

The impact of using a proton exchange membrane on alkaline fuel cell performance

El impacto de la utilización de una membrana de intercambio de protones en el rendimiento de pila de combustible alcalina

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ABSTRACT: A hydrogen fuel cell was designed in the laboratory, operating in potentiostatic mode (1 V, 1.23 V, 1.5 V and 5 V), obtaining characteristic parameters that allow improving hydrogen production by means of electrolysis. For this, a proton exchange membrane, Nafion 117, was adapted, which was subjected to an activation pretreatment, allowing us to compare its performance and function. Values for current density, degree of conversion, mass transfer coefficient and hydrogen flow generated in an instant (t) were obtained.

RESUMEN: Se diseñó una celda combustible de hidrógeno a nivel de laboratorio, operando en modo potenciostático (1 V, 1,23 V, 1,5 V y 5 V), obteniéndose parámetros característicos que permiten mejorar mediante una electrólisis la producción de hidrógeno. Para esto se adaptó una membrana de intercambio protónico, Nafion 117, la cual fue sometida a un tratamiento previo de activación, permitiendo comparar su funcionamiento y rendimiento. Se obtuvieron valores de densidad de corriente, grado de conversión, coeficiente de transferencia de materia y caudal de hidrógeno generado en un instante (t).

1. Introduction

Experimental electrochemical techniques for the study of electrode materials consist of measuring the system response to an imposed electrical signal (potential or current). The electrical signal disturbs the equilibrium state of the system and the resulting behavior is the answer, whose detection provides information about the properties of the system. The disturbance of the balance of an electrochemical system is achieved by varying electrode potential, the passage of electric current or by any excitation method such as changes in pressure, temperature, variation of electro-active species, etc. In general, a variation of the potential or the application of a current is used and the system responds to these disturbances with behavioral changes that may be followed by changes in the circulating current, electrode potential or the associated load [1, 2].

With this study, a fuel cell is characterized at laboratory level in potentiostatic conditions using preactivated steel electrodes coupled with and without a Nafion117 membrane, determining electrochemical parameters such as the current density, the working potential, the degree of conversion, the hydrogen flow rate and the production thereof in a given time.

2. Methodology

To evaluate the performance of the hydrogen fuel cell, preactivated steel (Pb-Sn 5%) electrodes were used for a period of 3 days in 1M H_2SO_4 solution to form an oxide film on the surface thereof, allowing better electrical conductivity and protecting it from corrosion as well [3, 4]. The steel anode consists of two steel plates, each with a surface of 73 cm^2 . A proton exchange membrane was used, Nafion 117, with a surface of 36 cm^2 , previously activated by four baths, each for an hour at a constant temperature between 70-80 ° C [5, 6].

Figure 1 shows the electrodes according to the design of the cell. Deionized water was used with 0.2 g KOH of 96% purity; and the total volume of the cell is 1000 cm^3 (1 L) and when performing the experiment 3 cm^3 of deionized water were used.

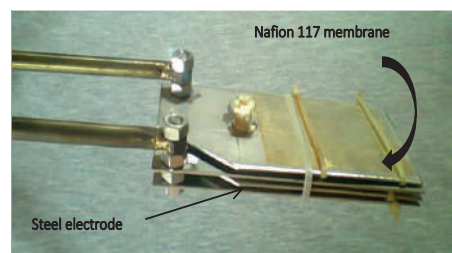


Figure 1 Steel electrodes with Nafion 117 membrane

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The electrodes are connected to a Interface 1000 Gamry potentiostat, trials were carried out at constant potential difference (potentiostatic mode) of 1 V, 1.23 V, 1.5 V for a period of 10 minutes and continuous samples were taken to determine the concentration and the variation of the volume of water within the cell [7, 8]. Figure 2 shows a photograph of the equipment configuration used. All assays were performed at 25 °C.

