Insights into Membrane Aging in PEM Electrolyzers: A Semi-Empirical Modelling Approach

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Objective – This study aims to address the degradation of proton exchange membrane (PEM) within an electrolyzer, a key factor limiting its lifetime and efficiency, by developing a semi-empirical model. The model integrates electrochemical factors, providing insights into membrane degradation.

Findings – The proposed model, validated with experimental data, reveals critical interactions that drive PEM aging and highlights the influence of various parameters on the performance of aged electrolyzer. It also identifies operational strategies that could help mitigating degradation, supporting optimized, durable electrolyzer performance, especially under dynamic operating conditions caused by renewable energy sources.

Originality – This work presents a novel equivalent electrical model specifically tailored to simulate PEM aging, establishing a predictive tool for setting optimal operating conditions. The model's unique approach offers valuable guidance for operators aiming to extend PEM electrolyzer lifespan under variable operational conditions.

Keywords - PEM electrolyzer, membrane aging, hydrogen production, modelling

1. Introduction

The development of green hydrogen production via water electrolysis pathways is essential for sustainable energy goals, aiming to reduce greenhouse gas emissions and global transition from fossil fuels-based to zero-carbon [1]. Water electrolysis technologies can be classified into two families: low-temperature electrolysis (LTE) and high-temperature electrolysis (HTE). LTE includes liquid alkaline, proton exchange membrane (PEM), and AEM (anion exchange membrane) electrolyzers, whereas HTE considers oxide-ion-conducting solid oxide electrolysis cell (O-SOEC) and proton-conducting solid oxide electrolysis cell (P-SOEC) electrolyzers [2]. Each of these electrolyzer technologies offers unique advantages and challenges in terms of performance, durability, and affordability when integrated with low-carbon electricity sources, but some are at earlier stages of development such as AEM and P-SOEC electrolyzers. In this work, PEM electrolyzers are considered because of their advantages: commercial technology, high current density at high efficiency, differential pressure operation, and dynamic operation capability when coupled with renewable energy sources [3]. However, their large-scale deployments face challenges, primarily due to the degradation of the membrane, which impacts efficiency and lifespan [4, 5]. According to the U.S. Department of Energy [6], PEM electrolyzers present currently 40,000 operation hours and the objective is to reach 80,000 operation hours by 2026. Besides, the current degradation rate is 4.8 mV/khr with the target of 2.3 mV/khr by 2026. On one hand, the sources of membrane degradations have been identified in the literature: operating conditions (temperature, current density) [4], current ripple from power electronics [5], dynamic operating conditions [7], gas bubble accumulation conditions [8], and start/stop conditions [9]. On the other hand, a few studies have addressed degradations modeling in PEM electrolyzers [4,9-11].

Relying on the current state-of-the-art above-mentioned, this study addresses membrane degradation due to current harmonics (including low and high-frequency ripple) from power electronics by developing a detailed model that captures the aging mechanisms through chemical and electrochemical factors. By analyzing these interactions, the model predicts aging impacts on electrolyzer performance and suggests operational strategies to mitigate degradation, extending device lifespan. The introduction of the semi-empirical additive term allows the model to capture the effects of membrane degradation, a critical factor in electrolyzer aging. This term, introduced for the first time in this work, has not, to the best

of the authors' knowledge, been covered in previous literature. The model also serves as a predictive tool, helping operators set optimal parameters for durability under dynamic load profiles common in renewable energy applications.

The plan of this research work is divided into four main sections. After the introduction providing the current state-of-the-art, the motivations, and the main contributions of this work, Section 2 highlights the PEM electrolyzer modeling considering aging phenomena. Then, in Section 3, the experimental test bench and the validation of the proposed model are presented. Finally, in Section 4, the conclusions of this work and a discussion about future challenges are given.

2. PEM electrolyzer modeling considering aging phenomena

Following the work presented in [12], the equivalent electrical model of an electrolyzer cell can be described as the superposition of different overvoltages, as shown in Fig. 1. This model expresses the nonlinear $V(I)$ characteristics of the electrolyzer through equations (1).

