presented in Section 3.1, this section is devoted to the analysis of the cell voltages and their responses according to static and dynamic operations. As in Section 3.1, the analysis is carried out by performing experiments on a commercial-400 W PEM electrolyzer (composed of three cells) to develop an accurate cell voltage static-dynamic model based on adaptive parameters according to the input current. The experiments consist of increasing and decreasing the current with a step of 1 A on each cell to investigate its behavior. This work on modeling each cell voltage instead of the stack voltage (as presented in [136] and Chapter 1) is motivated by the fact that cell voltage response and efficiency may undergo degradations during their operations due to dynamic solicitations (particularly important in RES) and low and highfrequency current ripple from power electronics (AC-DC and/or DC-DC converters) [49, 137]. Several works on performance degradation in PEM water electrolysis have been reported in the literature [103, 138–141]. These relevant works have demonstrated that PEM water electrolysis cells may be subjected to degradations due to dynamic operations and operating conditions (e.g. current density, temperature). However, the effects of current ripple from power electronics on PEM electrolysis cell performance are still a remaining key issue [49]; while many works have been reported for PEM fuel cells [131–133]. For this reason, cell voltage modeling is a powerful tool to study the degradation and wear effects from dynamic operations and current ripple.

3.2.1 Modeling issues: Dynamics and current ripple

Description of the experimental test rig

To analyze the dynamics of the three cells that are part of a commercial PEM electrolyzer, an experimental test rig has been realized at the GREEN laboratory, IUT de Longwy, as shown in Figure 3.12. The experimental test rig is composed by the following devices and components: (1) a laptop with a virtual control panel to control the DC power supply, (2) a DC power supply, (3) a 4-channel oscilloscope, (4) a pure water tank, (5) a commercial-400W PEM electrolyzer (composed of three cells), (6) a current probe to acquire the current at the input of the electrolyzer, and finally (7) two voltage probes to acquire the voltage of each cell. One voltage probe can acquire

up to two voltage measures. The specifications of the studied commercial PEM electrolyzer NMH2 1000 are provided in Table 3.1. Since the PEM electrolyzer NMH2 1000 system is manufactured for education purposes, it includes power electronics connected to the stack. The power electronics part is composed of a single-phase diode rectifier (to convert the AC voltage from the power grid (i.e., 230 V, 50 Hz) to a DC voltage) and a basic step-down DC-DC converter (to meet the low DC voltage required by the electrolyzer). The PEM electrolyzer system including the power electronics is shown in Figure 3.13.



Figure 3. 12. Experimental test setup.

In this work, only the stack of the PEM electrolyzer is considered and connected to an external DC power supply as depicted in Figure 3.12. The PEM electrolyzer features a solid polymer electrolyte based on fluoropolymer Nafion material from DuPont® company. The thickness of the membrane

is very thin (around 25 μ m), resulting in lower ohmic losses. The anode and cathode catalysts are based respectively on iridium and platinum materials; whereas current collectors at the anode and the cathode are made respectively in titanium (due to high anode potential) and carbon (low cathode potential) materials. Given that the low-pressure hydrogen storage tanks are based on metal hydride material (not shown in Figure 3.12), the outlet pressure of the PEM electrolyzer is set to 10.5 *bar*. The subsection 3.2.1 presents the responses of the PEM electrolyzer according to the input current and the current ripple issues on cell voltage efficiency.



Figure 3. 13. PEM electrolyzer system with power electronics.

Dynamics and current ripple issues

Based on the experimental test rig presented in Figure 3.12, experimental tests have been carried out to analyze the dynamic responses of the three cell voltages as a result of a step input current. The first cell corresponds to the cell on the top of the electrolyzer, the second cell is the middle cell, and finally, the third cell is located at the bottom (see Figure 3.12). The experiments have been carried out for two-step currents (i.e., from 0 to 10 A, and from 10 A to 0) to emphasize the direct and inverse dynamics of the electrolyzer. Both step currents have been achieved through the laptop with a virtual control panel to control the DC power supply. The obtained results are reported in Figures 3.14 and 3.15. For both tests, a large time scale (i.e., 5 s) has been chosen to highlight the dynamics and to observe the steady-state operation. The step current is applied at 1.25 s (Figure 3.14) and at 2.5 s (Figure 3.15).

First of all, based on Figure 3.2, at zero-current, the cell voltages are equal to 1.4 V corresponding to their reversible voltage. Therefore, the sum of these cell voltages enables obtaining the reversible stack voltage that is equal to around 4.2 V (as reported in [136]). At t=1.25 s, the current step is applied and an immediate rise in cell voltages can be observed. This immediate rise is related to the ohmic operation which can be modeled as a simple resistance, taking into consideration electrolyte resistance, and resistance of interconnects, end-plates, and contact [142]. As a result of this voltage rise, the cell voltages feature two different dynamics, one faster with the third cell, and another one slower with the first and second cells. Indeed, for the first and second cells, the dynamics last around 18.75 s; while for the third cell, the dynamic lasts around 8.75 s. Besides, in steady-state, the three cell voltages have the same value, around 2.6 V, corresponding to a stack voltage of 7.8 V.



Figure 3. 14. Response of the electrolyzer as a result of a rising electrical current from 0 to 10 A.

In comparison, in Figure 3.15, the cell voltages are equal to 2.6 V at 10 A corresponding to the end of the previous test. As a result of the inverse step current applied at 2.5 s, the same immediate rise can be noted. After that, it can be observed that the dynamics of the first and second cells are quite similar; whereas the third cell features a different dynamic. In this case, the voltage response of the third cell is slower compared to the first and second cell voltage responses. The first and second cells reach their steady-state operation in 7.5 s; while the third cell in 17.5 s. The steady-state voltages are equal to 1.4 V at zero-current. In summary, based on the rise or fall step current, the response voltages of the three cells show two different dynamics: slow and fast. The first and second cells present similar dynamics; while the dynamic of the third cell is different.



Figure 3. 15. Response of the electrolyzer as a result of a falling electrical current from 10 to 0 A.

These differences can be explained by the fact that some degradations have occurred over a long period of operation before the realization of these experiments. Indeed, the PEM electrolyzer stack has been supplied by the power electronics introduced in the previous subsection and shown in Figure 3.13. Due to their operation, power electronics generates low and high-frequency current ripple as depicted in Figure 3.16. The low-frequency component (around a hundred of Hertz) is due to the rectifier operation connected to the power grid; whereas the high-frequency component is due to the basic step-down DC-DC converter operating with a high switching frequency (around 20 kHz). In this case, the electrolyzer is supplied at low current (1 *A* representing the average value) and the current ripple is equal around 2 *A*, namely 200% of the average current. From Figure 3.16, it has to be noted that the voltage response of the electrolyzer is affected by the high current ripple since a small voltage ripple can be observed (around 0.4 *V*). In a previous work [129], the value of the equivalent double-layer capacitor modeling the dynamics of the studied PEM electrolyzer has been determined based on experimental data and by using a least-squares regression algorithm. The reported value is around 37 F and is higher compared to the values

reported for PEM fuel cells [117]. Based on the work reported in [131] focused on the interactions between PEM fuel cells and power converters, the authors have discussed the key role of the double-layer capacitor in filtering current ripple from power electronics. Since the value of the equivalent double-layer capacitor is quite high for this PEM electrolyzer, a large current ripple can be filtered. It may explain the reason for which the voltage ripple is small despite the high current ripple.



Figure 3. 16. Low and high-frequency current ripple in a PEM electrolyzer system.

