

TEMPERATURE IMPACT ON THE INTERNAL RESISTANCE OF A PEFC CONSIDERING THE ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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ABSTRACT

When coupled to different applications, a polymer electrolyte fuel cell (PEFC) work at a different operating temperature. In this study, the internal resistance of a PEFC is evaluated by using Electrochemical Impedance Spectroscopy (EIS) at moderate low current density, i.e., 0.5 A/cm², in the range of 40 – 80°C. The evaluation is carried out considering frequencies between 10kHz and 0.1Hz. An equivalent Randle circuit model is considered and the Nyquist and Bode diagram were obtained. Results show that the ohmic resistance and charge transport at low frequencies increase when the operating temperature is low, while the double layer capacitance increase at high temperatures.

Keywords: Electrochemical impedance spectroscopy, Temperature, Internal resistance, Membrane electrode assembly, Nyquist diagram.

1. INTRODUCTION

A polymer electrolyte fuel cell (PEFC) is an electrochemical device that convert the chemical energy present in the fuel into electrical energy and water in a clean and noiseless way [1]. Due to its modularity and adaptability, this type of fuel cell has gained research attention during the last years from experimental and modelling point of view [2, 3].

Several phenomena that occur inside a PEFCs during the energy conversion process such as the mass diffusion

and charge transport are carried out at different length and time scales simultaneously. The diffusion and transfer effects are affected when a fuel cell is analyzed at different frequencies [4]. The electrochemical impedance spectroscopy (EIS) arises as a powerful non-invasive technique used to analyze the individual effects and the internal losses in each process. The losses are originated by the resistances found in the constitutive elements of the cell. In general, the most significance losses originates from the ionic resistance of the membrane, the electron transport resistance in the layers and the contact resistances [5].

The EIS technique obtains the response of the cell when a signal perturbation of AC current is applied to an electrode. The response is evaluated in a wide range of frequencies allowing us to compute the real (*Re-Z*) and the imaginary (*Im-Z*) compounds of the system impedance. The magnitude and phase angle of the current are also evaluated in a Nyquist diagram. The analysis is supported by Randle's equivalent simplified circuits for the anode and the cathode, connected in series to a plane resistance emulating the membrane [6, 7].

An EIS gives detailed information that allows us to enhance the functions of a fuel cell. The enhancement can be achieved by optimizing the structure of the membrane electro assembly (MEA), optimizing the operating conditions, measuring the resistance of the fuel cell layers, studying the poisoning effects, etc. [8].

Several studies on internal resistance of a PEFC, that evaluates different current densities tells that the bigger transport and charge losses occur at the cathode electrode related to the oxygen reaction reduction (ORR) [9][10]. However, there is very few studies on the analysis at lower temperatures [11].

The objective of this study is to analyze the behavior of the internal resistance in a PEFC with a Nafion 212® MEA. The study is carried out evaluating different temperatures by means of the EIS technique.

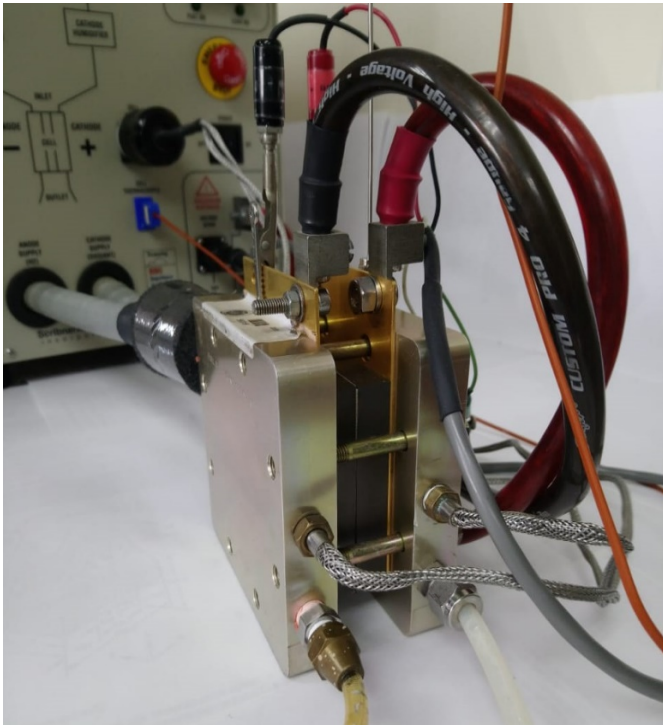


Fig.1. Single PEFC and data acquisition hardware used in this study

2. EXPERIMENTAL AND METHODS

2.1 Fuel Cell Test System

The current study is carried out using a fuel cell test system to evaluate the PEFC. This system allows us to obtain the operating parameters in real time. It contains flow controls, humidifier tanks, electrical heater loads with their respective control temperatures for the anode/cathode/cell. The frequency response is evaluated with a frequency response analyzer (FRA). For more detailed information readers are referred to [12].

