Characterisation of fuel cell state using Electrochemical Impedance Spectroscopy analysis

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Abstract

One of the most demanding research topics related to the Polymer Electrolyte Membrane Fuel Cell (PEMFC) concerns its reliability. Apart from the security aspects, it is basic to have a diagnosis of the internal state of the PEMFC in order to correct and optimise its operation.

The Fuel cell state and response depends on the imposed operating conditions, which are mainly given by temperatures, pressures, humidity, reactants concentrations and current.

This work explores the use of fuel cell experimental Electrochemical Impedance Spectroscopy (EIS) as a tool to characterise the fuel cell state, what can be very helpful for diagnosis purposes. With this objective in mind, a definition of "relevant characteristics" extracted from EIS response is done. "Relevant characteristics" can be used in order to characterize the fuel cell and also to find the parameters of simple equivalent circuits of its dynamical response. Besides, a complete equivalent circuit which permits a close fitting of the EIS response for all operating conditions is proposed and its evolution with operating pressure is studied.

1. Introduction

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EIS is a powerful characterisation technique for investigating the mechanisms of electrochemical reactions, measuring the dielectric and transport properties of materials and to explore the properties of the porous electrodes (MacDonald et al. [1]).

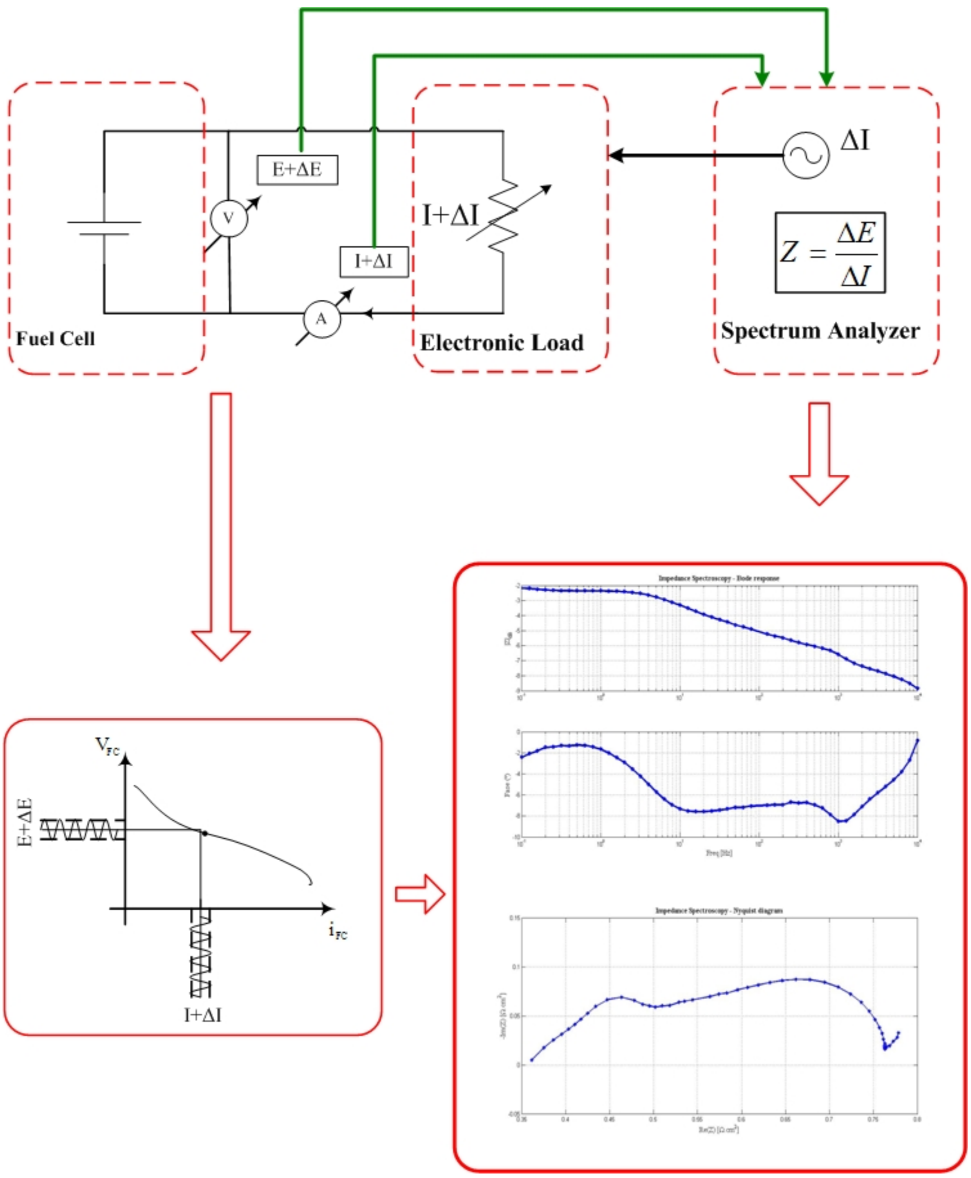


Figure 1 – EIS implementation and frequency response

EIS studies the system voltage response when a small amplitude Alternative Current (AC) load current, added to a base Direct Current (DC), is imposed to the system. The relationship between the resulting AC voltage and the AC imposed current sets the impedance of the system and is presented as a frequency response plot in Bode or Nyquist form (see figure 1).

The EIS characterisation technique has been used in different fields, including the fuel cell (see Paganin et al. [2] and Bautista et al. [3], Wagner et al. [4] and Diard et al. [5]). The power of this technique arises from: (i) it is a linear technique and the results are readily interpreted in terms of Linear System Theory, (ii) if measured over an infinite frequency range, the impedance contains all the information that can be gleaned from the system by linear electrical perturbation/response techniques, (iii) the obtained data can be analysed using frequency analysis tools and (iv) the experimental efficiency, defined as amount of information transferred to the observer compared to the information produced by experiment, is really high.

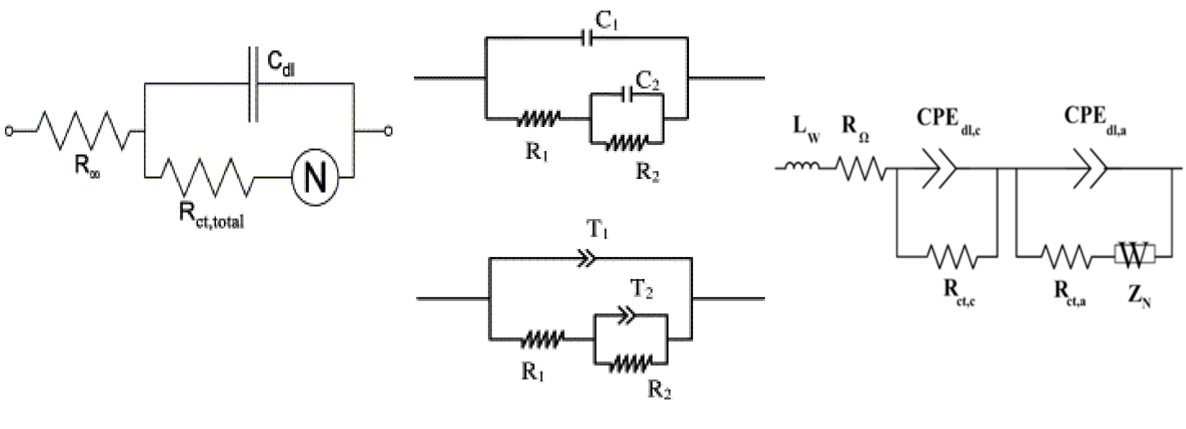
Many authors have studied a modelisation philosophy based on the search of electrical circuits, named “equivalent circuits”, consisting of an arrangement of different electrical components and having the same frequency response than the obtained by EIS tests (see Macdonald et al., 2005 [6]). Some works present equivalent circuits using electrical elements: like resistance (R), capacitance (C) or inductance (L). But other works use additional distributed elements that represent electrochemical or mass and ionic transport phenomena. For example, Warburg impedance represents the impedance of one-dimensional distributed diffusion of a species in an electrode. Another example is a Constant Phase Element (CPE), used for describing a distributed charge accumulation on rough irregular electrode surfaces (see table 1). The different components and parameters of the equivalent circuits often have an easy correspondence with the characteristics and behaviour of a real system. However, to obtain this correspondence can be a complicated task. In this work, this task is developed for a specific simple equivalent circuit.