Finally, to emphasize the effects of current ripple on PEM electrolyzer performance, cell voltage in a steady-state condition, static characterization of the cell voltage, and cell voltage efficiency have been plotted in Figure 3.17, 3.18, and 3.19 respectively. Figure 3.17 depicts the cell voltage in steady-state operation when the electrolyzer is supplied by the current shown in Figure 3.16. It

has to be noted that the voltage ripple is very small, around 0.15 V. For this current value (i.e., 1 A), the three cell voltages are equal and it enables justifying the value of the stack voltage ripple (around 0.4 V) in Figure 3.16. Then, Figure 3.18 shows a static characterization of the three cell voltages according to the input current. Based on the previous work [136], the current range has been limited to 10 A since the stack voltage remains constant above this value. It can be seen that the cell voltage curves show a disparity. At 10 A, the three cell voltages are similar despite some slight differences. Furthermore, while the cell voltages of cell 1 and 2 show a good agreement between each other, the third cell has a higher potential. This first observation allows linking with the previous observation on the different dynamics shown in Figure 3.14, and 3.15; where the dynamics of the first and second cells are similar; whereas the third cell has a different dynamic. Despite no works have been reported regarding the effects of current ripple on PEM electrolyzer performance, previous work on PEM fuel cells may explain this disparity between the cell voltages [143]. In this work, it has been noted a large disparity between the performance of the cell voltages as a result of a high-frequency current ripple (5 kHz, the average current value of 110 A, and 20% of current ripple). In Figure 3.19, it can be seen the impact of the current ripple on the cell voltage efficiency. The cell efficiency has been computed by dividing the thermoneutral voltage (i.e., 1.48 V) by each cell voltage. The first and second cells have a similar voltage efficiency; whereas the third cell voltage shows the worst performance due to a higher cell potential compared to the other cells.

In summary, this subsection enables confirming the motivations to carry out this research work in modeling each cell voltage to study performance degradation and wear effects.



Figure 3. 17. Cell voltage in steady-state operation when supplying by current ripple.



Figure 3. 18. Static characterization of the cell voltages.



Figure 3. 19. Cell voltage efficiency according to the input current.

3.2.2 Assessment of the parameters of the developed models

The model of each cell is developed by using the methodology presented in [32]. The equivalent electrical circuit is sketched in Figure 3.20.



Figure 3. 20. Equivalent circuit for a PEM electrolyzer

So, using the defined equations in Section 3.1.2, the current function *i*cell is determined by equation (3.4). For the activation overvoltage η act,c and η act,a the equations (3.5) and (3.6) respectively. So, the equivalent static-dynamic model of the electrolyzer voltage can be expressed as:

$$V_{\text{cell}}(t) = V_{\text{rev}} + i_{\text{cell}}(t) \cdot R_{mem} + \eta_{\text{act}}(t)$$
(3.15)

In this section, the parameters of the equation (3.15) are estimated for each cell of the PEM electrolyzer stack (cell 1, cell 2, and cell 3). These parameters are: *V*rev, *R*mem, η act,c(0), η act,a(0), *C*c, *C*a, *R*c, *R*a, τ c, and τ a. Using the Ohm's law, η act,c(0) and η act,a(0) are obtained as:

$$\eta_{\text{act,c}}(0) = R_c \cdot i_{cell}, \qquad \eta_{\text{act,a}}(0) = R_a \cdot i_{cell}$$
(3.16)

The parameters Rc and Ra have been determined by employing the equations (1.25) and (1.26). To make easier the construction of an electrical circuit, the capacitors are considered equal, so it is assumed Cc = Ca. Indeed, this assumption to consider the two capacitances equal leans on previous works reported in the literature regarding this important issue [129, 130].

To calculate the remaining five parameters, the cell voltage responses have been analyzed during dynamic tests. The static voltage-current curves of the three cells have been introduced in Figure 3.18 where the input current has been set to 10 A. Indeed, the cell voltages remain constant over this current value. The voltage dynamics have been studied by increasing the input current with a step of 1 A starting from 0 A up to reach 8 A and by decreasing it starting from 8 A to 0 A (keeping the same current step). Compared to the static characterization, to perform the dynamic tests, the input current has been limited to 8 A since the stack voltage has reached a value close to the rated stack voltage. As a result, there are no more dynamics. This issue has been discussed thoroughly in the previous work [136]. The obtained results are shown in Figures 3.21 and 3.22 for a rise step current, and Figures 3.23 and 3.24 for a fall step current. On one hand, in Figures 3.21, 3.22, 3.23, and 3.24, it can be noted that the cell voltage dynamics differ according to cell current. Indeed, cells 1 and 2 have the same behavior, compared to cell 3. It allows confirming our previous observations presented in Section 3.2.1. On the other hand, the maximum cell voltage (around 2.6 V) is reached by the cell 3 from 7 A; while the other cell voltages do not reach this value due to degradations as discussed in Section 3.2.1. It can be observed a slight voltage decrease when the third cell voltage has reached its maximum value, particularly noticeable in Figure 3.22. The same observation has been reported in the previous work [136], where a dynamic analysis of the stack voltage is presented. Finally, from the voltage variations point of view, they are meaningful up to 7 A with a disparity according to the number of the cell and the cell current.



Figure 3. 21. Cell voltage response as a result of a rise step current from 0 to 4 A.



Figure 3. 22. Cell voltage response as a result of a rise step current from 4 to 8 A.



Figure 3. 23. Cell voltage response as a result of a fall step current from 8 to 4 A.



Figure 3. 24. Cell voltage response as a result of a fall step current from 4 to 0 A.

After the analysis, a script has been developed by using MATLAB software to calculate the differential equations (3.5) and (3.6) to solve the equation (3.15). The script and the MATLAB command lsqcurvefit (based on the least-square regression algorithm) have been applied to adjust the parameters of the model to the data obtained experimentally for the different tests. The adjustment of the parameters has been performed three times to all different tests. In the first adjustment of the parameters, the results have shown that the variations of *V* rev and *R*mem are not significant for each cell. For this reason, these parameters have been estimated as constants in the three cells; *V* rev = 1.3898 *V* and *R*mem = 0.1029 Ω for cell 1; *V* rev = 1.3898 *V* and *R*mem = 0.1136 Ω for cell 2; *V* rev = 1.4123 *V* and *R*mem = 0.1396 Ω for cell 3. See Figures 2.25 and 2.26.



Figure 3. 25. Behavior and estimation of the parameter Vrev.



Figure 3. 26. Behavior and estimation of the parameter Rmem.

In the second adjustment, the estimated values for each cell in the first adjustment have been used. The adjustment has shown the behavior of the parameters τc and τa as a Gaussian function, which is a result of the dynamics behavior of the voltages tests. So, the parameter τc has been estimated as a current function:

$$\tau_{\rm c} = \begin{cases} 0.5568 \cdot exp \left[\frac{-(i_{cell} - 4.4731)^2}{0.4451} \right] + 1.0048 \quad for \; cell \; 1, \\ 1.1264 \cdot exp \left[\frac{-(i_{cell} - 4.4619)^2}{0.4525} \right] + 1.4771 \quad for \; cell \; 2, \\ 0.0827 \cdot exp \left[\frac{-(i_{cell} - 3.3822)^2}{0.1465} \right] + 0.3972 \quad for \; cell \; 3. \end{cases}$$
(3.17)

The parameter τa has been also estimated as a current function:

$$\tau_{\rm c} = \begin{cases} 0.0181 \cdot exp \left[\frac{-(i_{cell} - 1.2955)^2}{2.3718} \right] + 0.8509 \quad for \; cell \; 1, \\ 0.1009 \cdot exp \left[\frac{-(i_{cell} - 6.9142)^2}{2.1189} \right] + 0.8707 \quad for \; cell \; 2, \\ 0.0276 \cdot exp \left[\frac{-(i_{cell} - 3.7474)^2}{0.7212} \right] + 0.9825 \quad for \; cell \; 3. \end{cases}$$
(3.18)

In Figures 3.27 and 3.28 can be appreciated the behaviors and estimations of τc and τa , respectively.



Figure 3. 27. Behavior and estimation of the parameter $\tau_{\text{C}}.$



Figure 3. 28. Behavior and estimation of the parameter τ_a .