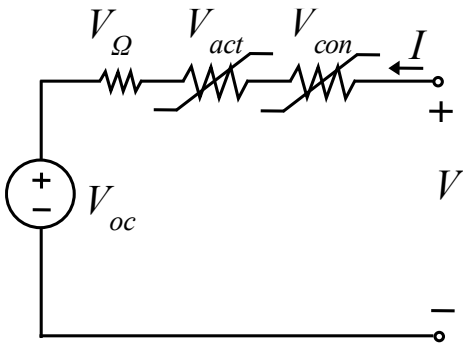

Figure 1 : equivalent electrical model of the PEM electrolyzer

$$V(I) = V_{oc} + V_\Omega + V_{act} + V_{con} \tag{1}$$

$$V_{oc} = k_{oc} \tag{2}$$

$$V_\Omega = I \cdot r \tag{3}$$

$$V_{act} = k_{act} \ln\left[\frac{I}{I_0} + \sqrt{\left(\frac{I}{I_0}\right)^2 + 1}\right] \tag{4}$$

$$V_{con} = k_{con} \cdot \ln\left[\frac{I_L}{I_L - I}\right] \tag{5}$$

Where $k_{oc}, r, k_{act}, I_0, k_{con}$, and I_L are constants dependent on the electrochemical characteristics of the PEM electrolyzer.

When this model is compared against the I-V curve of an electrolyzer cell subjected to aging phenomena, it does not provide a good fit to the experimental data, suggesting that corrections are needed. A better fit is achieved by introducing an additional aging term, which empirically models a series voltage term with nonlinear dependency on the current:

$$V(I) = V_{oc} + V_\Omega + V_{act} + V_{con} + V_{age} \tag{6}$$

Where

$$V_{age} = \frac{k_{age}}{1 + \gamma \cdot \exp(I)} \tag{7}$$

Here k_{age} and γ are empirical terms introduced to consider the aging effects on the electrolyzer.

3. Experimental setup and model validation

To carry out this work, a commercial-400 W PEM electrolyzer (NMH2 1000 from HELIOCENTRIS) was used and the experimental setup is shown in Fig. 2. Besides, the specifications of the PEM electrolyzer are summed up in Table 1. Since it is a commercial PEM electrolyzer, it includes its own power electronics. Therefore, the power electronic apparatus was removed, providing direct access to the stack and eliminating any filtering or control effects from the power interface. This modification ensured that the intrinsic electrical behavior of the electrolyzer could be directly analyzed. The PEM electrolyzer stack is fed in pure water (featuring a very low conductivity) and electricity from a DC power supply. Stack current and voltage are acquired by using current and voltage probes, respectively.

Figure 3 illustrates the improved model's fit to the obtained experimental data, demonstrating how the inclusion of the aging term effectively considers the degradation effects observed in the I-V characteristics of aged device. Similarly, Fig.

4 presents the fit of the model obtained with another type of device (SHC-300 from Shandong Saikesaisi Hydrogen Energy Co., Ltd) which is a liquid alkaline electrolyzer. Its specifications are given in Table 2. Also in this case, the best fit is obtained with the model that includes the aging term.

In both cases, the experimental data indicate that, as the current increases, the rate of increase in cell voltage is reduced but not zero. The inclusion of this additive term is required to consider the changes in electrochemical behavior due to membrane aging, as the base model (Equation 1) alone is insufficient to describe the shift in the slope of the I-V characteristics both at low voltages and at high voltages. The black-box approach adopted in this study consolidates the overall effects of aging into a single empirical term, making it possible to capture complex degradation mechanisms without requiring explicit modeling of each contributing factor. The formulation of this term enables the model to replicate changes in performance over time, providing a useful predictive tool for assessing the long-term operation of PEM and liquid alkaline electrolyzers.