Andreaus et al. (2002 [7], 2004 [8], see figure 2 (a)) have proposed a model of a fuel cell behaviour by means of an equivalent circuit that uses the following elements: R_{∞}, assumed to be the membrane resistance (estimated from high frequency resistance of EIS tests), $R_{ct,total}$, modelling the charge transfer resistance, C_{dl}, the double layer capacitance and N, the Nernst impedance (Warburg element) related to the mass transport limitations. Apart from the membrane resistance R_{∞} estimated value, in the work it is not detailed how the other parameters are obtained.

Table 1 – Typical elements and transfer functions used on equivalent circuits

Element	Transfer Function
Resistance	Z(s)=R
Capacitance	Z(s)=1/(s.C)
Inductance	Z(s)=s.L
Constant Phase Element (CPE)	$Z(s)=1/(s.C)^P$
Warburg	$Z(s) = R_w /(sT)^P .\tanh ((s.T)^P)$

Ciureanu et al. ((2001) [9] and (2003) [10], see figure 2 (b)), propose several models to describe the fuel cell behaviour. In this case, they start with a resistance and two parallel *RC* circuits in series with the ohmic resistance. C_1 is the double layer capacitance, R_1 is the charge transfer resistance, R_2 and C_2, stand for the diffusion process. Introducing a variation of this circuit, they replace the capacitors (C_1 and C_2) with CPE elements, because in a porous electrode, the capacitance due to the double layer charge is distributed along the



(a) Andreaus (b) Cireanu (c) Schiller

Figure 2 – Equivalent Circuit models

length of the pores. All parameters are obtained from EIS curve fitting software.

Schiller et al. ((2001, a) [11], (2001, b) [12], see figure 2 (c)), propose a model that represents the impedance response of a fuel cell during normal operating conditions. In this model, L_W is an inductance attributed to wiring, R_m is the membrane resistance, $CPE_{dl,c}$ and $CPE_{dl,a}$ are the approximations of the double layer capacitances at the cathode and anode, respectively. $R_{ct,c}$ and $R_{ct,a}$ are the charge transfer resistances associated with the cathode and anode reactions. Finally, the Nernst impedance (finite Warburg element) Z_N is used to represent the finite diffusion impedance. The adjustment of the equivalent circuit elements is done using a specific curve fitting algorithm.

In this work, the experimental setup description and the results obtained for different operating conditions are displayed in section 2. "Relevant Characteristics" definition is presented in section 3, and also, a procedure for obtaining these relevant characteristics when the operating pressure varies. In section 4, a simple equivalent circuit is presented and the procedure for the parameters determination from relevant characteristics is detailed. Also, a complete equivalent circuit is proposed and the evolution of its parameters is studied.

2. Experimental setup and results

In this section, the experimental setup is described and a brief description of the fuel cell system is also done. Then, the procedure of EIS tests is detailed and the experimental results for different operating conditions variations are showed.

2.1. Experimental setup description

To study the fuel cell response with EIS technique, different operating conditions were imposed to the fuel cell: current, temperature, pressure and relative humidity conditions. All tests were performed on a fuel cell with the following characteristics: Electrochem EFC05-01SP®, single fuel cell with 5 cm^2 of active area, 3 channels and 5 pass serpentine flow pattern, a membrane assembly with Nafion™ 115 and 1 mg Pt /cm^2 and Toray carbon fiber paper "TGP-H-060" as gas diffusion layer.

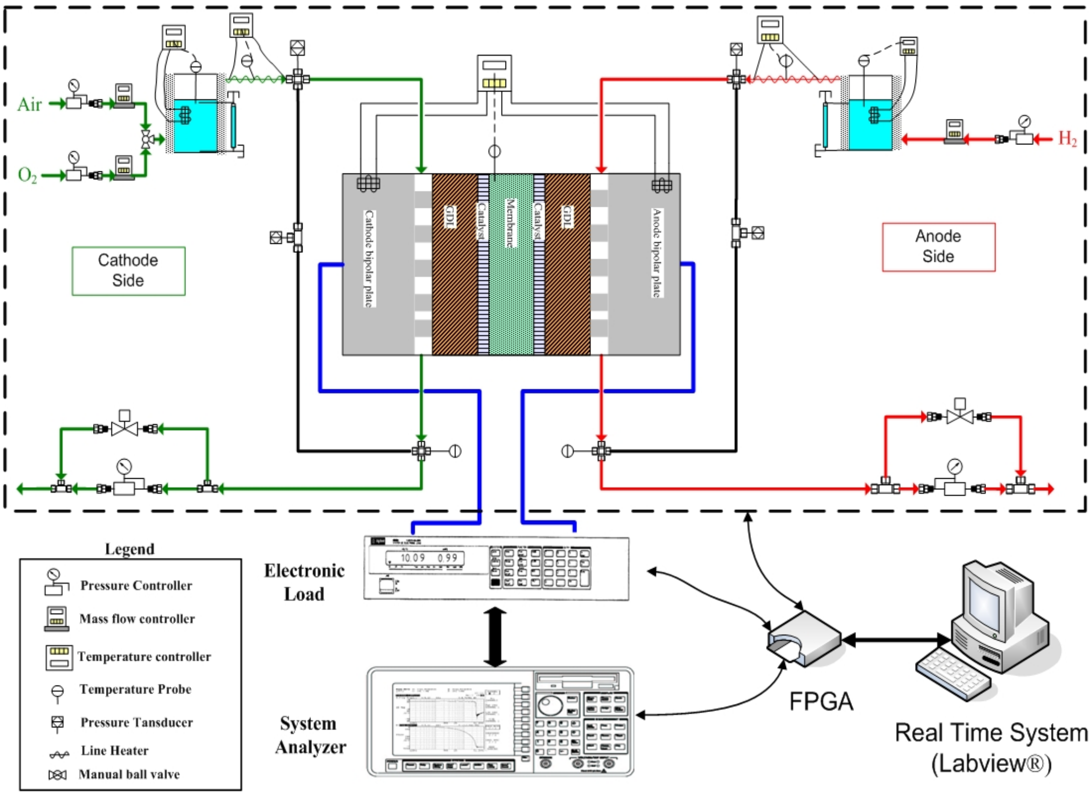


Figure 3 – Experimental setup description

In figure 3 a simplified scheme of the experimental setup used to obtain the cell response is presented. The test station consists of two reactant (anode and cathode) gas subsystems. Each subsystem contains: a mass flow controller, a membrane based humidification system with dew point sensors for control, inlet line heater to prevent condensation, absolute pressure transducer at the inlet, differential pressure transducer between the inlet and outlet of each reactant, and a back pressure regulator at the outlet of the fuel cell to control the system pressure. Each mass flow controller is calibrated for a specific gas (Hydrogen for the anode and synthetic air/Oxygen for the cathode).

