






Temperature-dependent Study for Hydrogen Crossover in a Polymer Electrolyte Membrane Used in a PEFC

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Abstract- Significance efforts are underway to improve fuel cell performance, with the Polymer Electrolyte Membrane (PEM) being an essential component of Polymer Electrolyte Fuel Cells (PEFCs). The losses within the PEM can be measured through hydrogen crossover. The temperature is a critical variable that directly affects the hydrogen crossover. In this study, the hydrogen crossover and corrected current density as a function of the temperature in a PEM of Nafion® 212 are analyzed. Linear Sweep Voltammetry (LSV) was the primary technique used in this study. Through this method, the hydrogen crossover is strongly affected by temperature. Specifically, with a rise in temperature from 40 °C to 80 °C, the hydrogen crossover increased by 41%. Furthermore, it was determined that the linear model depicted the best way the trend of the hydrogen crossover as a function of the temperature.

Keywords Hydrogen Crossover, Polymer Electrolyte Membrane, Polymer Electrolyte Fuel Cell, Linear Sweep Voltammetry, Temperature, Current density.

Nomenclature

Abbreviations

PEM	Polymer Electrolyte Membrane	n	Mole number
PEFC	Polymer Electrolyte Fuel Cell	R-squared	Coefficient of determination
LSV	Linear Sweep Voltammetry	RMSE	Root mean squared error
MEA	Membrane Electrode Assembly	F	Faraday constant, 96485 C/eq
CV	Cyclic Voltammetry	U	Voltage, V
EAS	Electrochemical active surface	kWl ⁻¹	Kilowatts per litre
I	Current density, mA/cm ²	I _L	Measured current, A
H ₂	Molecular hydrogen	I _{H2}	Limited current, A
T	Temperature	I _S	Short circuit current, A
N	Hydrogen flux	R _s	Electrical resistance of short, Ω

1. Introduction

Significant efforts are being made around the globe to tackle climate change and global warming, considering renewables and clean energy technologies to change the conventional energy matrix powered by fossil fuels [1]. According to energy demand, energy production for the year 2050 is estimated to be between 30% to 50% of renewable energies. Therefore, part of this production is expected to be using fuel cells. Fuel cells are one of the most innovative electrochemical devices [2], [3]. They use a reaction chemical energy to produce electrical energy [4]. This clean energy production will prevent greenhouse gas emissions because it only needs hydrogen and oxygen/air as reactants, with water and heat as byproducts. Using cogeneration systems in residential areas as another application for fuel cells can significantly improve system efficiency[5]. Studies indicated that this future technology would help to decarbonize the industrial transport and energy sectors [6], [7]. In some years, the new fuel cell generation will move from 4 kWl⁻¹ output passing to 5 kWl⁻¹. However, the target is up to 9 kWl⁻¹ [8].

PEFC can be utilized in numerous applications, such as mobile devices, vehicles, and stationary systems. Extending its operational lifespan to the greatest extent possible is crucial, which may range from 5 000 to 40 000 hours depending on the specific application. However, the longevity of the PEFC is primarily limited by the degradation of the Membrane Electrode Assembly (MEA) during long-term operation. A highly durable polymer membrane is thus a promising approach to increasing the lifetime of PEFC. For instance, chemical and electrochemical degradation can severely affect long-term operation, resulting from the attack of radicals and hydrogen peroxide generated within the cell that reacts with the membrane. By quantifying the hydrogen crossover current density in a polymer membrane, the durability of the PEFC can be assessed. Consequently, it has been evaluated in several studies due to its significant impact on the cell's durability [9].

1.1. Characteristics of PEFC

PEFC uses a solid electrolyte, which offers several advantages, such as a compact structure, simple operation and design, easy manufacture, and minimal corrosion [10]. Regarding operating conditions, PEFCs produce minimal noise, have a short start-up period, are lightweight, and have a high-power density with low temperatures [11]. The temperature explicitly affects each part of the membrane electrode assembly (MEA). Although, each layer in the MEA has its impedance [12].