In the last adjustment, the estimated values obtained in the first and second adjustment have been used. In this adjustment, the behavior of the parameter *C*c has been studied, which has shown a dependency of *i*cell and τ c. For this reason, *C*c has been estimated as a function of *i*cell, τ c, and τ a.

$$C_{\rm c}(i_{cell},\tau_c,\tau_a) = F(i_{cell},\tau_c,\tau_a) + H(i_{cell})$$
(3.19)

Where

$$F(i_{cell}, \tau_c, \tau_a) = \begin{cases} (2.04\tau_c - 31.37\tau_a) \cdot exp[0.52i_{cell}] + 8.47 \text{ for cell } 1\\ (10.78\tau_c + 2.42\tau_a) \cdot exp[0.23i_{cell}] - 7.59 \text{ for cell } 2\\ (2.10\tau_c - 2.86\tau_a) \cdot exp[0.69i_{cell}] - 1.56 \text{ for cell } 3 \end{cases}$$
(3.20)

The function H(icell) has the aim of estimating the residue between the function F and the data obtained in the data adjustment for the parameter Cc. Although, in first instance the function F is a good approximation for the parameter Cc it is necessary to improve accuracy since the values of

Cc for low current *i*cell is smaller compared to the values of Cc for high current. So, the function H has been calculated for each cell using Fourier's series. In Figure 3.29 can be appreciated the behavior and estimations of the parameter Cc.



Figure 3. 29. Behavior and estimation of the parameter Cc.

In Chapter 5, the parameter estimations presented in this section are used to experimentally validate the model introduced in Section 3.1.2.

CHAPTER 4

STUDY OF THE SELF-DISCHARGE PHENOMENON IN A PEM ELECTROLYZER

As mentioned in Chapter 1, there are different ways to model the voltage of PEM electrolyzer. Besides, it was discussed how voltage affects other electrolyzer parameters such as the gas crossover phenomenon and the efficiencies in the PEM electrolyzer (Faraday's efficiency, voltage efficiency, and energy efficiency). However, despite this extensive research on PEM electrolyzer modeling, no work in the literature has reported the phenomenon of self-discharge voltage in PEM electrolyzers.

The term "self-discharge" is sometimes associated with the chemical reactions discharging the surface and excluding any physical processes which cause the voltage drop [146, 147]. The phenomenon of self-discharge voltage has proven to be an important subject of study for any electrochemical device, particularly for batteries and supercapacitors. For batteries, the selfdischarge voltage is the main limitation to storing energy for a long time, so the efficiency and autonomy of systems are poor [148], which is a challenging issue when using batteries in electric vehicles, industries, and residences [149, 150]. To reduce battery self-discharge voltage, many strategies have been developed, such as optimizing materials for battery construction [150, 151] and developing different models with a high degree of reliability (i.e., by taking into account several variables or assimilating the battery like an electronic circuit) [152, 153]. On the other hand, for supercapacitors, besides being determinant for the duration of energy storage (i.e., rest phases), self-discharge voltage is an important indicator to quantify performance [154, 155]. As a result, by decreasing the effects of supercapacitors' self-discharge voltage, the lifespans of devices that depend on the power supply of supercapacitors are improved [156, 157]. Like batteries, different materials for the construction of supercapacitors have been used, and the development of models has been implemented as a strategy to decrease the self-discharge voltage [14, 158]. In comparison, the self-discharge phenomenon for fuel cells is usually neglected in the literature, and the first investigation about this important issue was reported in [159]. It has been highlighted that decreases of the Open-Circuit Voltage (OCV) of fuel cells are mainly caused by the leakage currents due to gas crossover through the membrane. On the one hand, currently manufactured membranes feature thin membranes to reduce the ohmic losses associated with the conduction of protons. On the other hand, the thinner the membrane, the higher the gas crossover and leakage currents [160, 161]. Over a long period of operation, gas crossover through the membrane may reduce the lifespan of the fuel cell and degrade the membrane (e.g., pinholes) [161]. Therefore, this phenomenon remains a major concern for electrolyzers and further investigations are required.

From this current state-of-the-art, it is important to start studying the phenomenon of self- discharge voltage that occurs in PEM electrolyzers, since it is significant when the electrolyzer is coupled with RES and should be useful for the development of future works as PEM electrolyzer emulators (i.e., by taking this phenomenon into account, more realistic behavior of the PEM electrolyzer voltage can be obtained). For this reason, this chapter is aimed at describing the self- discharge voltage met in a PEM electrolyzer through different experimental tests and developing a model enabling reproducing the self-discharge phenomenon according to the operating conditions, such as the current. This model has been developed based on models proposed in the literature for supercapacitors and batteries to describe the behavior of self-discharge voltage. The comparison between the developed model and the experimental data for different operating conditions has demonstrated the high reliability of the model in reproducing the self-discharge phenomenon.

4.1 Sighting of the self-discharge in a PEM electrolyzer

4.1.1 Description of the experimental test setup

To study the self-discharge voltage of a PEM electrolyzer stack, an experimental test rig has been designed and built at the GREEN laboratory, IUT de Longwy, as shown in Figure 4.1. The experimental test rig is composed of the following devices and components: (1) a laptop, (2) dSPACE control desk software, (3) a DC power supply, (4) a DS1104 controller board, (5) a commercial-400W PEM electrolyzer, (6) a voltage probe MTX 1032-B from the Metrix Company to acquire the stack voltage. The DC power supply is controlled through a virtual control panel installed on the laptop. The PEM electrolyzer is supplied from pure water featuring low water conductivity (less than 2 $\mu S.m^{-1}$). Higher water conductivity can contaminate and damage the electrolyzer. In this work, only the stack of the PEM electrolyzer is considered and connected to an external DC power supply as depicted in Figure 4.1. The studied PEM electrolyzer has a solid

polymer electrolyte based on fluoropolymer Nafion material from DuPont® company. The thickness of the membrane is very thin (around 25 μ m), resulting in lower ohmic losses and may influence the self-discharge phenomenon based on previous works reported for PEM fuel cells [160, 161] and electrolyzers [80, 162]. The acquired stack voltage from the voltage probe is then transferred into the DS1104 controller board. Finally, the experimental data are monitored and saved through dSPACE control desk software. The sampling time has been chosen to 1 *s* to collect the experiment data. Finally, the obtained experimental data are plotted by using Matlab-Simulink® software.



Figure 4. 1. Experimental test setup.
4.1.2 Self-discharge voltage issues

From the experimental test rig presented in Figure 4.1, several experimental tests based on different initial conditions (10, 20, 30, and 35 A) have been performed to emphasize the self-discharge phenomenon in a PEM electrolyzer. The obtained results are depicted in a single figure (Figure 4.2) to make easier their analysis for comparison purposes. The duration of the test was 5500 s. These tests have consisted of supplying first the PEM electrolyzer with a constant current (10, 20, 30, and 35 A) for hundred seconds, and then disconnecting the PEM electrolyzer from the DC power supply to observe the decrease of OCV. Based on Figure 4.2 it is important to point out that the duration in which a constant current is applied to the electrolyzer and the initial operating conditions influence the self-discharge phenomenon. As a result of the disconnection from the DC power supply, an immediate voltage drop can be observed in the stack voltage. This immediate decrease in the stack voltage can be explained based on a previous work where an equivalent electrolyzer [32]. The immediate voltage drop is due to the sum of the equivalent resistances modeling the anode, cathode, and electrolyte. This first voltage drops ends when the stack voltage has reached 4.2 V related to the OCV of the electrolyzer stack.

After that, the voltage drop related to the self-discharge phenomenon can be emphasized. This selfdischarge can be divided into two phenomena, one is related to an accelerated self-discharge and the second to a slow continuous self-discharge. These two phenomena are well known when characterizing batteries as reported in the literature [163, 164]. The accelerated self-discharge is commonly called OCV "depolarization"; while the slow continuous self-discharge is defined as OCV "relaxation". In Figure 3.2, it can be seen that the OCV for the test (35-0 A) decreases more quickly and continuously compared to the other tests at lower currents. This observation demonstrates that the initial operating conditions affect the self-discharge. To emphasize the two observed phenomena (OCV depolarization and relaxation), the results of each test have been plotted in Figures 4.3, 4.4, 4.5, and 4.6. The OCV relaxation occurs when the OCV has reached around 0.5 V. For each test, the time separating these two OCV phenomena can be apprehended. Depending on the initial operating conditions, the length of the OCV depolarization may be longer or shorter. For instance, in Figure 4.6, the length of the OCV depolarization is shorter (around 2850 *s*) compared to the other tests. A summary of the measured length of the OCV depolarization for each test is provided in Table 4.1.