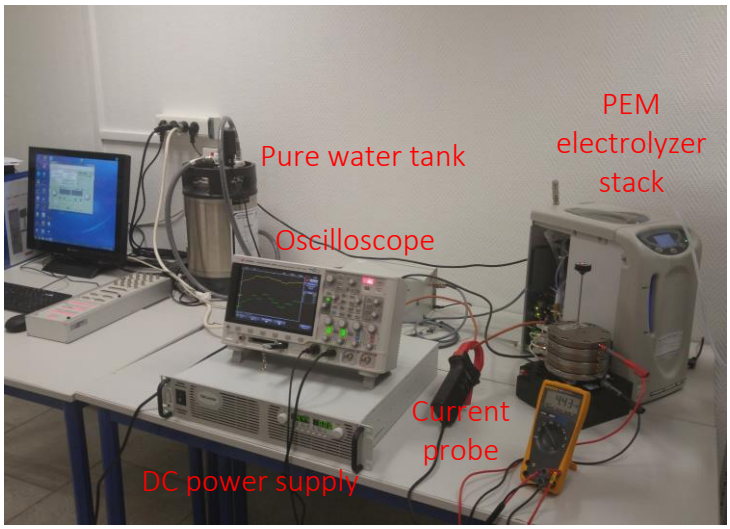

Figure 2: experimental setup implementing the 400 W PEM electrolyzer

Table 1. Specifications of the PEM electrolyzer stack

Parameters	Value	Unit
Rated electrical power	400	W
Stack operating voltage range	7.5-8	V
Stack current range	0-50	A
Delivery output pressure	0.1-10.5	bar
Cells number	3	-
Hydrogen flow rate range	0-1000	$ml.min^{-1}$

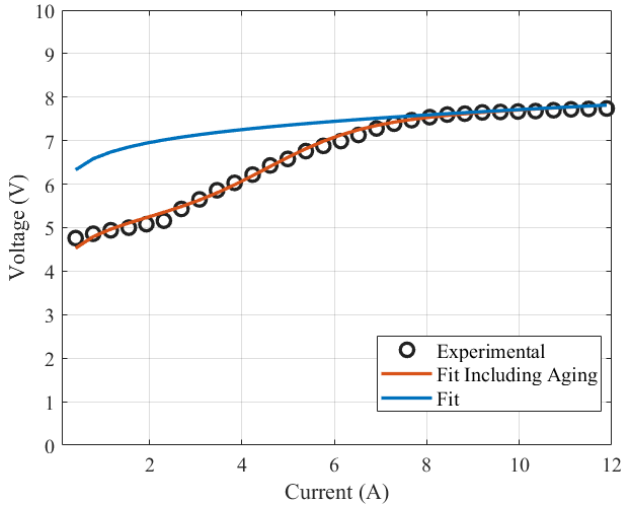

Figure 3: experimental data of the PEM electrolyzer (black circles) compared with the result of the model from (1) (blue line) and from the aged model (7) (orange line)

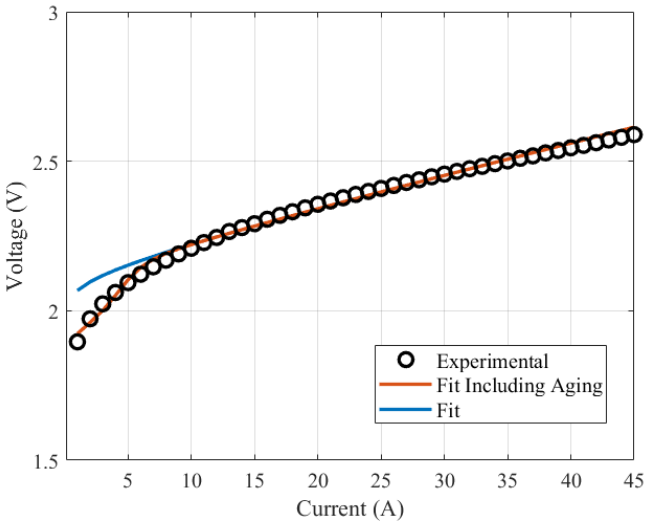

Figure 4: experimental data of the alkaline electrolyzer (black circles) compared with the result of the model from (1) (blue line) and from the aged model (7) (orange line)