The proton exchange membrane (PEM) plays a crucial role in the operation of a fuel cell by serving as an ionic conductor, gas barrier, and mechanical support. To avoid high ionic resistance and irreversible damage as part of the main failure effects of the membrane, this must be adequately hydrated. However, studies that evaluated the impact of relative humidity in fuel cells are conscious of affirm that, through numerical results, the water accumulation and flooding can have significant implications for current density production [13]. Other factors, such as gas pressure, humidity, and temperature, also can cause damage to the membrane [14]. For

this research, a Nafion® 212 membrane with a thickness of 50.8 µm was used. A comparative study [15] revealed that different electrolyte membranes require different work cycles. Nafion® 212 can be used for approximately 1200 cycles, while Nafion/SiO₂ can be used for around 2 700 cycles. Moreover, the gas permeation coefficient of hydrogen in Nafion® can be twice that of oxygen, and this indicator can increase as the relative humidity of the membrane increases [16]. Numerous efforts have been made to understand fuel cell lifetime. Simulation models [17] of cell operation have been developed and have verified that the membrane is one of the key factors for good performance.

1.2. Effect of Hydrogen Crossover in Fuel Cell

In the context of fuel cell performance, the phenomenon of hydrogen crossover presents a significant challenge, as it can lead to reduce durability and decreased cell efficiency. Hydrogen crossover occurs when a small number of hydrogen electrons pass through the PEM, causing a loss in performance. Experimental evidence suggests that hydrogen crossover is the most prevalent type due to the significantly higher presence of hydrogen flux than other gases [18]. This phenomenon occurs due to absorption/diffusion/desorption mechanisms that characterize low molecular weight species [19]. Hydrogen crossover can be analyzed through corrected current density. A high corrected current indicates higher values of hydrogen crossover. In this regard, a new membrane with a low hydrogen crossover will have a constant low current density. In contrast, a degraded membrane may present a short circuit, increasing hydrogen crossover levels [20]. The principle of hydrogen crossover is simple the loss of two electrons resulting from the crossover of a single hydrogen molecule is equivalent to the conduction of two electrons from the anode to the cathode. In a system with an operating current density of approximately 400 mA/cm², a fuel crossover current of 1 to 2 mA/cm² could be considered tolerable [21]. This translates to an efficiency loss of 0.25% to 0.5%.

Numerous studies have investigated the factors that influence the rate of hydrogen crossover, including temperature, relative humidity, pressure drop, and current density [22], [23]. The extent to which these factors affect hydrogen crossover depends on the usage time and the specific properties of the PEM material employed. Additionally, the rate of hydrogen crossover can generate secondary effects, such as the amount of heat released in the combustion, which is often linked to the catalytic activity of the PEM [24].

The principle of operation involves the transport of hydrogen from the anodic region to the cathodic region. Although the polymer membrane in the PEFC is designed to be impermeable to hydrogen and oxygen, small amounts of these gases can pass through the membrane [12]. When a direct reaction between hydrogen and oxygen occurs across the membrane, energy is lost as heat [25].

In addition to the mixed potential, gas crossover through the membrane, and internal currents generated by a short circuit, the open circuit behaviour of the fuel cell is also an important consideration. In cells that operate at low current densities, the efficiency losses associated with cycling work are significant, leading to performance losses in the open circuit [4].

1.3. Techniques for Hydrogen Crossover

Multiple methods are available for calculating hydrogen crossover in fuel cells, each with advantages and limitations. The steady-state current density is a simple implementation technique. However, it requires accurate measurement of the anode and cathode current densities, which may be challenging under certain conditions such as high humidity or low current densities. On the other hand, mass spectrometry is a non-electrochemical method but is highly accurate and quantitative in measuring hydrogen crossover. This method requires specialized equipment and needs more time than other techniques. Finally, a mixed process known as differential electrochemical mass spectrometry provides detailed insight into the mechanisms and pathways of hydrogen crossover. However, it also requires specialized equipment and may be subject to interference from other gases in the fuel cell [26].

At last, a method called isotope labeling can be mentioned. It is a powerful technique where control of the labeling process is crucial to analyze isotope ratios. As is the case with the previous techniques, special equipment is a prerequisite [22,23,24]. Each method will depend on the specific goals, requirements, and availability of equipment and expertise. Following our work scope, we have used linear sweep voltammetry.