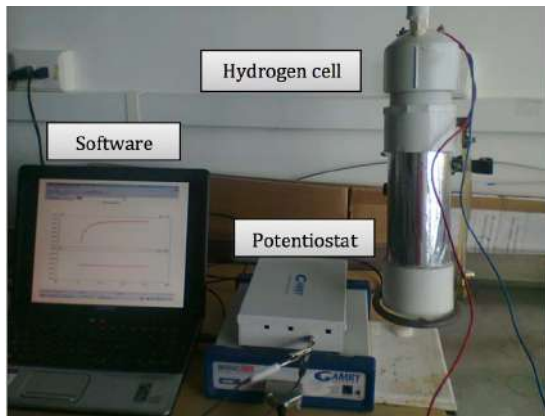


Figure 2 Photograph of the measurement setup

3. Results and discussion

In Figure 3, the current density in potentiostatic mode for 1, 1.23 and 5 V is shown when the Nafion 117 membrane is not used.

It can be seen that the potential applied to the cell is directly proportional to the current density, this means, as the potential increases, the current density does too. Following the parameters set by the electrochemistry, high current densities do not favour energy efficiency, so in this experiment the potentials at 1, 1.23 and 5.0 V, allow us to obtain higher energy efficiency [9, 10].

Figure 4 shows the current density when the coupled hydrogen fuel cell with the Nafion 117 membrane is used.

A similar behavior was evidenced in Figure 3, where the current density increases as the working potential is increased; from the above, we can determine that the optimal working potential in potentiostatic conditions with or without Nafion 117 membrane is 1 V [11]. It is evident that Figures 3 and 4 show a behavior in which as the applied potential increases, the current also increases.

3.1. Optimal working potential

The cell voltage depends on the current density (current / surface of the electrodes) and the lower it is, the lower the voltage that has to be applied to the cell [12].

In Figure 5 current density is shown, operating at 1 V with and without Nafion 117 membrane, showing a similar behavior.

It was observed that the current density is lower when the polymer (Nafion 117) is used, this is due to chemical pretreatment conducted to the membrane, which contributes to good moisture and the activation of the sulfonic groups it presents [13, 14].

From the foregoing, it can be determined that the electrolyte has properties that favor mass transport in the electrode surface, for generating low current densities favoring increased energy efficiency; such decrease of current density is related to the use of low potentials [15, 16].

The separation between the electrodes is another factor that greatly influences the energy efficiency, because a separation of more than 3 mm in the electrodes causes increases in the current density; this was experimentally checked.

In these devices where a process of reduction of water to hydrogen by electrolysis is carried out, it is observed that the optimal working potential tends to decrease when the process is put into practice, since the difference of theoretical potential reached this class of devices that operates below 100 ° C is 1.23 V [17, 18]. To prevent electrochemical overpotential, special catalysts are required, including those of ruthenium, that have good properties. Although greater efficiency at high temperatures is obtained, no tests were conducted, due to the lack of proper equipment.

3.2. Degree of conversion

For a hydrogen type proton production cell (PEM), operating at maximum reaction rate, meaning at such potential that the current density is no less than the limiting current density, conversion of the reactive species (deionized water) increases exponentially over time and depends on the mass transfer coefficient k and the specific area of the electrode a , as shown in Eq. (1).

$$X(t) = 1 - e^{-ka_e t} \quad (1)$$

Where, k (s^{-1}) is the mass transfer coefficient; a , is the specific area of the electrode and t is time (s) [19, 20].

Figure 6 shows the evolution of the degree of conversion using hydrogen fuel cell with and without Nafion 117 membrane.

The degree of conversion in a fuel cell with a Nafion 117 membrane is greater than the one without it, this is due to the total current consumed by the cell, it also favors the reaction speed of the applied work potential. A factor in increasing the reaction rate and therefore in increasing the degree of chemical conversion was the pre-treatment performed to the Nafion 117 membrane, proving that the proton exchange done by the hydrophilic part of the membrane (sulfonic acid group) was conducted easily [20, 21].