Test	Length of the OCV		
	depolarization		
0-10 A	3950 s		
0-20 A	3350 s		
0-30 A	3150s		
0-35 A	2850 s		

Table 4. 1. Summary of the measured length of the OCV depolarization.

Based on the previous works reported for self-discharge in batteries [146, 148] and supercapacitors [155, 156], the studied PEM electrolyzer features a higher self-discharge rate. Indeed, lead-acid and lithium-ion batteries feature a low self-discharge rate (noticeable in terms of days, weeks, or even months); while supercapacitors a higher self-discharge rate (noticeable in terms of hours or days). In supercapacitors, the high self-discharge is due to their organic electrolyte. For batteries, the self-discharge rate strongly depends on the temperature and the wear (decrease in the number of charge/discharge cycles) due to deep discharges [146]. The higher the temperature, the higher the self-discharge rate. The same phenomenon has been reported when the batteries are subject to deep discharge. In comparison, for supercapacitors, it has been highlighted that their self-discharge rates are dependent on their double-layer capacitance values, as well as on the temperature [147]. The higher the temperature, the higher the self-discharge rate; whereas the smaller the double-layer capacitance value, the higher the self-discharge rate.

As it has been emphasized in previous works [32, 136], when supplying the PEM electrolyzer with dynamic current profiles, the electrolyzer behaves as a capacitor because of the charge doublelayer effect. Indeed, between the electrode and the electrolyte, there is a layer of charge, which can store electrical charge, and therefore, energy. The accumulation of charges generates an electrical voltage, which corresponds to the activation overvoltage both at the anode and at the cathode. Thus, when the current immediately changes, the activation overvoltage both at the anode and the cathode takes some time before following the change in current due to the reaction kinetics. Besides, the PEM electrolyzer features two dynamics, the first one slower related to the anode, and the second one faster related to the cathode. These two different dynamics can be modeled by two RC branches where their constant times depend on the values of the two resistors considering the values of both capacitances equal [130]. Given that the dynamics both at the anode and cathode change according to the operating conditions, the values of both RC branches cannot be considered constant. For this reason, in [136], the parameters of both RC branches have been assessed through mathematical modeling whatever the operating conditions. The reported values for the double-layer capacitance are similar to the ones for supercapacitors (between 3 and 69 *F*) [136]. Starting from this analysis and the previous observations reported for supercapacitors, the high-self discharge rate depicted in Figure 4.2 can be explained. Indeed, the low double-layer capacitance value of the PEM electrolyzer leads to an accelerated and slow continuous self-discharge.

Finally, based on previous works reported for PEM electrolyzers [80, 162] and the knowledge of the authors on this topic, the self-discharge phenomenon in PEM electrolyzers is mainly induced by the leakage currents due to gas crossover through the membrane. Indeed, a part of the current at the cathode side has not been combined with the protons to generate hydrogen. Hence, this current goes back to the anode through the membrane that, at low current densities, is more permeable to gas crossover, as demonstrated in the literature [80, 162]. Besides, it is important to point out that gas crossover is strongly dependent on temperature, pressure, and membrane thickness, as emphasized in the literature [80, 106]. In the case under study, the PEM electrolyzer features a very thin membrane (i.e. around 25 μ m). As highlighted in [106], the thinner the membrane, the higher the gas crossover. Therefore, the thin membrane of the PEM electrolyzer may explain the high self-discharge rate observed in Figure 4.2.

To conclude, despite these first observations, further investigation is required to understand the self-discharge rate of PEM electrolyzers and the parameters affecting the self-discharge rate such as temperature and accelerated wear linked to their operating conditions (static and dynamic).



Figure 4. 2. Self-discharge tests according to different initial conditions (10, 20, 30, and 35 A).



Figure 4. 3. OCV depolarization and relaxation (10-0 A).



Figure 4. 4. OCV depolarization and relaxation (20-0 A).



Figure 4. 5. OCV depolarization and relaxation (30-0 A).



Figure 4. 6. OCV depolarization and relaxation (35-0 A).

4.2 Mathematical model

As mentioned in the beginning of this chapter, there are no reported models for the self-discharge voltage of the PEM electrolyzer. For this reason, this chapter is also focused on developing a model to describe the self-discharge voltage behavior.

As can be seen, there is a lag time in the experimental data before self-discharge voltage occurs, see Figure 4.2. For this reason, it is assumed that the voltage in the electrolyzer has normal behavior before the self-discharge voltage occurs. Therefore, taking into account the model for voltage

developed in [32, 136], which describes a static-dynamic behavior of the voltage drop in small periods (i.e. time lapses around 50 s) into a PEM electrolyzer, the static-dynamic model for the voltage before the self-discharge voltage occurs can be expressed as:

$$V(t) = \begin{cases} V_0 & \text{if } t < tc \\ V_{rev} + i(t) \cdot R_{mem} + \eta_{act}(t) & \text{if } t \ge tc \end{cases}$$
(4.1)

where V_0 is the initial voltage of the PEM electrolyzer (i.e., it is the value obtained before disconnecting the PEM electrolyzer from the power source). Vrev is the OCV, [V]. *i* is the current in the cell [A], Rmem is the membrane resistance [Ω]. η act is the activation overvoltage, [V]. *t* is the time in [s]. Finally, t_c is the time that the electrolyzer remains connected to the energy source, [s].

Furthermore, due to the experiment carried out, the current function can be expressed as the step function:

$$i(t) = \begin{cases} A_1 & \text{if } t < tc \\ A_2 & \text{if } t \ge tc \end{cases}$$

$$(4.2)$$

where both A_1 and A_2 take constant values, [A]. Besides, the activation overvoltage is expressed as $\eta \text{act} = \eta \text{act,c} + \eta \text{act,a}$, where $\eta \text{act,c}$ is:

$$\eta_{act,c} = \left(\frac{\tau_c}{C_c}\right) \cdot \left[(A_2 - A_1) \cdot \left(1 - exp\left[\frac{t_c - t}{\tau_c}\right] \right) + f_1(t) \right] + g_1(t)$$
(4.3)

And $\eta_{act,a}$:

$$\eta_{act,a} = \left(\frac{\tau_a}{C_a}\right) \cdot \left[(A_2 - A_1) \cdot \left(1 - exp\left[\frac{t_c - t}{\tau_a}\right] \right) + f_2(t) \right] + g_2(t)$$
(4.4)

where *C*c and *C*a are capacitance for cathode and anode, [*F*], both capacitances are considered equal based on a previous work reported in [130]. τ c and τ a are time constants, [*s*]. The functions $f_1(t)$ and $f_2(t)$ are given by:

$$f_1(t) = A_1 \cdot \left(1 - exp\left[\frac{-t}{\tau_c}\right]\right), \quad f_2(t) = A_1 \cdot \left(1 - exp\left[\frac{-t}{\tau_a}\right]\right) \tag{4.5}$$

and the functions $g_1(t)$ and $g_2(t)$ as:

$$g_1(t) = \eta_{\text{act},c}(0) \cdot exp\left[\frac{-t}{\tau_c}\right], \qquad g_2(t) = \eta_{\text{act},a}(0) \cdot exp\left[\frac{-t}{\tau_a}\right]$$
(4.6)

To model the self-discharge voltage, the models of supercapacitors and batteries reported in [146, 147] have been taken into consideration. In addition, the behavior of the self-discharge voltage curve has been taken into account, which has a voltage drop rate and subsequently a stable behavior (see Figure 4.2). Thus, the proposed model for the self-discharge voltage is the Verhulst's equation given by:

$$\frac{dV}{dt} = r \cdot V \cdot \left(1 - \frac{V}{K}\right) \tag{4.7}$$

where r is the rate of voltage drop (self-discharge voltage). K is the voltage that the electrolyzer maintains after the self-discharge phenomenon, [V]. Equation (4.7) has the analytical solution:

$$V(t) = \frac{K \cdot V(0) \cdot exp[r \cdot t]}{K + V(0) \cdot exp[r \cdot t]}$$
(4.8)

Therefore, by considering Equations (4.1) and (4.8), the self-discharge voltage model for PEM electrolyzer is expressed as:

$$V(t) = \begin{cases} V_0 & \text{if } t < t_c, \\ V_{rev} + i(t) \cdot R_{mem} + \eta_{act}(t) & \text{if } t_c \le t < t_{\tau}, \\ \frac{K \cdot V(t_{\tau}) \cdot exp[r \cdot t]}{K + V(t_{\tau}) \cdot exp[r \cdot t]} & \text{if } t \ge t_{\tau}. \end{cases}$$

$$(4.9)$$

where t_{τ} indicates the time in which the self-discharge phenomenon begins in the PEM electrolyzer, [*s*].