There are also temperature readings in fuel cell inlet and outlet gas channels, humidifiers and line heaters. These measurements are done using K Type thermal couples. Temperatures of the fuel cell, humidifiers and line heaters are controlled by Proportional Integral Derivative (PID) controllers. The cooling of the cell is attained by natural convection. All the measurements and the control are made in real time by means of a LabView® control system. Electrochemical Impedance Spectroscopy experiments are done controlling the imposed operating current with an electronic load (TDI®) and a system analyzer (HP®).

2.2. Experimental Results

Two sets of experimental data were obtained, one with H_2/O_2 and the other with H_2/Air as reactants.

In table 2, base operating conditions for the two sets are presented. Starting from these base operating conditions, different variations are studied: nominal current variation, cathode and anode pressure variation (having both the same value), cell temperature and relative humidity. All these variations are done maintaining the other operating conditions at their base values.

Table 2 – Base Operating Conditions

	T_{FC} [ºC]	P_{FC} [Bar]	I_{FC} [A]	Φ_{fuel} [SLPM]	Φ_{oxid} [SLPM]	RH [%]
Air	60	1.0	1.0	0.34	0.83	100
Oxygen	80	1.5	2.0	0.34	0.17	100

In order to obtain the EIS response, the following procedure is applied:

- The desired operating point is imposed (current, temperature, pressure, etc.).

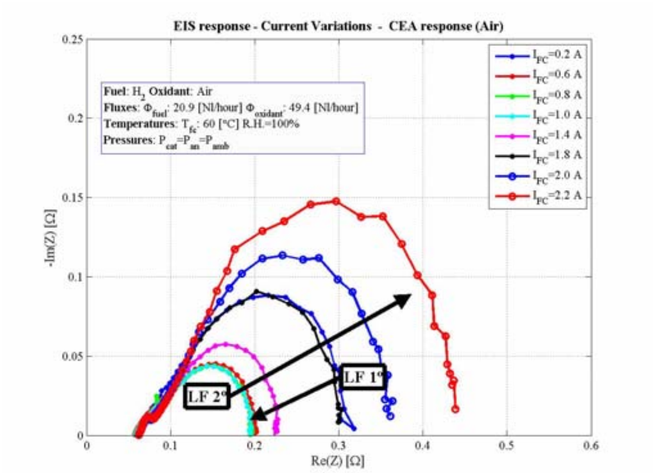
- In the system analyzer, the sinusoidal variation of current is configured (range of frequencies, number of frequency points, module of sine wave, etc.) and is imposed to the electronic load.
- A measurement of resulting voltage is passed to the system analyzer from the electronic load.
- The impedance spectrum is obtained on the system analyzer and Bode and Nyquist graphs are showed.
- All obtained data is stored on the real time control system.

The experimental data obtained is summarised in table 3, where the distribution of figures is also indicated.

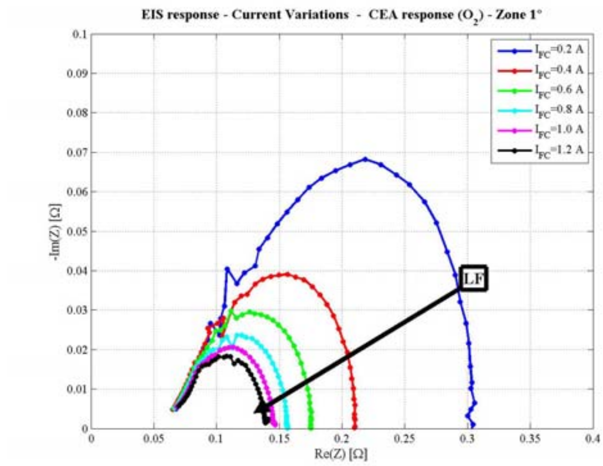
Table 3 – Experimental data description

Operating condition under variation	**H_2/Air reactants supply**	**H_2/O_2 reactants supply**
Current	Figure 4 (a)	Figure 4 (b, c, d)
Pressure	Figure 5 (a)	Figure 5 (b)
Temperature	Figure 6 (a)	Figure 6 (b)
Relative humidity	Figure 7 (a, b, c)	Figure 7 (d)

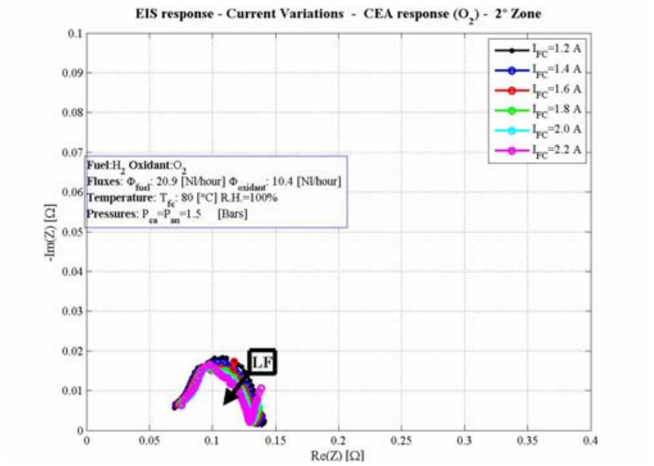
In the following sections only the pressure variations will be considered to illustrate the proposed analysis methodology. The EIS response of the fuel cell system when the operating pressure changes is shown in figure 5 (a) for the H_2/Air reactants supply operation and in figure 5 (b) for the H_2/O_2 reactants. Both cases present the same trend of the frequency response with operating pressure changes: when the pressure increases, the low frequency part of EIS diminishes in comparison with the high frequency part which remains constant.



(a) H_2/Air



(b) H_2/O_2 (1º zone)



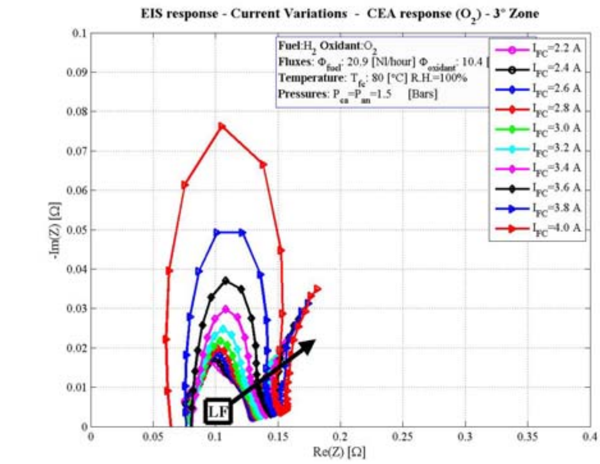
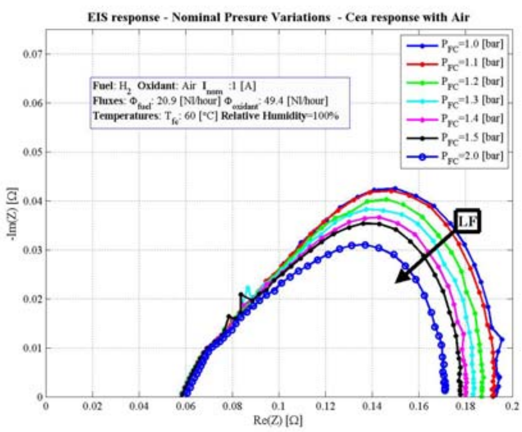
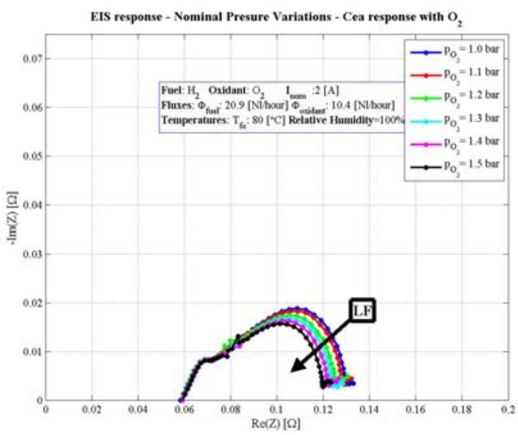