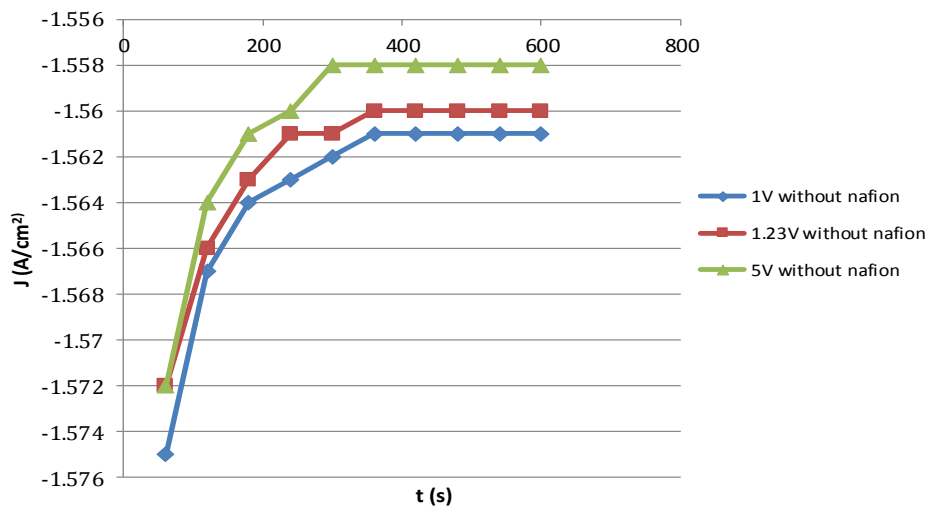


Figure 3 Current density versus time in potentiostatic conditions without Nafion 117

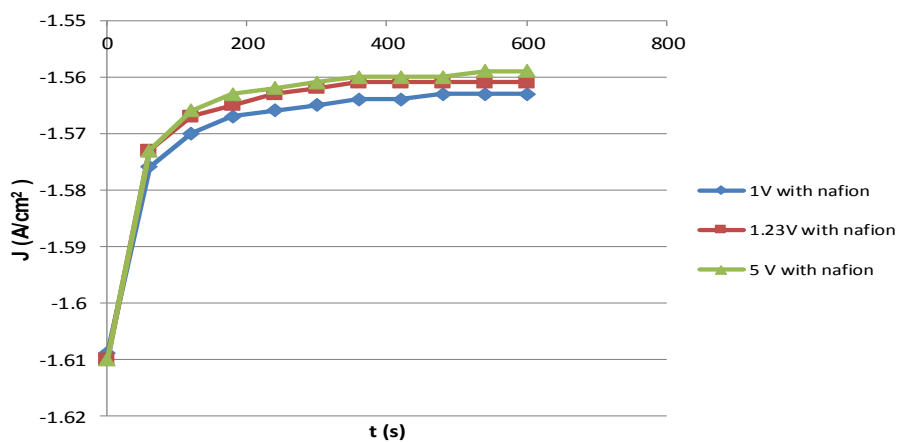


Figure 4 Current density vs time with Nafion 117 under potentiostatic conditions

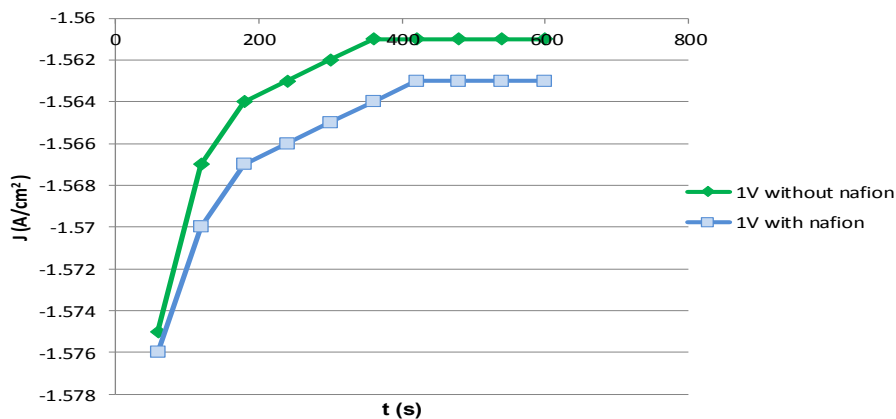


Figure 5 Current density vs time with and without Nafion 117 under potentiostatic conditions