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Results

First of all, the developed model and its parameters from Chapter 3 have been tested by using the experimental data. From these data, the PEM electrolyzer stack voltage can be obtained by simulations. Besides, to assess the effectiveness of the model in reproducing the real behavior of the electrolyzer, the relative error *E*r and the mean error *E*m have been calculated for all different experimental tests as follows:

$$E_{\rm r} = \left(\frac{100}{N_d}\right) \cdot \sum_{k=1}^{N_d} \left| \frac{V_{exp,k} - V_{sim,k}}{V_{exp,k}} \right|, \qquad E_m = \left(\frac{1}{N_d}\right) \cdot \left(\sum_{k=1}^{N_d} |V_{exp,k} - V_{sim,k}|\right)$$
(5.1)

where N_d is the number of experimental data, $V \exp_k k$ is the *k* experimental measurement [*V*], $V \sin_k k$ is the *k* simulation data from the model [*V*].

In Figure 5.1, a comparison between the developed model and the experiments is reported. In this comparison, an input current from 0 to 5 *A* in a time from 0 to 50 *s* has been considered. The comparison between the obtained simulation data with the experimental data; for the input current from 0 to 1 *A* with a $t_c = 10 s$ has shown a Er = 1.3% and Em = 0.07 V; for the input current 1 to 2 *A* with a $t_c = 10 s$ has shown a Er = 0.95% and Em = 0.05 V; for the input current 2 to 3 *A* with a $t_c = 10 s$ has shown a Er = 0.66% and Em = 0.04 V; for the input current 3 to 4 *A* with a $t_c = 10 s$ has shown a Er = 0.06 V; for the input current 4 to 5 *A* with a $t_c = 10 s$ has shown a Er = 0.06 V.



Figure 5. 1. Comparison of the stack voltage between the experiments (solid line) and the model (dashed line) considering a current range from 0 to 5 *A*.

In Figure 5.2, the results obtained by simulation and the experimental data have been compared for a current range from 5 to 7 *A* in a time from 0 to 50 *s*. The comparison between the model with the experimental data; for the input current 5 to 6 *A* with a $t_c = 8 s$ has shown a Er = 0.8% and Em = 0.06 V; for the input current 6 to 7 *A* with a $t_c = 1 s$ has shown a Er = 0.18% and Em = 0.013 V.



Figure 5. 2. Comparison of the stack voltage between the experiments (solid line) and the model (dashed line) considering a current range from 5 to 7 A.

On the other side, in Figure 5.3, the model and the experiments have been compared with an input current from 8 to 5 *A* in a time between 0 and 50 *s*. The comparison between the model and the experiments; for the input current 8 to 7 *A* with a $t_c = 17.5 \ s$ has shown a Er = 0.66% and $Em = 0.05 \ V$; for the input current 7 to 6 *A* with a $t_c = 12.5 \ s$ has shown a Er = 1.42% and $Em = 0.1 \ V$; for the input current 6 to 5 *A* with a $t_c = 20 \ s$ has shown a Er = 0.64% and $Em = 0.04 \ V$.



Figure 5. 3. Comparison of the stack voltage between the experiments (solid line) and the model (dashed line) considering a current range from 8 to 5 A.

In Figure 5.4, the model has been compared with the experiment data for a current range from 5 to 0 *A* in a time from 0 to 50 *s*. The simulation comparation with the experimental data; for the input current 5 to 4 *A* with a $t_c = 15 \ s$ has shown a Er = 1.29% and $Em = 0.08 \ V$; for the input current 4 to 3 *A* with a $t_c = 15 \ s$ has shown a Er = 1.64% and $Em = 0.1 \ V$; for the input current 3 to 2 *A* with a $t_c = 15 \ s$ has shown a Er = 1.47% and $Em = 0.08 \ V$; for the input current 2 to 1 *A* with a $t_c = 15 \ s$ has shown a Er = 1.47% and $Em = 0.08 \ V$; for the input current 2 to 1 *A* with a $t_c = 15 \ s$ has shown a Er = 1.47% and $Em = 0.08 \ V$; for the input current 2 to 1 *A* with a $t_c = 15 \ s$ has shown a Er = 1.93% and $Em = 0.1 \ V$; for the input current 1 to 0 *A* with a $t_c = 20 \ s$ has shown a Er = 2.7% and $Em = 0.13 \ V$.



Figure 5. 4. Comparison of the stack voltage between the experiments (solid line) and the model (dashed line)considering a current range from 5 to 0 A.

The mathematical model has been compared with the experiments obtained for different current steps from 0 to 3 A, 0 to 6 A, 0 to 10 A, 10 to 0 A, and 2 to 10 A. The results are reported in Figures 5.5 and 5.6. The aim is to estimate the accuracy of the model in replicating the PEM stack voltage for different current steps, different from those used to develop the model.

In Figure 5.5, simulations results are reported in a time from 0 to 50 *s*. The comparison between the model and the experiments; for the input current 0 to 3 *A* with a $t_c = 4.5 s$ has shown a Er = 4.2% and Em = 0.2 V; for the input current 0 to 6 *A* with a $t_c = 11 s$ has shown a Er = 3.95% and Em = 0.25 V; for the input current 0 to 10 *A* with a tc = 2 *s* has shown a Er = 3.9% and Em = 0.29 V.



Figure 5. 5. Comparison of the stack voltage between the experiments (solid line) and the model (dashed line) considering a current range from 0 to 3 A, 0 to 6 A, and 0 to 10 A.

In Figure 5.6, the model is tested for the last current steps in a time from 0 to 50 s. The comparison of the model with the experimental data; for the input current 10 to 0 A with a $t_c = 4 s$ has shown a Er = 2.52% and Em = 0.12 V; for the input current 2 to 10 A with a $t_c = 11 s$ has shown a Er = 4.19% and Em = 0.29 V.



Figure 5. 6. Comparison of the stack voltage between the experiments (solid line) and the model (dashed line) considering a current range from 10 to 0, and 2 to 10 A.

In Figures 5.7, 5.8, 5.9, and 5.10, the data obtained from the developed model have been compared with experimental data for different current ranges. In Figures 5.7, and 5.8, rise current steps have been investigated, from 0 to 4 A, and from 4 to 8 A, respectively. In comparison, in Figures 5.9, and 5.10, fall current steps have been considered, from 8 to 4 A, and from 4 to 0 A, respectively. From Figures 5.7 and 5.8, it has to be noted that the model enables replicating accurately the real voltage response of cells 1 and 2. Regarding cell 3, slight differences can be observed but the dynamics are reproduced with accuracy. Note also that, in Figures 5.9, and 5.10, the comparison between the model and the experimental data shows a good agreement despite some errors that can be observed and are more significant in contrast to the comparison provided in Figures 5.7 and 5.8. Indeed, as shown in Figures 5.14 and 5.15, the cell voltage responses present different behaviors according to rise or fall current steps. In the case of a fall current step, it can be observed in Figures 5.9 and 5.10 that the cell voltage responses are not similar according to the input current. For this reason, accurate modeling of these responses is complex and some errors between the model and the experiments are noticeable. The relative errors Er and the mean errors Em for the different tests

reported in Figures 5.7, 5.8, 5.9, and 5.10 are summarized in this section. The objective is to discuss the obtained global results for each cell and to provide some future perspectives.



Figure 5. 7. Comparison of the voltage of the cells between the experiments (solid line) and the model (dashed line) considering a current range from 0 to 4 A.