Figure 4 - EIS results with Current variations

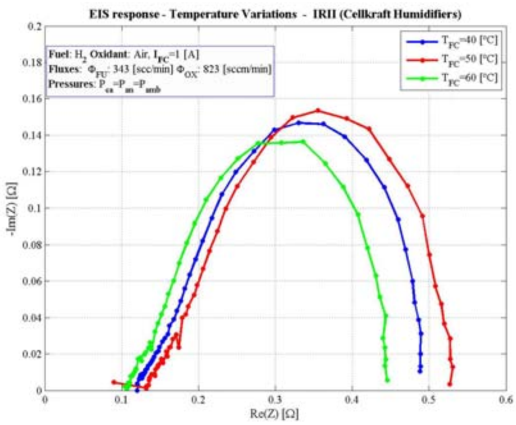


(a) H_2/Air

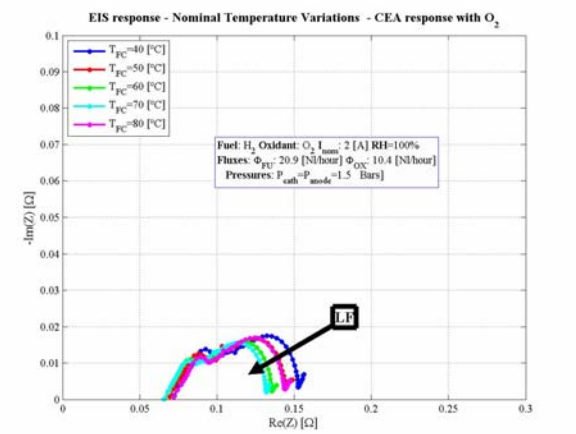


(b) H_2/O_2

Figure 5 - EIS results with pressure variations

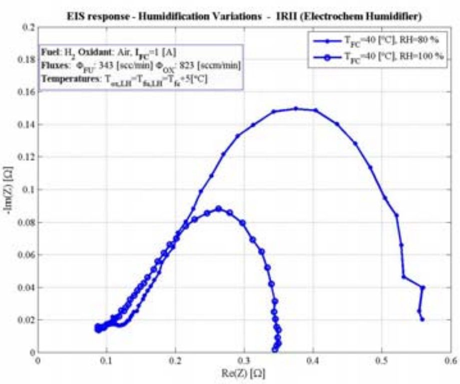


(a) H_2/Air

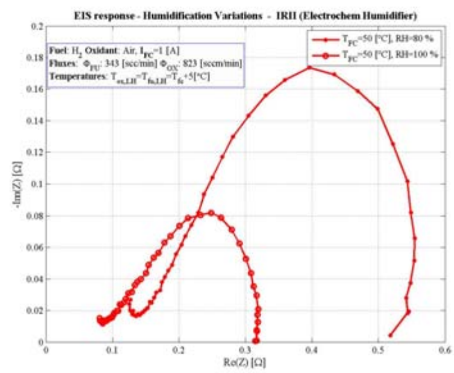


(b) H_2/O_2

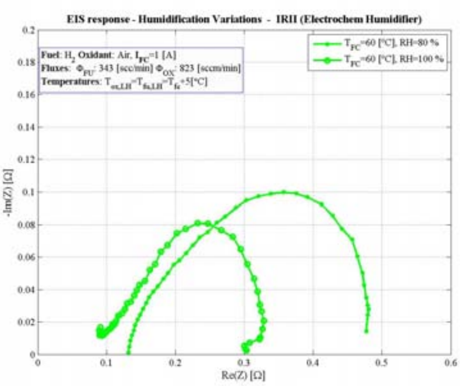
Figure 6 - EIS results with Temperature variations



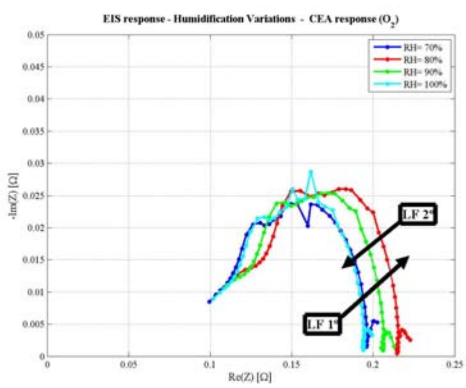
(a) H_2/Air (T_{FC}=40 ºC)



(b) H_2/Air (T_{FC}=50 ºC)



(c) H_2/Air (T_{FC}=60 ºC)



(d) H_2/O_2

Figure 7 - EIS results with relative humidity variations

3. Characterisation of frequency response

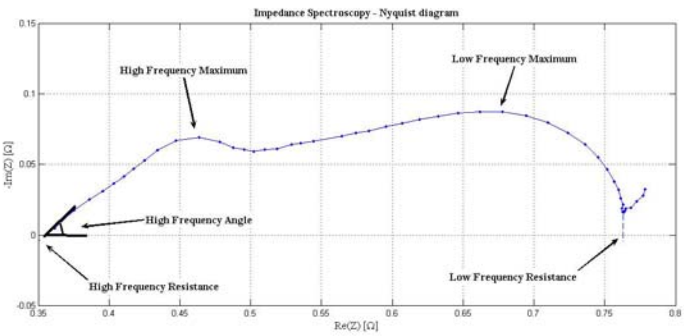
A typical EIS fuel cell response can be seen in figure 8, where the *relevant characteristics* of Bode and Nyquist plots are showed. These *relevant characteristics* are defined as:

Nyquist response (see figure 8 (a))

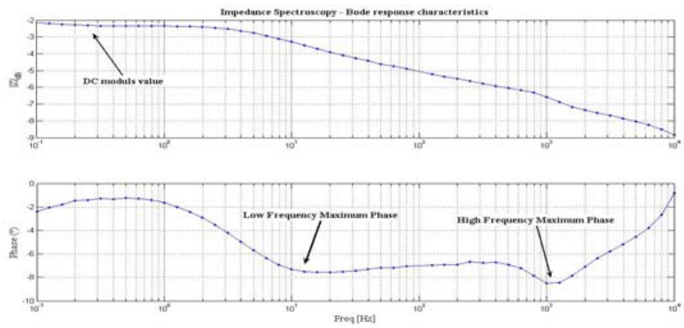
- Low frequency Resistance (R_{LF})
- Low frequency Maximum (imaginary part) ($f_{max,LF}$).
- High frequency Maximum (imaginary part) ($f_{max,HF}$).
- High frequency Resistance (R_{HF}).
- High frequency angle (ϕ_{HF}).