2.2 Single Cell Hardware

The cell is formed by a chromium-beryllium framework with an effective area of 25 cm². The graphite end-plates have triple serpentine channels type with a width and depth of 1mm (for both). The MEA is the so-

called five layer in which all the layers form a unity. The electrolyte is a polymer membrane Nafion® 212 with a thickness of 50.8 μm. The Nafion membrane is covered by to catalyst layers with 60wt% of platinum nanoparticles, on order to enhance the electrochemical reactions. At both sides, two gas diffusion layers of woven carbon cloth with MPL - W1S1005 are placed.

2.3 Operating parameters

Ultra-pure hydrogen was used as fuel while, medical oxygen was employed as oxidant. During the purging period nitrogen was used. The inlet pressure for the gases was established at 3.79x10⁵ Pa and the water for humidification is ASTM type I (minimum resistivity 18 MΩ/cm). All the impedance tests were carried out varying the inlet temperature of the reactant gases and of the cell from 40 to 80°C in steps of 10°C. The relative humidity was established at 100% and gas flow was configured at 0.14 SLPM for hydrogen and 0.73 SLPM for oxygen. Both gas flows were set according to [4].

2.4 Impedance Measurement

The EIS test was carried out by using the FRA, which is a test system available in the fuel cell test system. The frequency sweep moves from 10 kHz to 0.1 Hz in a logarithmic scale obtaining ten data per cycle. The integration time was 0.3 s with one cycle per integration. The amplitude of the employed alternating current (AC) was of 5% of the established direct current (DC). In the current study, a DC current of 0.5 A/cm² was used.

2.5 Mathematical Model

There are several models to analyze the response to the EIS tests, however the most widely model used is the one related to equivalent circuits [13][14]. The model for the current study is the so-called Randle, which consists of an electrical resistance connected in series (R_s) with a parallel circuit ($R_{ct} - C_{dl}$) in an electrochemical half-cell. R_s represents the cell ohmic resistances, R_{ct} corresponds to the charge transfer resistance in the electrolyte/electrode interface. Additionally, a constant phase element (CPE) is considered for this analysis which is represented by the double-layer capacitance of the system (C_{dl}). Finally, a low frequency resistance (R_{lf}) is associated to the system. In Figure 2, a description of the equivalent system is presented and the related correlations to determine the parameters are presented. Also, a brief physical description of the Nyquist diagram is added.

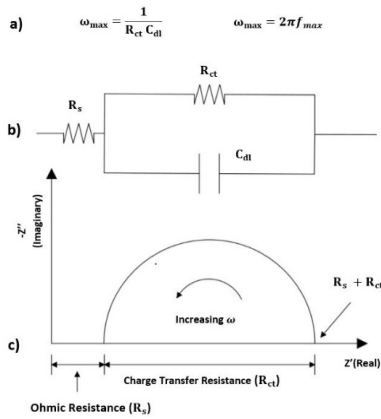


Fig.2. a) Equations to correlate the frequency, resistance and capacitance. b) Equivalent circuit of Randle for a half-cell. c) Complex plane representation of the impedance data.

3. RESULTS AND DISCUSSIONS

The obtained impedance results are presented in a Nyquist diagram in Figure 3 (left side), and their corresponding bode diagram are also included (right side). The impedance is also evaluated at different temperatures and presented in Table 1. Considering Figure 2c, the cell ohmic resistance (R_{ohm}) is localized in the intersection of the curve with the axis Re-Z from the Nyquist diagram at high frequency, which is related to the resistance of the Nafion®212 membrane. Taking into account that the contributions of the other cell components are at a minimum.

It is observed that when the operating temperature of the cell decreases, the ohmic resistance increases producing a decrement in its performance. For a constant current density of 0.5 A/cm², there is a ohmic resistance change of 23.3 mΩcm² when the temperature changes from 40 to 80°C. It was observed that when the temperature varies according to the mentioned range, the operating voltage increases from 0.710 to 0.752 V, i.e., the voltage drop in R_s varies in 12 mv. However, in the second column from Table 1, it is observed a voltage change of 42 mV; this voltage drop difference is originated by the charge and mass effects.

On the other hand, the charge-transfer resistance (R_{tc}) in the electrolyte/electrode interface is the sum of the charges transfers due to hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) at the anode and cathode, respectively. According to Figure 2c, it is possible to estimate the mentioned resistance as the distance between the intercepts in the horizontal axis from the Nyquist diagram. It is observed, according to Table 1, that the R_{tc} increases when the operating temperatures is low. This is mainly due that at low

temperatures the reaction rate of the electrode is low and the kinetics of the ORR is reduced. The ORR is much slower than the HOR, and therefore the losses in the cathode are bigger than the losses in the anode. The maximum transfer charge resistance was of about 21 mΩcm² when the temperature is changing from 40 to 80°C for a current density of 0.5 A/cm².