Figure 5. 8. Comparison of the voltage of the cells between the experiments (solid line) and the model (dashed line) considering a current range from 4 to 8 A.



Figure 5. 9. Comparison of the voltage of the cells between the experiments (solid line) and the model (dashed line) considering a current range from 8 to 4 A.



Figure 5. 10. Comparison of the voltage of the cells between the experiments (solid line) and the model (dashedline) considering a current range from 4 to 0 A.

Finally, the mathematical model has been compared with the experiments obtained for different current steps from 0 to 3 *A*, 0 to 10 *A*, and 10 to 0 *A* to analyze its reliability in predicting the different cell voltages. The results are reported in Figure 5.11, where it can be observed that the response obtained with the developed mathematical model show a good agreement with the experimental data. Indeed, for some cases, the dynamic and static behavior of the cell voltages can be reproduced with accuracy. However, since these experimental data have not been taken into consideration when determining the parameters of the model in Figure 3.20, some estimation errors are noticeable particularly during the transient states but in steady-state conditions, the model accurately since the studied PEM electrolyzer features different dynamics depending strongly on the operating conditions (i.e. current values, and step current between two operations) as shown in Figures 3.14 and 3.15. In summary, despite some estimation errors are noticeable in the cell voltage transients, the developed model enables recreating the real cell voltage response according to dynamic operations.



Figure 5. 11. Comparison of the voltage of the cells between the experiments (solid line) and the model (dashedline) considering a current range from 0 to 3 A, 0 to 10 A, and 10 to 0 A.

To validate the model introduced in Chapter 4, the parameters of Equation (4.9) have been estimated using an m-file in Matlab® together with the command lsqcurvefit, which is based on the least-square regression algorithm. The values of the parameters are shown in Table 5.1.

Parameter	Value	Unit
Vrev	0.21	V
C_c	800	F
C_a	800	F
$ au_c$	180	S
$ au_a$	2558.9	S
$\eta_{\rm act,c}(0)$	$5.5719 \cdot \log\left[9.1933 \cdot \left(\frac{1}{i}\right)\right]$	V
$\eta_{\rm act,a}(0)$	$8.2919 \times 10^{-6} \cdot i^{4} + 9.8489 \times 10^{-4} \cdot i^{3} - 0.0314 \cdot i^{2} - 0.0027 \cdot i$ + 3.6606	V
	+ 3.0000	
r	-4.1226×10^{-4}	(-)
K	0.3941	V

Table 5. 1. Calculated parameters for self-discharge voltage model.

As can be seen in Table 5.1, the values of $\eta \operatorname{act}, c(0)$ and $\eta \operatorname{act}, a(0)$ depend on the current input *i*, which agrees with the work reported in [136, 165].

After calculating the parameters, the effectiveness of the model in reproducing the real behavior of the self-discharge voltage in the PEM electrolyzer has been evaluated. To carry out this evaluation, a comparison between the experimental data and the model has been developed using the mean absolute percentage error Er and the mean absolute error Em by using (5.1).

To observe the comparison between the experimental data and the model simulations, an m-file was developed in Matlab®. The results are shown in Figures 5.12, 5.13, 5.14, and 5.15. In these figures, the OCV depolarization and relaxation are emphasized. In Figure 5.12 can be appreciated the comparison between the curve of the experimental data from 10 to 0 *A* and the curve generated by the model. To generate this simulation, the values $A_1 = 10 A$, $A_2 = 0 A$, $V_0 = 6.78 V$, $t_c = 155 s$, and $t_\tau = 3200 s$ have been used.



Figure 5. 12. Comparison between the experimental data from 10 to 0 A and the simulation of the model.

In Figure 5.13, the comparison between the curve of the experimental data from 20 to 0 *A* and the curve generated by the model is shown. To perform the simulation, the values $A_1 = 20 A$, $A_2 = 0 A$, $V_0 = 7 V$, $t_c = 210 s$, and $t_\tau = 2600 s$ have been used.



Figure 5. 13. Comparison between the experimental data from 20 to 0 A and the simulation of the model.

In Figure 5.14 can be observed the comparison between the curve of the experimental data from 30 to 0 *A* and the curve generated by the model. To develop this simulation, the values $A_1 = 30 A$, $A_2 = 0 A$, $V_0 = 6.9 V$, $t_c = 190 s$, and $t_\tau = 2400 s$ have been used.



Figure 5. 14. Comparison between the experimental data from 30 to 0 A and the simulation of the model.

Finally, in Figure 5.15, the comparison between the curve of the experimental data from 35 to 0 *A* and the curve generated by the model is shown. To perform the simulation, the values $A_1 = 35 A$, $A_2 = 0 A$, $V_0 = 7.1 V$, $t_c = 170 s$, and $t_t = 2300 s$ have been used.



Figure 5. 15. Comparison between the experimental data from 35 to 0 A and the simulation of the model.

5.2 Discussion

Based on the results reported in the previous section, in Table 5.2 is provided to summarize the relative and mean error of the model according to different tests carried out. From this table, it can be noted that the maximum mean error obtained with the model is equal to 0.29 V (i.e. 4.19%) for a current step from 2 to 10 A; whereas for the other tests (Figures 5.1, 5.2, 5.3 and 5.4), the mean error is very low (less or equal than 0.13 V). The maximum errors are obtained for larger current steps (Figures 5.5 and 5.6) since these experimental data have not been directly used to develop the adaptive model. Hence, the estimation of the parameters of the model is not optimal, and errors between the experimental data and the model can be observed. Despite this, the model can provide a good approximation of the real behavior of the electrolyzer. Besides, the obtained errors are particularly noticeable during the transient phenomena, which are complex to model according to the input current. To conclude, these obtained results demonstrate the effectiveness of the model to reproduce the real behavior of the PEM electrolyzer while reducing the errors between the model and the model and the experiments. Further improvements can be made to increase the reliability of the model in

predicting the dynamic behavior of the electrolyzer during dynamic operations, how can be the theory of control and mathematical analysis.

Input current	t_c	Er	Em	Simulation
0 to 1 A	10 <i>s</i>	1.3%	0.07 V	
1 to 2 A	10 <i>s</i>	0.95%	0.05 V	
2 to 3 A	10 <i>s</i>	0.66%	0.04 V	Figure 5.1
3 to 4 A	10 <i>s</i>	0.98%	0.06 V	
4 to 5 A	10 <i>s</i>	0.88%	0.06 V	
5 to 6 A	8 <i>s</i>	0.8%	0.06 V	Eigura 5 2
6 to 7 A	1 <i>s</i>	0.18%	0.01 V	Figure 3.2
8 to 7 A	17.5 s	0.66%	0.05 V	
7 to 6 A	12.5 s	1.42%	0.01 V	Figure 5.3
6 to 5 A	20 s	0.64%	0.04 V	_
5 to 4 A	15 s	1.29%	0.08 V	
4 to 3 A	15 s	1.64%	0.1 V	
3 to 2 A	15 s	1.47%	0.08 V	Figure 5.4
2 to 1 A	15 s	1.93%	0.1 V	
1 to 0 A	20 s	2.7%	0.13 V	
0 to 3 A	4.5 <i>s</i>	4.2%	0.2 V	
0 to 6 A	11 <i>s</i>	3.95%	0.25 V	Figure 5.5
0 to 10 A	2 <i>s</i>	3.9%	0.29 V	
10 to 0 A	4 <i>s</i>	2.52%	0.12 V	Eigene 5 (
2 to 10 A	11 <i>s</i>	4.19%	0.29 V	Figure 5.6

Table 5. 2. Summary of the performance of the model.