Bode response (see figure 8 (b))

- Low frequency Maximum Phase ($\varphi_{max,LF}$).
- High frequency Maximum Phase ($\varphi_{max,HF}$).



(a) Nyquist Characterisation



(b) Bode Characterisation

Figure 8 – Relevant Characteristics from EIS response

These characteristics of the frequency response are selected after the observation of EIS evolution at different operating points (from figure 5 to figure 8) and searching its possible use as indexes of fuel cell condition. Also, as will be explained in section 4, the obtained indexes can be used in order to search the values of equivalent circuit elements.

The variation of the relevant characteristics when the operating pressure changes, is detailed in table 4 and table 5.

Table 4 - Evolution of relevant characteristics with pressure variation (H_2/Air)

P_{fc} [Bar]	R_{LF} [Ω]	f_{maxLF} [Hz]	f_{maxHF} [Hz]	R_{HF} [Ω]	φ_{maxLF} (°)	$f_{\Phi maxLF}$ [Hz]	φ_{maxHF} (°)	$f_{\Phi maxHF}$ [Hz]
1	0.197	5.01	794.33	0.0580	-17.05	10.00	-8.19	794.33
1.1	0.194	5.01	794.33	0.0576	-16.95	7.94	-8.21	794.33
1.2	0.189	5.01	794.33	0.0576	-16.37	10.00	-8.16	794.33
1.3	0.184	6.31	794.33	0.0579	-16.04	10.00	-8.13	794.33
1.4	0.181	5.01	794.33	0.0578	-15.39	10.00	-8.17	794.33
1.5	0.179	6.31	794.33	0.0581	-15.08	10.00	-8.08	794.33

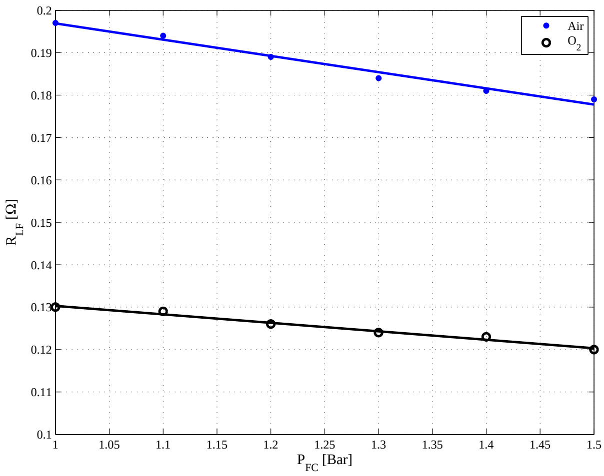
Table 5 - Evolution of relevant characteristics with pressure variation (H_2/O_2)

P_{fc} [Bar]	R_{LF} [Ω]	f_{maxLF} [Hz]	f_{maxHF} [Hz]	R_{HF} [Ω]	φ_{maxLF} (°)	$f_{\Phi maxLF}$ [Hz]	φ_{maxHF} (°)	$f_{\Phi maxHF}$ [Hz]
1	0.130	7.94	1000	0.0583	-10.12	12.59	-6.93	1000
1.1	0.129	7.94	1000	0.0586	-9.94	12.59	-6.91	1000
1.2	0.126	10.00	1000	0.0587	-9.57	15.85	-6.86	1000
1.3	0.124	10.00	1000	0.0591	-9.35	15.85	-6.78	1000
1.4	0.123	12.59	1000	0.0593	-9.14	15.85	-6.75	1000
1.5	0.120	12.59	1000	0.0590	-8.95	15.85	-6.73	1000

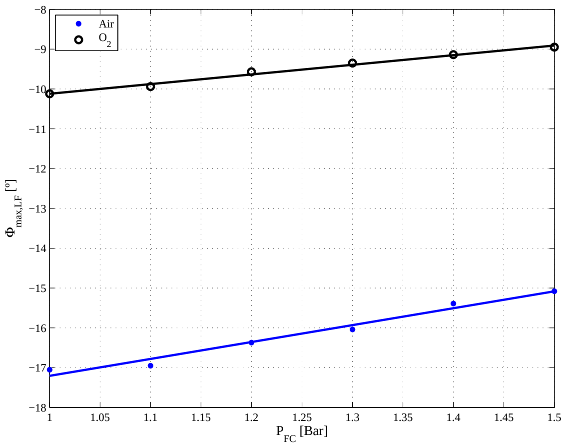
The pressure variation affects specially the low frequency response: low frequency resistance, low frequency maximum arc and low frequency maximum phase. This evolution is probably due to changes in the diffusion processes and reaction concentration. An increment of total pressure, gives an increment on the partial pressure of gases and the refilling of reacting gases is faster (reduction of diffusion and activation losses). In figure 9, significant variations of the relevant characteristics most affected by operating pressure can be observed.

Pressure variation affects the low frequency behaviour without distinction of working with H_2/Air or H_2/O_2 as reactants. Both working situations give similar trends to the low frequency resistance (R_{LF}, figure 9 (a)), reducing the value as pressure increases (what is due to an increase of the reactants concentration on the active layer).

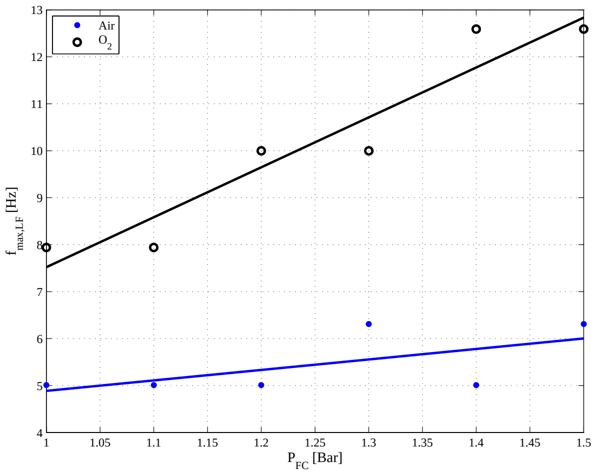
Also, on both situations, the low frequency maximum Phase ($\phi_{max,LF}$, figure 9 (b)) has the same trend. Also, the evolution of the low frequency maximum phase freq. ($f_{\phi max,LF}$, figure 9 (c)) has the same trend for both curves, although this trend is more discernible for H_2/O_2 situation than for H_2/Air.



(a) Low frequency resistance (R_{LF})



(b) Low frequency Maximum Phase ($\phi_{max,LF}$)



(c) Low frequency Imaginary Maximum frequency ($f_{max,LF}$)

Figure 9 – Relevant characteristics with operating pressure variation

4. Equivalent circuit design

In this section, the selection of the topology of an equivalent circuit modelling the fuel cell behaviour is studied. In the first part, a simple equivalent circuit is presented and the steps for initial values calculation are presented, too. Then, the parameters of this circuit are adjusted using specialized software (Z-View® [13]). After that, a complete equivalent circuit model is described and its parameters are determined.