Table 2. Specifications of the liquid alkaline electrolyzer stack

Parameters	Value	Unit
Rated electrical power	150	W
Operating voltage range	1.6-2.6	V
Current range	0-45	A
Delivery output hydrogen pressure	0.1-10.5	Bar
Cells number	1	-
Hydrogen flow rate range	0-310	$ml.min^{-1}$
Electrolyte	32 % weight KOH	-

To further validate the model under dynamic conditions, the experimental setup (Fig. 2) was used to observe the transient voltage response of the electrolyzer (see Fig. 5). A step change in current was applied, and the corresponding voltage response was recorded. The results exhibited a first-order transient behavior, where the voltage followed an exponential response with a time constant dependent on the double-layer capacitance (phenomenon appearing between the electrodes and the PEM) of the electrolyzer. It should be noted that membrane degradation influences not only steady-state characteristics but also transient performance, affecting the electrolyzer response time to current variations.

To replicate these experimental observations, the system was simulated using a discretized version of the nonlinear function provided by the proposed model (Eq. 6). The dynamic behavior is described by the following equation:

$$v_{k+1} = v_k + \frac{\Delta T}{\tau} \cdot (V(i_k) - v_k) \quad (8)$$

Where v_{k+1} is the voltage at time step *k+1*, v_k is the voltage at time step *k*, ΔT is the discretization time step, τ is the system time constant, i_k is the current at time step *k*, and $V(i_k)$ is the steady-state voltage calculated from (6) based on the instantaneous current value i_k.

The transient response was computed in MATLAB environment and compared with the measured data. The simulation adequately reproduced the experimental voltage evolution, demonstrating that the model effectively captures the impact of aging on both steady-state and dynamic behavior. The comparison between experimental and simulated results, illustrated in Fig. 5, shows a strong correlation in both the magnitude and time constant of the voltage response.

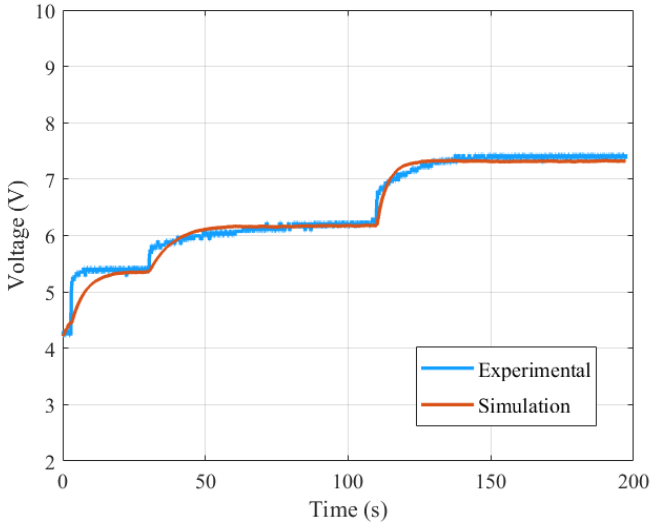

Figure 5: voltage transient of the PEM electrolyzer, experimental data (blue line) compared with the result of the simulation (orange line)

4. Conclusion

This study presents a semi-empirical model for analyzing the aging mechanisms in electrolyzers, with a particular focus on membrane degradation and its impact on overall performance. By introducing a novel empirical aging term into the electrochemical model, this approach successfully captures the nonlinear behavior associated with aging, particularly changes in the I-V characteristics.

The modified model has been validated against experimental data, demonstrating its ability to provide predictive insights into degradation effects. The proposed model not only describes long-term degradation effects in electrolyzers but also accurately predicts transient electrical responses. This aspect is particularly significant for applications where electrolyzers operate under fluctuating sources, such as those powered by renewable energy sources. The validated dynamic response further strengthens the model predictive capabilities, making it a valuable tool for assessing both performance degradation and real-time operational strategies to mitigate aging effects.

Future work could expand this model further by incorporating additional degradation factors and addressing profoundly the dynamic behavior of the electrolyzer. Besides, the influence of fluctuating operational conditions and long-term dynamic inputs could be considered to enhance its accuracy and applicability in real-world renewable energy applications scenarios.

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