In Tables 5.3, 5.4, and 5.5, a summary of the relative and mean error for each cell is provided according to the different tests performed. Based on table 5.3, it can be noted that the maximum mean error obtained for the cell 1 is equal to 0.12 V (i.e. 5.37%) for a current step from 0 to 10 A; whereas for the other tests (Figures 5.7, 5.8, 5.9, and 5.10), the relative error is very small (less than 5%). From Table 5.4, it has been reported that the maximum mean error obtained for the cell 2 is equal to 0.1 V (i.e. 6.14%) for a current step from 10 to 0 A; while for the other tests (Figures 5.7, 5.8, 5.9, and 5.10), the relative error is very small (less than 5%). From the table 5.10), the relative error is very low (less than 5%). From the table 5.5, it can be observed that the maximum mean errors obtained for the cell 3 is equal to 0.16 V (i.e. 6.02%) and 0.1 V (i.e. 5.3%) for a current step from 0 to 10 A and 0 to 3 A respectively; whereas for the other tests (Figures 5.7, 5.8, 5.9, and 5.10), the relative error is very low (less than 5%).

The maximum errors are obtained for larger current steps (Figure 5.11) since these experimental data have not been employed to determine the parameters of the developed mathematical model. Therefore, the assessment of the different parameters of the model is not optimal, and errors between the experimental data and the model are noticeable. Furthermore, the obtained errors are meaningful during the transient states, which are complicated to model with accuracy according to the current of the electrolyzer. To conclude, based on the results reported in Tables 5.3, 5.4, and 5.5, the developed mathematical model with adaptive parameters reproduces with accuracy the real behavior of the PEM electrolyzer while decreasing the cell voltage errors between the model and the experiments for each cell. Further improvement using other modeling techniques can be made to increase the reliability of the model in predicting the dynamic behavior of the electrolyzer during dynamic operations.

Based on this preliminary work, it would be interesting to take into consideration other key operating parameters such as the temperature. Indeed, as emphasized in the literature [144], the operating temperature has a strong influence on the performance of PEM electrolyzers, affecting at the same time the reversible voltage, the activation overvoltage both at the anode and cathode, and the ohmic overvoltage. The higher the operating temperature, the lower the reversible voltage, and other over voltages (i.e., activation and ohmic). As a result, the performance of the PEM electrolyzer can be enhanced by featuring a higher energy efficiency. From the dynamics point of view, the rise in temperature strongly affects the activation over voltages leading up to faster chemical kinetics. In summary, within the framework of our work, a change in operating temperature will affect our model since we have only considered the change in electrolyzer current. Therefore, the assessment of the different parameters of our model based on temperature change will enable us to enhance its reliability in predicting cell voltage responses.

Finally, this work can be useful to develop a real-time PEM electrolyzer emulator in hardware- inthe-loop applications to test power electronics connected to RES as it has been reported for PEM fuel cell stack [145].

Input current	tc	Er	Em	Simulation
0 to 1 A	5 s	1.94%	0.03 V	
1 to 2 A	5 s	1.83%	0.03 V	Eiguro 57
2 to 3 A	5 s	1.00%	0.02 V	Figure 5.7
3 to 4 A	5 s	1.36%	0.03 V	
4 to 5 A	5 s	0.96%	0.02 V	
5 to 6 A	4.5 s	1.06%	0.02 V	Eigura 5 9
6 to 7 A	2.93 s	0.80%	0.02 V	Figure 5.8
7 to 8 A	2.68 s	0.84%	0.02 V	
8 to 7 A	3.32 s	0.89%	0.02 V	
7 to 6 A	2.77 s	1.33%	0.03 V	Eigura 5.0
6 to 5 A	2.96 s	0.66%	0.01 V	Figure 5.9
5 to 4 A	2.94 s	1.20%	0.02 V	
4 to 3 A	4.2 s	1.62%	0.03 V	
3 to 2 A	5.85 s	1.17%	0.02 V	Eigura 5 10
2 to 1 A	3.97 s	1.11%	0.02 V	Figure 5.10
1 to 0 A	4.59 s	4.38%	0.07 V	
0 to 3 A	1.75 s	4.39%	0.08 V	
0 to 10 A	1.05 s	5.37%	0.12 V	Figure 5.11
10 to 0 A	2.3 s	2.67%	0.04 V	

Table 5. 3. Summary of the performance of the model for cell 1.

Table 5. 4. Summary of the performance of the model for cell 2.

Input current	t _c	Er	Em	Simulation
0 to 1 A	5 s	2.21%	0.03 V	
1 to 2 A	5 s	0.48%	0.01 V	Eigura 5 7
2 to 3 A	5 s	0.62%	0.01 V	Figure 5.7
3 to 4 A	5 s	1.00%	0.02 V	
4 to 5 A	5 s	0.72%	0.02 V	
5 to 6 A	4.5 s	0.86%	0.02 V	Eigura 5 9
6 to 7 A	2.93 s	0.88%	0.02 V	Figure 5.8
7 to 8 A	2.68 s	0.68%	0.02 V	
8 to 7 A	3.32 s	2.08%	0.04 V	
7 to 6 A	2.77 s	1.41%	0.03 V	Eigung 5.0
6 to 5 A	2.96 s	1.59%	0.03 V	Figure 5.9
5 to 4 A	2.94 s	4.85%	0.07 V	
4 to 3 A	4.2 s	1.52%	0.04 V	
3 to 2 A	5.85 s	2.91%	0.07 V	Eigura 5 10
2 to 1 A	3.97 s	2.23%	0.05 V	Figure 5.10
1 to 0 A	4.59 s	1.20%	0.02 V	
0 to 3 A	1.75 s	3.95%	0.07 V	
0 to 10 A	1.05 s	4.77%	0.11 V	Figure 5.11
10 to 0 A	2.3 s	6.14%	0.1 V	

Input current	tc	Er	Em	Simulation
0 to 1 A	5 s	2.57%	0.04 V	
1 to 2 A	5 s	1.03%	0.02 V	Eiguro 57
2 to 3 A	5 s	1.23%	0.03 V	Figure 5.7
3 to 4 A	5 s	0.69%	0.02 V	
4 to 5 A	5 s	1.14%	0.03 V	
5 to 6 A	4.5 s	1.66%	0.04 V	Eigura 5 9
6 to 7 A	2.93 s	1.84%	0.05 V	Figure 5.8
7 to 8 A	2.68 s	0.37%	0.01 V	
8 to 7 A	3.32 s	2.32%	0.05 V	
7 to 6 A	2.77 s	4.11%	0.08 V	Eigura 5.0
6 to 5 A	2.96 s	3.64%	0.07 V	Figure 5.9
5 to 4 A	2.94 s	4.89%	0.07 V	
4 to 3 A	4.2 s	1.54%	0.04 V	
3 to 2 A	5.85 s	4.9%	0.13 V	Eigura 5 10
2 to 1 A	3.97 s	1.81%	0.04 V	Figure 5.10
1 to 0 A	4.59 s	1.97%	0.05 V	
0 to 3 A	1.75 s	5.3%	0.1 V	
0 to 10 A	1.05 s	6.02%	0.16 V	Figure 5.11
10 to 0 A	2.3 s	3.42%	0.06 V	

Table 5. 5. Summary of the performance of the model for cell 3.

With respect to the model developed for the self-discharge voltage phenomenon, a summary of the relative error and mean error is presented in Table 5.6. On the one hand, a relative error E_r of less than 5 % is presented for the tests of 10-0 A, 20-0 A, and 30-0 A. While the test 35-0 A has obtained a relative error of 5.69 %, this being the highest relative error obtained within these comparisons. On the other hand, a mean error E_m of less than 0.075 V is obtained for each one of the experimental tests. Therefore, in general, there is an average relative error $E_r = 4.6$ % and an average mean error $E_m = 0.0603$ V for the experimental tests, which validates the model.

As can be seen, the behavior of the self-discharge voltage curve is expected to be asymptotically stable for large periods. Furthermore, the behavior presented by the self-discharge voltage in a PEM electrolyzer has a great similarity with the curve described by Verhulst's equation. Besides, as highlighted in [166], the self-discharge phenomenon in supercapacitors does not obey to usual empirical equations. For this reason, the developed model is based on physical reasoning taking into consideration the real physical phenomenon governed by supercapacitors and electrolyzer operation. As a result, the model achieves high accuracy.

Finally, recommendations to prevent the phenomenon of self-discharge voltage in a PEM electrolyzer are presented in the next subsection as a result of the analysis of the experimental data.