4.1. Simple equivalent circuit

The first simple equivalent circuit is a combination of few elements (see figure 10): resistances (R_m and R_{tc1}), capacitance (C_{dc1}) and a Warburg element (W_1). These elements are selected in order to the represent resistive effects of membrane proton conduction

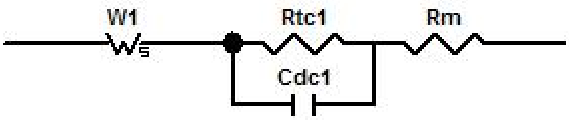


Figure 10 – Simple equivalent circuit

resistance (element R_m), the charge transfer resistance and accumulation (R_{tc1} in parallel with C_{dc1}), and the diffusion effects (Warburg element, W_1). Here, Finite Length Warburg element is used, which has a following transfer function:

$$W_1(s) = \frac{R_{W_1} \tanh((s.T_{W_1})^{P_{W_1}})}{(s.T_{W_1})^{P_{W_1}}} \qquad (1)$$

where "s" is the Laplace complex frequency and "R_{W1}" is the finite resistance at low frequencies, "T_{W1}" is a time constant related by some authors to the diffusion effects (Bautista et al., [3] and Diard et al. [5]) with the following equation:

$$T_{W_1} = \frac{L^2}{D} \qquad (2)$$

where "L" is the effective diffusion thickness, and D is the effective diffusion coefficient of the particle. "P_{W1}" is an exponent related with the roughness of the diffusion media (Podlubny [14]).

If the diffusion effects are considered influential at low frequency range, Warburg element is adjusted using low frequency information extracted from *relevant characteristics* defined in section 3. Then, if the accumulation and transfer of charge is reflected at high frequency range, the parallel between R_{tc1} and C_{dc1}, can be determined form high frequency information of section 3. Also, resistive effects at high frequency intersection with real axes can be associated with membrane resistance R_m, among other ohmic effects.

4.2. General procedure of the equivalent circuit parameters adjustment

Once the EIS test is done and the frequency response is obtained, the relevant characteristics of this response are calculated. Then, considering an equivalent circuit and making a separation of different effects as function of their frequency range, the relevant characteristics help to find parameter values of the selected equivalent circuit.

In order to illustrate the general procedure used to obtain the parameters of the simple equivalent circuit from the relevant characteristics, an example with all necessary steps is presented.

The procedure is applied to the first curve of pressure variation in H_2/O_2 supply, with operating pressure: P_{FC}=1.0 [Bar]. The resulting frequency response is showed in figure 6.(b) and relevant values obtained from corresponding test are showed in table 5.

The following steps are used in order to relate relevant characteristics and equivalent circuit parameters:

- The high frequency resistance (R_{HF}, intersection with the real axis at high frequency) is an estimation of the ohmic effects, mainly proton conduction resistance of the membrane:

$$R_m \approx R_{HF} \approx 0.058\,\Omega \quad \textbf{(3)}$$

- The high frequency maximum frequency ($f_{max,HF}$) helps to find the charge accumulation and transfer time constant (τ_{dc1})

$$f_{\max,HF} \approx \frac{1}{2\pi\left(R_{ct1}C_{dc1}\right)} \rightarrow \tau_{dc1} = R_{ct1}C_{dc1} \approx \frac{1}{2\pi f_{\max,HF}} \approx \frac{1}{2\pi(794.3)} \approx 200\ \mu s \quad (4)$$

- Using the resistance associated with this high frequency arc ($R_{max,HF}$), the charge transfer resistance (R_{ct1}) is calculated as follows:

$$R_{ct1} \approx R_{\max,HF} - R_m \approx 0.009\,\Omega \quad (5)$$

- Combining the information of the charge transfer resistance (R_{ct1}), the charge accumulation and the transfer time constant (τ_{dc1}), the double layer capacitance is determined:

$$C_{dc1} \approx \frac{\tau_{dc1}}{R_{ct1}} \approx 22\ mF \quad (6)$$

- The Warburg resistance (R_{W1}) is established from the resistance difference between the low frequency resistance (R_{LF}) extracted from table 4, the membrane and the charge transfer resistance:

$$R_{w_1} \approx R_{LF} - R_m - R_{ct1} \approx 0.13\,\Omega \quad (7)$$

- The Warburg exponent (P_{W1}) is determined using a combination of one relevant characteristic ($Im_{w,max,LF}$, imaginary part of low frequency arc) and a trigonometric expressions from Warburg transfer function (equation (1)):

$$\mathrm{Im}_{w_{\max,LF}} = -\frac{1R_{w_1} sen(\frac{P_{w_1}\pi}{2})}{2.(\cos(\frac{P_{w_1}\pi}{2})+1)} = -\tfrac{3}{8}R_{w_1}.\tan(\tfrac{P_{w_1}\pi}{2}) \Rightarrow P_{w_1} = -\tfrac{4}{\pi}\arctan\left(-\frac{2.\mathrm{Im}_{w_{\max,LF}}}{R_{w_1}}\right) = 0.4 \quad (8)$$

- Finally, the Warburg time constant (T_{W1}) is given by the following equation:

$$T_{w_1} \approx \frac{1}{R_{w_1} w_{\max,LF}^{P_{w_1}}} \approx 0.099\,[seg] \qquad (9)$$

With the frequency response, the relevant characteristics definition and the proposed equivalent circuit, this procedure can be applied to *all working situations* in order to obtain the parameters of the equivalent circuit.

After this parameter estimation, the equivalent circuit is constructed in Zview® software in order to compare with the real response. Also, this tool allows curve fitting with Non Linear Least Squares algorithm, refining the initial values of the equivalent circuit to new ones. In table 6 and figure 11, a comparison is made between the response obtained with the parameters of the initial procedure and the parameters estimated by Zview®.

Table 6 - Simple equivalent circuit adjustment for H_2/O_2 situation (P_{FC}=1.0 [Bar])

Element	**Initial**	**Estimated (Zview®)**
R_{W1} [Ω]	0.13	0.135
T_{W1} [sec]	0.099	0.092
P_{W1}	0.4	0.42
R_{tc} [Ω]	0.009	0.0085
C_{dc} [F]	0.022	0.035
R_m [Ω]	0.058	0.056

The comparison shows that the initial parameter estimation based on the described procedure is a good tool for curve fitting on frequency response.

However, using the Zview® software, the information obtained from relevant characteristics and equivalent circuit parameter procedure are improved giving a better curve fitting.