The mass transport effects that occur in the low frequency side can be neglected due to that the experiment was carried out at a moderate low current density and only one cell was analyzed. Therefore, for the conditions established in this experiment, most of the total resistance of the cell is due to the resistance of the charge transfer reaction. If a larger number of cells is analyzed and higher current density values are considered, the mass transport effects appear as mentioned by Zhu et al. [5] and Yuan et al [15]. For the mentioned reason, the spectrum shown in Figure 3 (left side) has a single high-frequency arc which agrees with the equivalent circuit in Figure 2(b).

According to the equivalent circuit, C_{dl} is obtained with the charge transfer resistance and the frequency at the maximum capacitive reactance by using the equations in Figure 2(a). For more detailed information about C_{dl} , the reader is referred to [16].

According to the obtained results, at higher temperatures the system has higher values of C_{dl} in comparison with at low temperatures. This C_{dl} is associated with activation polarization according to Sudarshan [17]. Due to the higher values of C_{dl} the operating density current range increase. Finally, the Bode diagrams shows the variability of the data as a function of the frequency. It is noticeable that at low frequencies the system increases the total impedance. However, the performance at 80°C is superior to that at 40°C, as shown in Fig. 3 (right). It is also possible to observe that the inflexion point of the magnitude occurs in the vicinity of the maximum offset angle.

Table 1. Summary of H₂/O₂-PEFC properties as a function of temperatures anode/cell/cathode at 1.2x H₂/2.5 O₂, 3.79x10⁵ Pa, 100% RH, 0.5 A/cm².

Operating Temperature [°C]	Operating Voltage [V]	R_s [Ωcm ²]	R_{tc} [Ωcm ²]	R_{if} [Ωcm ²]	C_{dl} [F]
40/40/40	0.710	0.1038	0.132	0.236	0.0152
50/50/50	0.743	0.0956	0.120	0.215	0.0168
60/60/60	0.750	0.0882	0.116	0.204	0.0173
70/70/70	0.755	0.0840	0.111	0.195	0.0228
80/80/80	0.752	0.0805	0.115	0.195	0.0220

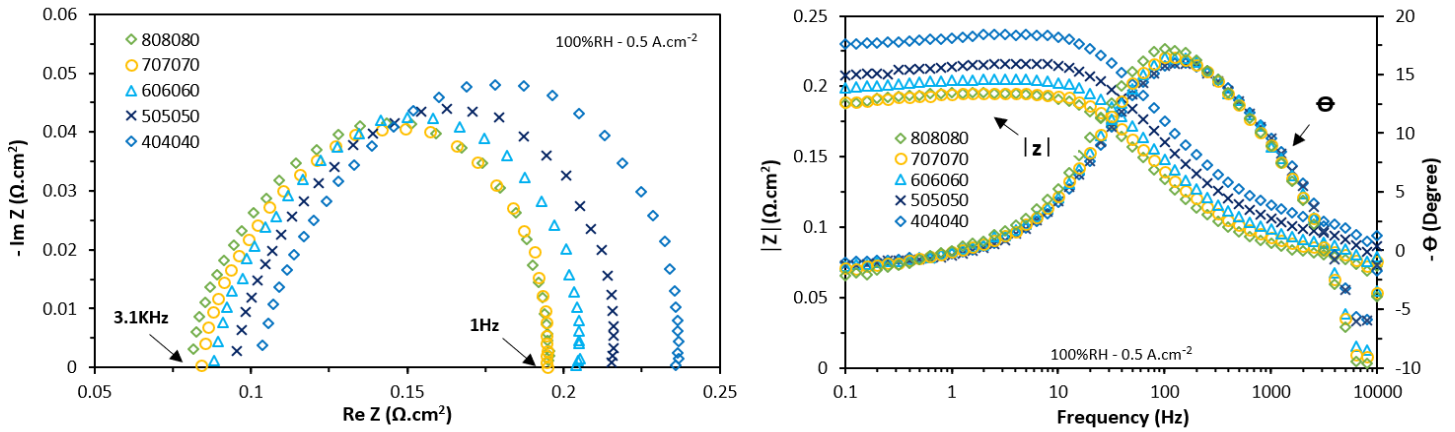


Fig. 3. Left: In situ AC impedance spectroscopy. Right: Bode diagrams for the impedance magnitude and phase angle. Both: Results at different temperatures for the range 10kHz to 0.1Hz at 0.5A/cm² with 100 %RH.

4. CONCLUSIONS

The electrochemical impedance spectroscopy was applied to a Nafion 212 membrane PEFC. A range of temperatures of 40 – 80°C, was considered, and it is concluded that the ohmic resistance, transfer charge resistance and the resistances at low frequencies increase at low temperatures. This is due to the slow kinetics of the oxygen reduction at the cathode side. The double layer capacitance increases at high temperatures, due the low resistances associated to the membrane. On the other hand, the total impedance of the system decreases at high frequencies, while the maximum value appears at low frequencies.

ACKNOWLEDGEMENT

The authors kindly acknowledge the financial support from FIMCP-CERA-05-2017. In addition, Åforsk project No 17-331 is gratefully acknowledged.

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