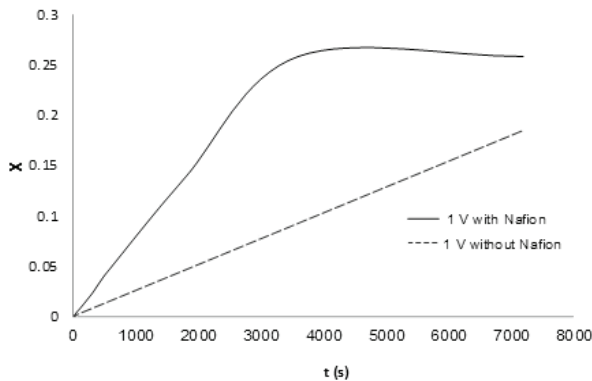


Figure 6 Degree of conversion for a prototype hydrogen PEM cell with and without membrane Nafion117

In the graph, it can be seen that the conversion degree in a cell membrane possessing Nafion 117 is between 25-30% and varies with time. Although the values are relatively low, these are normal for this type of device and it is due to saturation of water by the polymer. This means that the proton conductivity of the Nafion membrane is best when there is sufficient hydration [15, 22-24].

It is noted that Figure presents a level close to 28% conversion and then decreases maximum, indicating that the calculated coefficient k can undergo variations not affecting the electrochemical process.

3.3. Mass transfer coefficient

From the representation of $\ln(1-X)$ versus time, the mass transfer constant k is determined, as shown in Figure 7 for a working potential of 1V.

k values of $1.14 \times 10^{-6} \text{ s}^{-1}$ were obtained when the fuel cell Nafion 117 membrane is used and 3.8×10^{-7}

s^{-1} when operated without it.

From the adjustment of the experimental data for the potential of 1V it was evident that the coefficient of matter is greater in a hydrogen-producing cell with a Nafion 117 membrane, showing that the current distribution is more homogeneous and there is low ionic migration. This increase of the mass transfer coefficient, matches the use of Nafion 117 membrane and with the decrease of the current passing through the circuit with the applied voltage, thus being linked to higher gas bubble generation, which facilitates the transfer of material to the electrode surface and the activation process of the sulfonic groups of the polymer with the 2 M sulfuric acid solution [12, 25]. This is demonstrated by the large amount of hydrogen generated in the process of electrolysis.

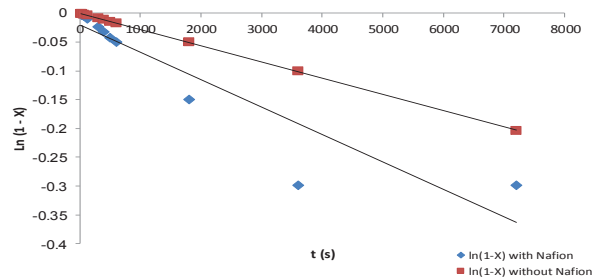


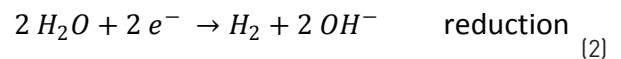
Figure 7 Schematic presentation of the method for determination of mass transfer coefficient, k

3.4. Hydrogen production

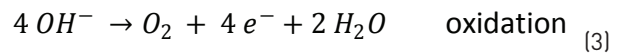
The volume of the hydrogen generated in the fuel cell was determined. The Nafion 117 membrane in addition to driving protons (H^+) also plays an important role in the separation of hydrogen and oxygen in the hydrogen fuel cell [25], shown by the amount of hydrogen generated in the research.