Currently, a wide range of tests are available to analyze hydrogen crossover in PEFC. Some of the most employed methods include linear sweep voltammetry (LSV), volumetric method, gas chromatography, cyclic voltammetry (CV), and mass spectrometry [29]. Among these, LSV and CV are frequently employed during PEFC evaluation. LSV is typically used to evaluate the electrochemically active surface (EAS), while CV is employed to quantify the level of hydrogen crossover [30].

1.4. Linear Sweep Voltammetry

The LSV involves the introduction of humidified hydrogen through the anode section and humidified nitrogen through the cathode section. A potentiostat is employed to apply a known potential to oxidize the hydrogen crossover in the cathode, which functions as an anode during this process. At the same time, the current density is recorded for each applied linear potential, which is established in incremental steps [31].

1.5. PEFC performance

Operating temperatures strongly influence fuel cell performance and affect several essential factors, including kinetics, catalyst tolerance, heat transfer, and water management. As a result, PEFCs that operate at high temperatures are viewed as the future of fuel cells [4].

Hydrogen crossover is one of the significant challenges which can lead to reduced cell efficiency, cathode potential depression, and the formation of aggressive peroxide radicals [12]. When hydrogen and oxygen directly interact, peroxide radicals can accelerate the degradation of the catalytic layer and the polymer membrane [32].

1.6. Highlights of Hydrogen Crossover in PEFC

The study of hydrogen crossover in fuel cells is significant in the field of materials for this technology. The goal is to

reduce the number of hydrogen molecules permeating the membrane. Accurate measurement of hydrogen crossover is crucial for improving the performance and durability of fuel cells. The literature shows a direct correlation between these two factors, where an increase in temperature can cause degradation of the cell internal components over time. To better understand this relationship, a model was developed to evaluate the effects of temperature on hydrogen crossover in fuel cells [9].

Accordingly, the effective monitoring of hydrogen crossover in polymer membranes is critical in a specific period. Among the electrochemical methods utilized for hydrogen crossover detection, Linear Sweep Voltammetry, Cyclic Voltammetry, and Potential Step method have been employed. Linear Sweep Voltammetry is the most widely used technique due to its flexibility and ease of operation [23].

Understanding how temperature affects hydrogen crossover is essential to optimize fuel cell operation. For this reason, thermal degradation poses a significant challenge in the development and commercialization of fuel cell technology. On the other hand, by studying the relationship between temperature and hydrogen crossover, researchers can gain valuable insight into the underlying mechanisms of fuel cell degradation and develop effective strategies to mitigate it. It is anticipated that this study will lead to improved durability of fuel cells, which will, in turn, enhance their commercial viability. Ultimately, improving the durability of these electrochemical devices is critical for advancing the field of fuel cell technology and promoting the adoption of this sustainable energy source [33].

While other factors, such as relative humidity and pressure gradient, can influence fuel cell performance, temperature is the primary factor contributing to degradation, particularly thermal degradation. Therefore, this research is focused only on the impact of temperature on hydrogen crossover to understand better the catalytic activity inside the fuel cell.

1.7. Relationship with Other Existing Works

There are other studies in which similar techniques have been used to assess hydrogen crossover. In a study [34] a Nafion® 211 membrane was used and evaluated under different conditions. It was found that temperature and relative humidity directly affect the hydrogen crossover through the membrane. A significant reduction in the electrochemical area in the catalytic layer of the cell was observed. The author suggests that the lifetime of the fuel cell is related to the hydrogen crossover. In another gas characterization study, the hydrogen crossover was evaluated using permeability coefficients. Mathematical models were also developed, and comparison showed linear correlations are the best model between current density, partial pressure, and temperature. In this case, a Nafion® 112 membrane was used [20].

The use of the LSV technique as a method of identifying hydrogen crossover can even determine the degree of membrane degradation. A study evaluated pinholes detected and localized by linear sweep voltammetry. In addition, open circuit experiments were used to quantify hydrogen crossover [35]. There are several ways to evaluate the hydrogen crossover. However, we focus only on those of an electrochemical and non-electrochemical nature.