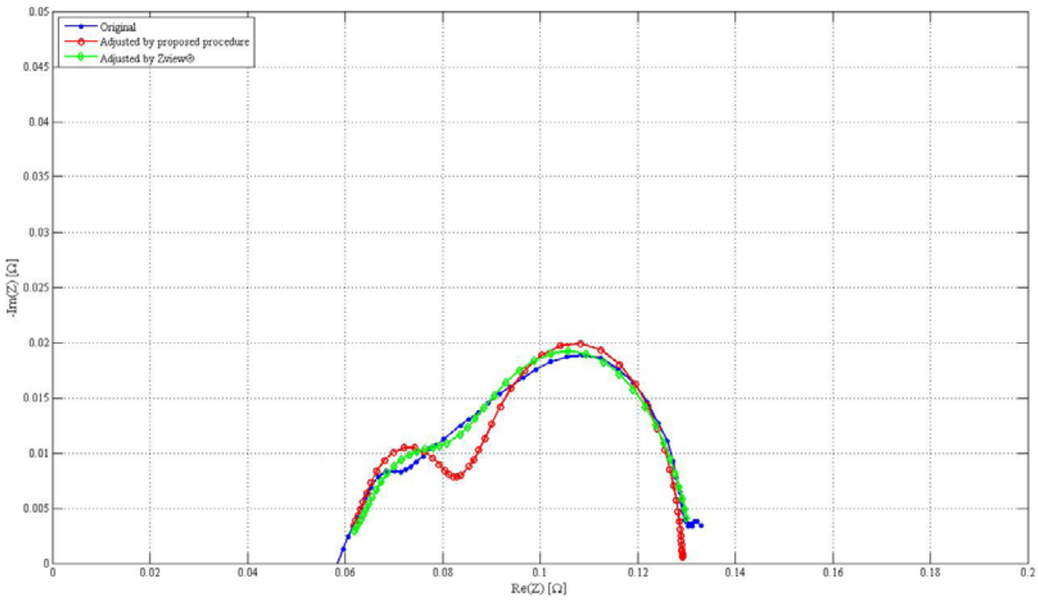


Figure 11 - Comparison of simple equivalent circuit result effect

4.3. Complete equivalent circuit

In order to obtain a better adjustment of the frequency response, a complete equivalent circuit is defined.

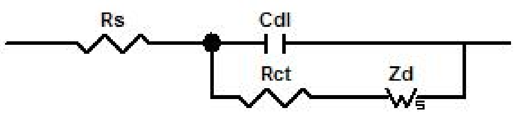


Figure 12 – Randles equivalent circuit

A well known equivalent circuit for a single-step charge transfer reaction in the presence of diffusion is the "Randles equivalent circuit" (see J. Ross Macdonald et al. [6]), where R_s is the electrolyte resistance, C_{dl} is the double layer capacitance, R_{ct} is the charge transfer resistance and Z_d is the diffusion impedance, generally, using a Warburg impedance.

Considering one “Randles equivalent circuit” for the anode and another for the cathode, a proposal of a complete equivalent circuit to study the experimental EIS response is done (see figure 13). Here, taking into account the influence of the electrode roughness on charge accumulation, a CPE (Constant Phase Element) is used in replacement of planar capacitance.

The elements of the complete equivalent circuit are: L_W, which represents the wiring inductance, $R_{tc,1}$ and $R_{tc,2}$ which are the representation of the charge transfer resistances (for the anode and the cathode). $CPE_{dl,1}$ and $CPE_{dl,2}$ are the double layer charge representation, Z_{W1} and Z_{W2} are the diffusion impedances, and R_m is the membrane resistance. Some of the initial values of the complete equivalent circuit parameters are obtained from the simple equivalent circuit adjustment and the other elements have a known initial values. The total

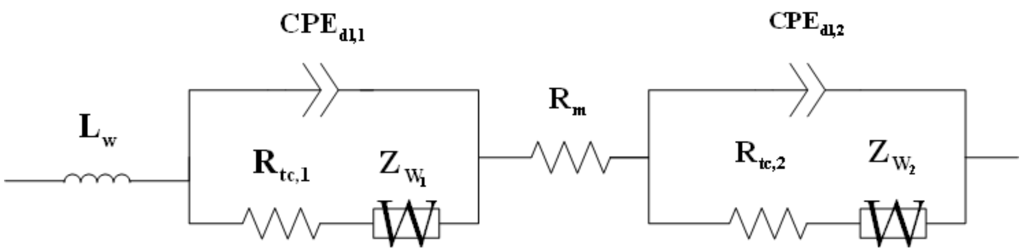


Figure 13 – Complete equivalent circuit proposes

parameter adjustment is done with the curve fitting software Zview®.

The main advantages of this complete equivalent circuit are the symmetry and the high quality of the adjustment for all operating condition variations. The principal disadvantages are the higher number of parameters to adjust, in comparison with the relevant characteristics, and the phenomena interpretation and separation of apparent at different frequency domain effects. As the information has only two relevant frequency zones, and the equivalent circuit has four frequency variable elements (2 CPE and 2 Warburg elements) there is an overlapping of the frequency responses of these effects.

The comparison between the responses obtained with the simple equivalent circuit and with the proposed procedure results in figure 11 and the results for the complete equivalent circuit for the same operating condition (H_2/O_2 as reactants, P_{FC}=1.0 [Bar]), is showed on figure 14. The fitting of the complete equivalent circuit is better than the simple equivalent circuit, probably due to a higher number of free parameters to adjust the response.

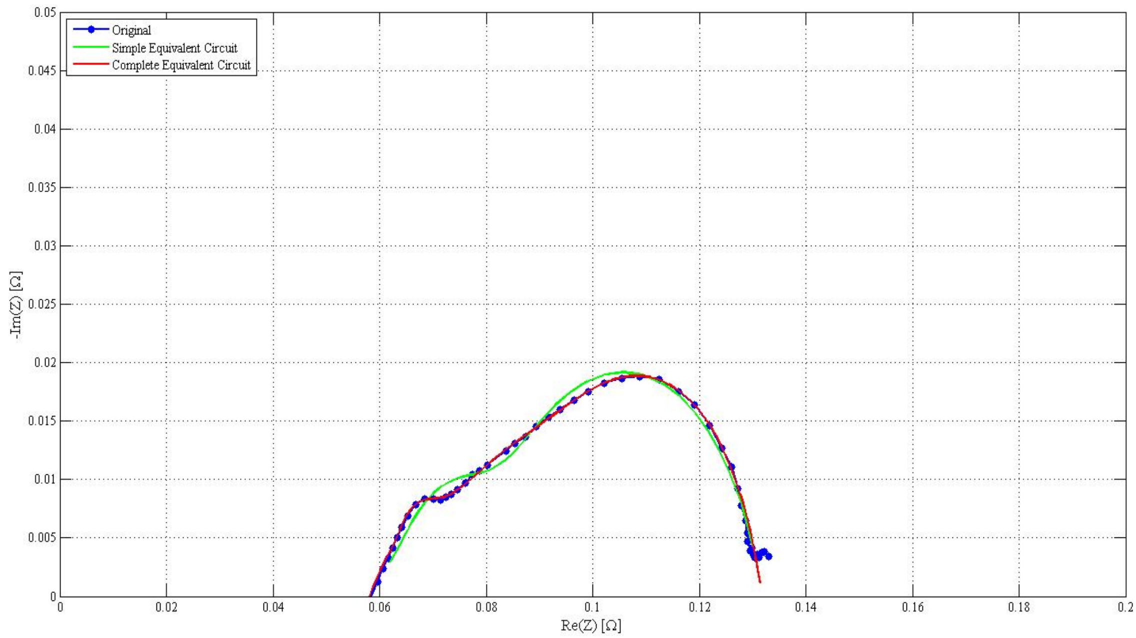


Figure 14 – Comparison between simple and complete equivalent circuit

Table 7 – Complete equivalent circuit parameter evolution with pressure H_2/O_2 situation