Input current	Er	Em
10-0 A	3.55 %	0.0528 V
20-0 A	4.43 %	0.0489 V
30-0 A	4.70 %	0.0745 V
35-0 A	5.69 %	0.0648 V

Table 5. 6. Summary of the relative and mean errors.

5.2.1 Self-discharge prevention

Over the last years, research has been intensified to develop different solutions to reduce the selfdischarge of supercapacitors by bringing improvement to the electrode, separator, or electrolyte [167, 168]. Indeed, as highlighted in Section 4.1, the self-discharge of supercapacitors is an important issue due to the fast self-discharge, low energy efficiency, and loss of stored energy. Like supercapacitors, self-discharge in PEM electrolyzers is a major concern given that gas crossover through the membrane and leakage currents may decrease the lifespan of the electrolyzer and lead to the degradation of the membrane (e.g. pinholes) as reported for PEM fuel cells [159, 161]. Besides, when the electrolyzer is reconnected to a power supply with low OCV (as a result of a self- discharge), high overshoot may occur, causing likely deterioration of the PEM electrolyzer [169]. In Figure 5.16, the voltage overshoot (around 9 V, 12.5 % higher than the rated voltage of the electrolyzer (i.e. 8 V)) is shown when reconnecting the DC power supply (current step from 0 to 20 A). Besides, at the beginning of the test, it can be highlighted that the OCV is very low (close to 0 V) as a result of the self-discharge. To prevent the self-discharge issue in PEM electrolyzers, several potential solutions can be adopted:

 A compromise must be found for the thickness of the membrane to reduce the selfdischarge. A thin membrane leads to lower resistance, increasing consequently the gas crossover and leakage currents. In comparison, an increase of the membrane thickness (improving the permeability of the membrane against gas crossover), leads to higher losses in the membrane; and as a result, a decrease in energy efficiency [80, 162].

- 2. The operating temperature must be as low as possible to enhance the protective function of the membrane against gas crossover. A higher operating temperature leads to lower resistance and consequently contributes to gas crossover, as highlighted in previous works focused on the effect of the temperature on Faraday's efficiency [33].
- 3. The operating pressure must be as small as possible to limit the gas crossover.
- 4. To avoid the limitation of the operating conditions (pressure, temperature) while keeping a thinner membrane, the self-discharge can be compensated by supplying the PEM electrolyzer with a small current (contributing to a constant OCV).



Figure 5. 16. Stack voltage overshoot when connecting to the DC power supply as a result of a selfdischarge.

CONCLUSION

The objective of this thesis has been to establish the theoretical bases that justify the possibility of building an electronic emulator for a PEM electrolyzer. This device is intended to save money (due to the high cost of PEM electrolyzers) and test novel power conversion topologies and their control without employing a PEM electrolyzer that might be degraded during experiments. A mathematical model has been proposed and developed to show that there is a relation between a PEM electrolyzer and an electronic circuit. Thus, with this electronic circuit, it is possible to reproduce the static and dynamic behaviors of the PEM electrolyzer.

To propose a model, a study of the main characteristics of PEM electrolyzers has been carried out. This study has covered different types of electrolyzers (i.e., alkaline, PEM, and solid oxide), advantages, disadvantages, their basic operations, and how these devices can be coupled to different energy sources. After that, a review of different mathematical models for PEM electrolyzers has been made to analyze the reported models to describe the electrical domain presented in a PEM electrolyzer. This review has taken into account the different efficiency parameters (Faraday, voltage, and energy) and the specific energy consumption, which are important indicators of performance for a PEM electrolyzer. Furthermore, with this part of the work, it is observed that the dynamic models for the voltage-current of a PEM electrolyzer are scarce. Therefore, knowing the importance of the dynamic study of the voltage of a PEM electrolyzer and the lack of this type of model in the literature, it has been decided to propose and develop a static-dynamic model.

In this thesis, it has been investigated the dynamic behavior of voltage in a PEM electrolyzer to develop an accurate static-dynamic mathematical model, both for the stack and cells. The experimental tests have demonstrated the presence of dynamics for input current steps from 0 to 8 A and no dynamics for input currents higher than 8 A. The originality of the modeling approach consists in modeling the electrical domain to increase the reliability of the model in predicting the cell and stack voltage. This approach is motivated by the fact that the cells composing the PEM electrolyzer may be subjected to degradations during its operation due to current ripple from power

electronics and dynamic solicitations when coupling with renewable energy sources. It has been demonstrated that the current ripple can degrade cell voltage performance. By performing different dynamic tests at different input currents, mathematical models with adaptive parameters have been developed for the stack and each cell. Then, a comparison between the model and experiment data have demonstrated the performance of the model in predicting the voltage behavior as a result of dynamic tests, both for the stack and cells. The obtained mean errors are lower than 4.2% for the stack and 6% for the cells, which shows the accuracy of the model. However, for future studies, it would be interesting to test the model under different input signals like straight, sine or cosine, and triangular (generally met with power electronics). Besides, to increase the reliability of the model, it would be interesting to employ other modeling techniques that could bring improvements in replicating the transient states of the PEM electrolyzer as control theory, which can be useful to optimize the PEM electrolyzer. The developed mathematical models with adaptive parameters could be implemented in hardware-in-the-loop applications for different purposes such as investigation of new power converters and their control, and analysis of the degradation and wear effects of the cells mainly provoked by the dynamic operating conditions met when coupling with renewable energy sources and current ripple from power electronics.

After modeling for electrolyzer, a new data collection has been performed but with a greater amount of time at each current input. These experiments have demonstrated the existence of the self-discharge voltage phenomenon for the PEM electrolyzer. As mentioned in this thesis, this phenomenon results in a decrease of the Open-Circuit Voltage that occurs when an electrochemical device is disconnected from the power source. Besides, no previous works have been reported in the literature about this phenomenon for electrolyzers. For this reason, a chapter is mainly focused on investigating the self-discharge voltage that occurs in a PEM electrolyzer and model this phenomenon. Therefore, by taking into account this voltage drops in the modeling, simulations with a higher degree of reliability are obtained when predicting the behavior of PEM electrolyzers. Thus, it is concluded that building an emulator based on this model is feasible.

FUTURE WORKS

As can be seen, the model developed in this thesis has shown high accuracy when reproducing the static and dynamic behaviors of a PEM electrolyzer. However, this model might have better performance. The ideas for the model to obtain greater reliability are as follows:

- To consider the temperature within the model as a function of time, since during the experimental tests, it has been observed how this parameter affects the operation of the PEM electrolyzer through the decrease of the cell voltages, and so the stack voltage. The lower the stack voltage, the higher the energy efficiency of the PEM electrolyzer.
- To propose a sensitivity analysis for the adaptive parameters used for the model. The goal is to use inverse methods by the ordinary least squares (OLS).

In addition to being able to extend the theoretical work, with the development of this investigation, it is already possible to start building the first prototypes of the emulator. In Figure 5.17 is shown a prototype of an electronic circuit for the emulator of a PEM electrolyzer and in Figure 5.18 it can be appreciated the performance testing of the emulator prototype for a PEM electrolyzer.



Figure 5. 17. Prototype of an electronic circuit for the emulator of a PEM electrolyzer.



Figure 5. 18. Performance testing of the emulator prototype for a PEM electrolyzer.
THESIS ACHIEVEMENTS

Throughout this thesis, several academic achievements as lectures, scientific articles and disclosure articles have been achieved.

Lectures:

• Congreso Nacional de Control Automático 2019.



• XIII Coloquio de Ecuaciones Diferenciales y sus Aplicaciones.



Scientific articles:

• Memorias del Congreso Nacional de Control Automático 2019 [170].



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Estimation of temperature gradient method for a particular PEM electrolyser system

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Review Article

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

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• Research article in International Journal of Hydrogen Energy [136].



Development of an adaptive static-dynamic electrical model based on input electrical energy for PEM water electrolysis

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• Research article in Journal of Renewable Energy [165].



Cell voltage static-dynamic modeling of a PEM electrolyzer based on adaptive parameters: Development and experimental validation



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Article Self-Discharge of a Proton Exchange Membrane Electrolyzer: Investigation for Modeling Purposes

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Disclosure articles:

• Science popularization article in Supplement Campus.



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