2. Experimental and Methods

2.1. Laboratory equipment

The study was conducted on a Fuel Cell Test System 850e multi-range, allowing the real-time evaluation of PEFC. The system includes a current-load controller, tanks for humidifying the reactant gases, heaters for the anode, cell, and cathode, mass flow controller, and PEFC response meters. An 850 Auto-Multigas valve was used to supply and exchange reactants automatically. Hydrogen was fed at the anode side, and nitrogen was provided at the cathode side. The system also used an 885e Potentiostat to perform linear sweep voltammetry tests to obtain the hydrogen crossover. All the mentioned systems were connected to a computer, which controlled the variables involved in the study using FuelCell software.

Regarding the fuel cell used in this study, Nafion® 212 was part of the Proton Exchange Membrane (PEM). The PEM had an active surface area of 25 cm² and a thickness of 50.8 microns. In addition, the tested cell comprised two gas diffusion layers made of carbon cloth and a catalyst layer with 0.5 mg/cm² of platinum composition.

2.2. Experiment Setup

Before the experimental part, the PEFC systems were purged with nitrogen for 20 minutes to eliminate residual impurities. The output line is evaluated to ensure no obstructions inside the system. The configuration of the parameters for the experiment setup is shown in Table 1. Part of the practice is the assignment of the counter electrode, adjusted to the anode, and the working electrode to the cathode. This configuration was chosen because the reaction occurs more slowly at the cathode. On the other hand, according to previous studies that suggest a low scanning rate

reduces errors in the results [36], the scanning speed was set to 1 mV/s. By applying a voltage sweep, it is possible to obtain a corrected current density that provides information regarding the crossover through the membrane. Fig. 1 shows a flow chart with the steps to be followed before the test is carried out in the fuel cell.

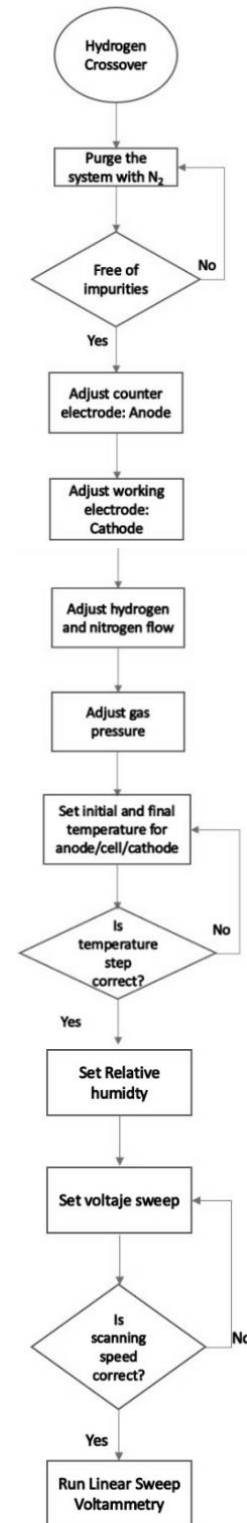


Fig. 1. Flow chart for the experiment setup.

2.3. Corrected Current Density and Hydrogen Crossover

The corrected crossover current density was determined using the linear sweep voltammograms and the methodology

Table 1. Fuel Cell Setup Parameters

Setup Fuel Cell Software	
Hydrogen flow	0.1 l/min
Nitrogen flow	0.1 l/min
Gas pressure	3.79 x 10 ⁵ Pa
Initial temperature anode/cell/cathode	40 °C/40 °C/ 40 °C
Final temperature anode/cell/cathode	80 °C/80 °C/80 °C
Temperature step	10 °C
Relative humidity	100 %
Voltage sweep	0.0 to 0.8 V
Scanning speed	1 mV/s

presented [20]. To obtain I_L , it is necessary to consider the contribution of the limiting current, which occurs at the point where the hydrogen desorption reaction takes place, approximately 0.1 V, and the short-circuit current. Equation (1) includes the limiting current I_{H_2} and the short-circuit current (I_S) to calculate the limiting corrected current density.