Element	P_{FC}=1.0 Bar	P_{FC}=1.1 Bar	P_{FC}=1.2 Bar	P_{FC}=1.3 Bar	P_{FC}=1.4 Bar	P_{FC}=1.5 Bar
R_{tc1}	0.063	0.063	0.063	0.064	0.065	0.064
R_{W1}	0.036	0.034	0.031	0.029	0.027	0.026
T_{W1}	0.020	0.017	0.014	0.013	0.011	0.011
P_{W1}	0.31	0.32	0.33	0.33	0.34	0.35
$T_{CPE,1}$	0.002	0.002	0.002	0.002	0.002	0.002
$P_{CPE,1}$	0.65	0.67	0.69	0.66	0.66	0.67
R_m	0.058	0.058	0.058	0.058	0.058	0.058
L_W	0.000021	0.000021	0.000022	0.000021	0.000021	0.000021
$T_{CPE,2}$	0.0001	0.0002	0.0002	0.0002	0.0002	0.0003
$P_{CPE,2}$	1.65	1.61	1.60	1.59	1.60	1.54
R_{tc2}	0.00012	0.00015	0.00016	0.00016	0.00015	0.00019
R_{W2}	0.035	0.032	0.031	0.030	0.031	0.029
T_{W2}	0.064	0.060	0.055	0.051	0.048	0.045
P_{W2}	0.48	0.48	0.48	0.48	0.47	0.48
SSE	0.012	0.058	0.025	0.057	0.097	0.022

In table 7, all adjusted parameters for the different operating pressures are shown. Also, the Sum of Squared Error (SSE) is presented, calculated as:

$$SSE = \sum_{\omega_i=\omega_0}^{\omega_f} \left(y_{real,\omega_i} - y_{est,\omega_i} \right)^2 \qquad (10)$$

where $y_{real,\omega i}$ ($y_{est,\omega i}$) is the real (estimated) complex value at frequency ω_i, and ω_0 and ω_f are the initial and final frequency points.

Using the complete equivalent circuit response, a descriptive evolution of some of the estimated parameters with the pressure changes is searched.

With the information collected in table 7, the parameter behaviour is studied. In order to find possible representative parameters, an iterative process is applied. Starting with the parameters that have low value variations when pressure changes, the curve fitting is repeated maintaining their values fixed to their mean values. This analyzed parameter is maintained fixed if the total response is not qualitative degraded. Then, other parameters are tested and the process continues until a minimal number of parameters having a real influence in the EIS is attained, while the equivalent circuit still presents a good fitting with the experimental response.

Table 8 – Complete equivalent circuit parameter simplification with pressure (H_2/O_2)

Element	P_{FC}=1.0 Bar	P_{FC}=1.1 Bar	P_{FC}=1.2 Bar	P_{FC}=1.3 Bar	P_{FC}=1.4 Bar	P_{FC}=1.5 Bar
R_{tc1}	0.063					
R_{W1}	0.031					
T_{W1}	0.014					
P_{W1}	0.33					
$T_{CPE,1}$	0.0021					
$P_{CPE,1}$	0.67					
R_m	0.058					
L_W	2.1E-07					
$T_{CPE,2}$	0.00018					
$P_{CPE,2}$	1.6					
R_{tc2}	0.00015					
R_{W2}	0.036	0.034	0.031	0.029	0.028	0.026
T_{W2}	0.064	0.060	0.055	0.050	0.047	0.045
P_{W2}	0.48					
SSE	0.044	0.069	0.087	0.097	0.12	0.086

In table 8, the final result is presented: after the described iterative process, $\boldsymbol{R_{W2}}$ and $\boldsymbol{T_{W2}}$ parameters are found to be representative of the evolution of the system when pressure changes. These are two of the three parameter values of one Warburg element of the equivalent circuit. In figure 15, the selected parameter evolutions are shown and both present similar trend to low frequency relevant characteristics when the pressure changes (see figure 9).

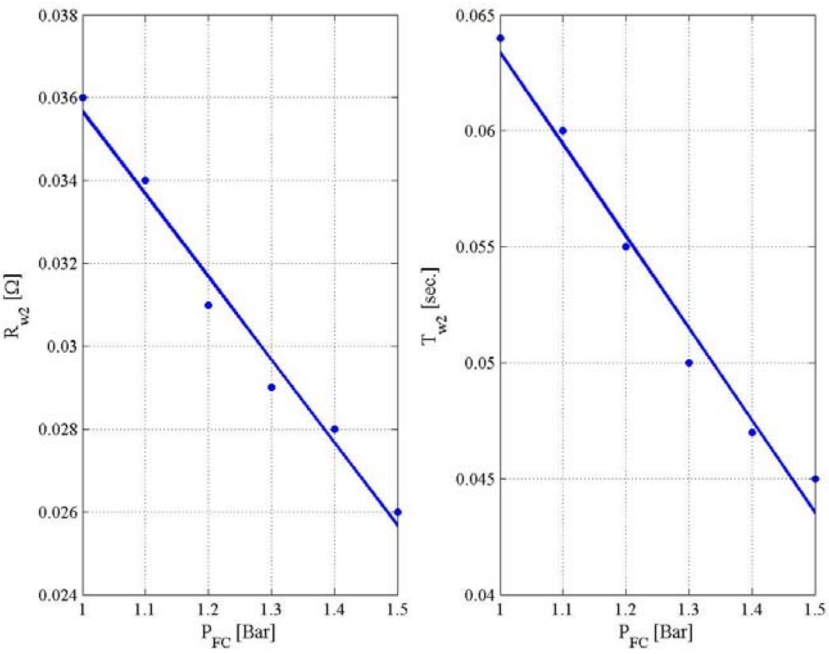


Figure 15 – Selected parameters evolution with operating pressure

5. Conclusions

An experimental set of EIS response applied to a single fuel cell with H_2/O_2 and H_2/Air as reactants at different operating conditions (current, pressure, temperature and relative humidity) were obtained. Definition of some relevant characteristics of EIS response is presented as useful tool in order to obtain possible indicators of the fuel cell operating state. A simple equivalent circuit is proposed and its parameters are obtained using a general procedure combining EIS shape and the relevant characteristics defined. Then, a complete equivalent circuit is presented in order to obtain a better experimental data fitting. Finally, after an iterative process, the complete equivalent circuit representative parameters are found. These representative parameters have a clear evolution with the change of the operating conditions, making possible the use them as fuel cell state indicators.

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Nomenclature

AC	Alternative Current
C	Capacitance (F)
CPE	Constant Phase Element
D	Diffusion coefficient ($cm^2.s^{-1}$)
DC	Direct Current
EIS	Electrochemical Impedance Spectroscopy
f	Frequency (Hz)
H_2	Hydrogen
I	Current (A)
L	Inductance (H) or Length (cm)
O_2	Oxygen
P	Pressure (Bar) or Warburg exponent
PEMFC	Polymer Electrolyte Membrane Fuel Cell
PID	Proportional Integral Derivative
R	Resistance (Ω)
RH	Relative Humidity (%)
S	Laplace complex frequency
SSE	Sum of Squared Error (Ω^2)
T	Temperature (ºC) or Time constant (s)
W	Warburg impedance
y	Complex value
Z	Impedance (Ω)

Greek Symbols

ϕ	Angle (º)
φ	Phase (º)
Φ	Volumetric flow (SLPM)
τ	Time constant (s)
ω	Angular frequency ($rad.s^{-1}$)

Subscripts

0	Initial Value
a	Anode
c	Cathode
ct	Charge Transfer
dl	Double Layer
est	Estimated Value
f	Final value
FC	Fuel Cell
fuel	Fuel side
HF	High Frequency
i	Actual Value

LF	Low Frequency
m	Membrane
max	Maximum
N	Nernst
oxid	Oxidant side
real	Real Value
W	Warburg

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