Since the hydroxide aqueous solution used as supporting electrolyte has a $\text{pH} > 7$, the half reactions occurring at each electrode are as follows. Below are shown in the following Eqs. (2), (3) and (4):

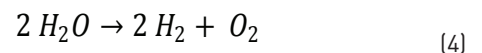
Cathodic reaction.



Anodic reaction.



Overall reaction.



The hydrogen produced in the fuel cell prototype was accumulated in water for it to be possible to calculate its volume, with a high yield, but is very susceptible to contamination by CO_2 , which presents a disadvantage for an application on an industrial scale. The studies were performed at constant temperature (300 K), applying Henry's law [9, 13], as shown in Eq. (5):

$$M = K P \quad (5)$$

Where P is the partial pressure of the gas in equilibrium with the solution (mm Hg) and M is the molar concentration of dissolved gas in the liquid phase, K ($7.8 \times 10^{-4} \text{ M / mmHg}$) is known as Henry's constant and depends on the solute and solvent and temperature. M is the molar concentration

of gas, which in this case is hydrogen, K is the Henry constant is equivalent to $(7.8 \times 10^{-4} \text{ M} / \text{mm Hg})$ and P is the partial pressure of hydrogen, equivalent to 0.0104 atm (7.94 mm Hg).

The total volume of generated hydrogen is 14.66 L . According to Henry's law, due to the amount of deionized water spent being equal to only 3 cm^3 in 10 min ; 43.99 cm^3 was generated at a rate of $4.39 \text{ cm}^3 / \text{min}$ [15, 21]. Table 1 shows the results obtained.

Table 1 Estimated volume of hydrogen generated

| Volume | L, cm^3 |
|---|----------------------|
| Total volume of hydrogen generated (L) | 14.66 L |
| De-ionized water usage (cm^3) | 3 cm^3 |
| Hydrogen production in test (cm^3) | 43.99 cm^3 |

3.5. Hydrogen production in an instant (t)

To find out hydrogen production from the initial instant to a time t ; the hydrogen flow rate up to said instant is integrated, as reflected in Eq. (6) and shown in Figure 8 [14].

$$V_{H_2} = \int_0^t m_{H_2} dt \quad (6)$$

V_{H_2} hydrogen volume in cm^3 , m_{H_2} is the hydrogen flow rate ($4.39 \text{ cm}^3 / \text{min}$) and t is time in minutes.

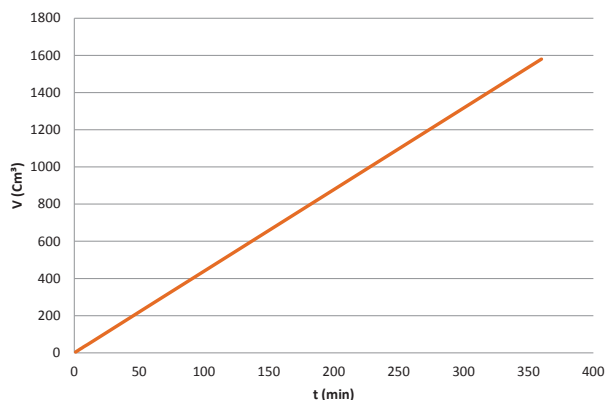


Figure 8 Generated hydrogen volume vs time

The volume generated by the hydrogen production cell is linear with respect to time indicating that hydrogen production is high at a laboratory scale, which can be an inconvenient at the time of storage, since adequate tanks for handling it must be present, where no blasting is possible.

4. Conclusion

The Nafion 117 membrane allows for the current distribution to be more homogeneous and for there to be low ionic migration in a cell for producing hydrogen, with the possibility of checking the calculated material coefficient.

The degree of conversion in a hydrogen production cell with a Nafion 117 membrane is greater, resulting in a 25% - 30%, indicating that the polymer can generate hydrogen with high purity.

The Nafion 117 membrane allows the decrease of current densities; it can benefit small working potential and low current, supporting energy efficiency of the cell.

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