$$I_L = I_{H_2} + I_S = I_{H_2} + \frac{U}{R_S} \quad (1)$$

Using the results obtained and equation (2), it is also possible to determine the hydrogen crossover flux, where n represents two eq/mole, the number of equivalents per mol, and $F=96485$ C/eq represents the Faraday constant. Additional details can be found in [36]. Based on the obtained hydrogen crossover values, empirical correlations are proposed to describe the behaviour of the corrected current density and the hydrogen crossover as a function of the temperature.

$$N_{H_2} = \frac{I_L}{n \cdot F} \quad (2)$$

3. Results and Discussion

3.1. Linear Sweep Voltammogram Temperature-Dependent

Five linear sweep voltammetry tests were conducted for a temperature range between 40°C and 80 °C with intervals of 10 °C. The results obtained are shown in Fig. 2, which exhibits a typical behavior of linear sweep voltammetry. The test contains two regions: the low and high potential. The short-circuit current and hydrogen crossover in the low potential region increase with increasing voltage. The second region is entered when the tipping point is reached, where only the short-circuit current experience an increment [31].

Additionally, at elevated temperatures, better and more homogeneous hydration can be achieved [37]. The limiting current I_{H_2} was found to be between 0.9 and 1.4 mA/cm², which appears approximately at 0.1 V and is associated with the hydrogen desorption reaction [23]. After this point, the current increases linearly I_S , known as a short circuit. This process is mainly characterized by a gradual rise in hydrogen

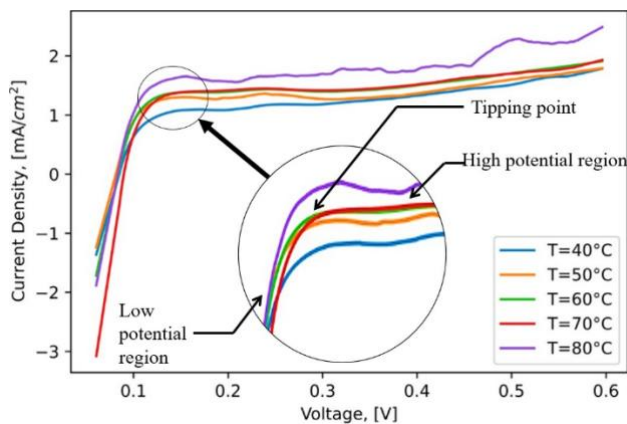


Fig. 2. Linear Sweep Voltammograms for current density temperature-dependent.

crossover as the voltage increases. In the curve corresponding to the temperature of 80°C, noise appeared in the data. The primary cause of the noise observed is water formation inside

the cell [38]. Water comes from the humidification of the gases, and when passing through the PEFC, water condensation is produced. The absorbed water in the membrane lengthens the polymer chain, increasing its volume and allowing for greater hydrogen diffusion.

3.2. Hydrogen Crossover Temperature-Dependent

The trend of the data shown in Fig. 3 indicates that the temperature has a proportional effect on the hydrogen crossover. The permeability coefficient of the gas depends on the temperature, and the diffusion coefficient is affected by the particle's movement. At higher temperatures, the particles have more energy and collide more quickly with the membrane surface, causing an increase in hydrogen diffusion [9, 32]. It is supported by a study where high temperatures strongly affect kinetic reactions, slightly increasing the current density and charge transfer coefficient [31]. However, working at high temperatures accelerates the degradation of the proton exchange membrane as the hydrogen crossover increases each time. Moreover, this increase causes a reduction in the active area of the catalyst [19] and the formation of hydrogen peroxide during cell operation [17].

The current density was between 0.9 to 1.3 mA/cm² for the evaluated temperature range, which is consistent with the values reported in the literature. Reference [20] reported corrected current density values ranging from 0.7 to 2.1 mA/cm² for a temperature range between 25°C and 85°C. Similar results are found by Cheng et al. [12]. Other studies have reported that the hydrogen permeation rate for a new and thin polymer electrolyte membrane is around 1 mA/cm², and for membranes subjected to high load and work rate can exceed 10-20 mA/cm². It should be noted that referring to corrected current density is analogous to hydrogen crossover since both are proportional. However, a high increase in current in a fuel cell reduces the hydrogen concentration on the electrode. Experimentally, the forces involved in the fuel cell, also known as driving forces, are smaller and produce a decrease in hydrogen crossover [39]. It is crucial to indicate

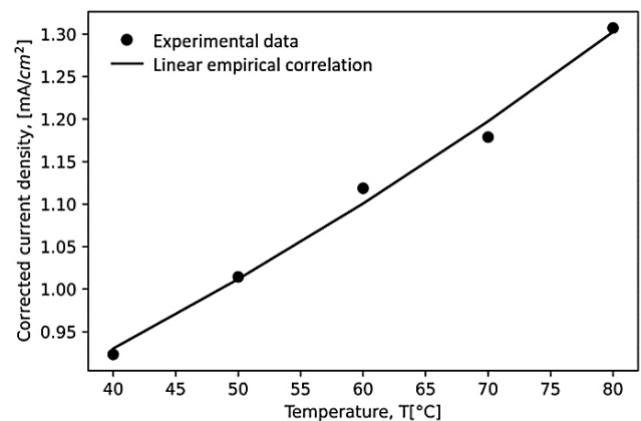


Fig. 3. Corrected current density as a function of the temperature for Nafion® 212

that the results may vary depending on the operating conditions to which the experimentation is subjected. Therefore, the hydrogen crossover rate varies based on the conditions the PEFC membrane is exposed [40]. According to

the collected data, the obtained results follow a consistent growth trend along with the temperature.

Based on the experimental data, this study proposes three correlations to quantify the corrected current density as a function of temperature. The proposed correlations are presented in Table 2. The R-squared and RMSE parameters were analyzed; following these criteria, the model that best describes the data trend is the linear function. It is important to note that the validity of the proposed model is limited to a temperature range of 40 °C to 80 °C under a relative humidity of 100 %. To calculate hydrogen crossover, it is necessary to multiply the obtained correlations by a factor of 5.18×10^{-6} .

R-squared and root mean square error is used to evaluate the accuracy and quality correlations between temperature and current density. R-squared is a measure of the proportion of the variability in the current density that is explained by temperature in the model. It ranges from 0 to 1, with higher values indicating a better fit between the model and data. However, R-squared alone does not indicate the magnitude of the error between the predictions and the data. This is where RMSE comes in; it measures the average difference between predicted and actual values. A lower RMSE indicates a better fit between the model prediction and the real data. The complementary measures are used together to evaluate the accuracy and quality of the correlation between temperature and current density. As a result, the linear model is the best fit for these indicators.

Table 2. Correlations proposed for corrected current density temperature-dependent.

Type of function	Equation	R-squared	RMSE
Linear	$0.009324T + 0.5491$	0.9916	0.01567
Exponential	$0.6641e^{0.00842T}$	0.9912	0.01605
Power	$0.1472T^{0.4948}$	0.9863	0.02004

4. Discussion.

The next generation of studies is focused on addressing issues such as investigating membrane degradation to visualize perforations or fractures that may occur due to the work cycles. On the other hand, we can also address how the ratios obtained would be affected if the effect of relative humidity and the internal fuel Moving on to the area of materials; arduous research is carried out to improve the structure of the membranes and reduce the hydrogen crossover, thus obtaining more commercial fuel cells. Finally, what is currently under review is the impact that hydrogen crossover can have on other fuel cell elements.

Several factors may alter the results regarding the different levels of noise that may be encountered in the data collection. The elements can be internal to the fuel cell or external from low-purity gases or impurities in the system. It is essential to

employ techniques such as filtering or averaging to mitigate the effect of noise on the data. In addition, one must be consistent in collecting the data in an orderly and controlled manner so that noise can be avoided and the experimental phase is reproducible.

5. Conclusion

This study aimed to investigate the impact of temperature on hydrogen crossover through Nafion® 212. The corrected current density was used as a suitable parameter to analyze hydrogen crossover since both are directly proportional. The experimental results revealed that the linear model was the most appropriate for describing the effect of temperature on corrected current density and hydrogen crossover. Moreover, the findings indicated that hydrogen crossover and corrected current density increases with temperature; a 41% increment was observed between 40°C and 80°C. Finally, the study suggests that excessive humidification of the reactant gases may lead to water formation inside the polymer electrolyte fuel cell due to water condensation. The water production can result in noise in the final collected data.

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