

## Symmetrical electrode mode for PEMFC characterisation using impedance spectroscopy

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### Abstract

This paper investigates a single complete proton exchange membrane fuel cell (PEMFC) as a whole, modelling it by an electrical equivalent circuit (EC) using the electrochemical impedance spectroscopy (EIS) technique. The cell tested was a PEM single cell with a Nafion 117 membrane. The measurements were carried out with the fuel cell working in an electrode “symmetrical mode” (SM), that is, with the same gas injected in both electrodes, with different gases supplied to anode/cathode compartments (O<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/H<sub>2</sub>). The working temperature of the cell was (40–70 °C), and the humidification conditions of reactant gases were 45 ± 5 and 100% relative humidity (RH).

This study obtains the structure of the EC and its parameters values, and offers a physical interpretation relating these parameters to several processes occurring in the system. The relations of properties, such as membrane conductivity or the resistance to the charge transfer process as a function of the working parameters of the fuel cell, such as temperature, reactant gases injected and their humidification conditions are also studied.

The efficiency of EIS for the modelling and characterisation of PEMFC working in SM is also discussed.

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**Keywords:** PEMFC; Impedance spectroscopy; Equivalent circuit; Membrane conductivity; Charge transport; Mass transport

### 1. Introduction

Among the different types of fuel cells, the PEMFC has been attracting much interest as an energy source for residential applications and electric vehicles. It is capable of achieving high-power densities working at low temperatures, e.g. 60 °C.

PEMFC EIS electrode symmetrical mode characterisation achieves a double objective:

- it gives a deeper quantitative/qualitative understanding of the fuel cell system that permits improvement in the design and operation of the fuel cell; and

- it leads to a better understanding of the performance of these systems which depend on a complex group of structural and functional characteristics, which interact internally to provide the optimum situation for the entire process.

Modelling electrochemical systems by an EC is a procedure used in the EIS technique that offers an explanation of the macroscopic or microscopic properties of the electrochemical system analysed. EIS is a method to characterise the electrochemical properties of materials and their interfaces with electronically conducting electrodes [1]. Due to the complexity of the electrode behaviour inside a fuel cell, and the influence of several factors, such as electrical conductivity and interface structures, EIS has been demonstrated to be a useful and powerful technique to study the different processes that occur in the fuel cell. It also allows us to evaluate the electro-

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chemical processes independently in order to determine the influence of each component on fuel cell performance [2]. The EIS furnishes data to relate the electrochemical system properties to its ac impedance frequency response.

Suitable model treatments have been developed for the impedance response of gas diffusion electrodes [3,4]. Nafion membranes have been studied with this technique to evaluate the behaviour of the membrane as a function of water content [5]. Model experimental systems of the catalyst–Nafion interface have been studied [6], while the response of gas diffusion electrodes has been studied in a half-cell mode. Impedance techniques have also been used to examine the response of a single cell [7,8]. However, evaluation of a complete single cell incorporating bipolar plate structure is not available in the literature.

The EC obtained by the EIS technique will be used as a tool for the diagnosis of design and operation of the fuel cell. For this purpose, an experimental set-up in the SM configuration [8,9] is implemented in this investigation. This procedure has been used in such a manner as to enable the study and characterisation of any electrochemical cell, to gain better knowledge of the processes that occur in each electrode, electrolyte and interface of the fuel cell. This “symmetrical mode” operation is one of the fundamental and easy approaches to determine these processes without the necessity of fuel cell operation, which works with  $H_2/O_2$  injected in anode/cathode compartments (“normal mode”). Further, the “symmetrical mode” was also chosen due to technical limitations of the monitoring devices. For example, the internal electric resistance in “normal mode” operation is of order of milliohm, requiring very sensitive and accurate measurements, and is thus too sophisticated and remote from the objective of this work.

Very few investigations have evaluated a complete single PEMFC in SM, there are few systematic EIS studies related to the effects of temperature and humidity, and there are few physical interpretations of each component of the equivalent circuit obtained [8,9]. The EIS of a PEMFC in a “symmetrical mode” depends strongly on humidity condition. In this investigation, two humidity values are considered:  $45 \pm 5$  and 100% RH. However, the drier condition is the more appropriate one since at 100% RH, the EIS spectrum depicted revealed less reliable information. The objective of this work is the determination of the impedance behaviour of a complete single cell of PEM type working in SM, studying the effect of temperature at  $45 \pm 5\%$  RH, which would allow qualitative–quantitative knowledge of the electrical transport properties of each cell component to be gained.

## 2. Experimental technique

### 2.1. Cell hardware

From a physical viewpoint, a complete single PEMFC is made primarily of an electrolyte (a polymer exchange mem-

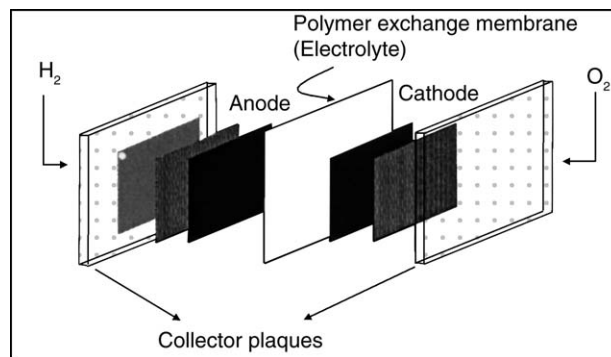


Fig. 1. Parts of a complete single cell PEMFC.

brane), two electrodes (anode and cathode), two gas diffuser plates and two metallic collector plates. This is shown in Fig. 1.

Impedance measurements were conducted on a complete single cell consisting of a Dupont Nafion<sup>®</sup> 117 membrane (thickness, 183  $\mu\text{m}$ ), two identical electrodes made of the catalytic layer ( $0.7 \text{ mg Pt cm}^{-2}$ ) and carbon Vulcan<sup>®</sup> dust ( $600 \text{ m}^2 \text{ g}^{-1}$ ), integrating the membrane electrode assembly (MEA). The home-made (by Instituto Cerámica y Vidrio (ICV)-CSIC, Spain) electrodes-membrane assembly (MEA) of  $25 \text{ cm}^2$  (labelled CSIC) was assembled with a total thickness of 783  $\mu\text{m}$  [10]. Two toroid gaskets are used to make gas compartments watertight and the Toray carbon paper (thickness, 300  $\mu\text{m}$ ) is used as gas diffuser plates. It was sandwiched between two collector plates of aluminium 70–75 with a thickness of 1 cm each. Gas distribution is provided through channels machined on each plate of  $800 \mu\text{m} \times 600 \mu\text{m}$  rectangular section; plates that are also used as current collectors.

### 2.2. Polarisation curve test “normal mode”

In order to obtain a typical polarisation curve, the cell is used in the “normal mode” operation of the PEMFC:  $(-)\text{H}_2$ , Pt/C//Nafion membrane//Pt/C,  $\text{O}_2(+)$ . This complete single fuel cell was developed using ICV–Instituto de Automática Industrial (IAI)–CSIC technology. A programmable discrete electronic load for a single cell of 10 W developed at IAI–CSIC with decreasing resistance values with 20 s between measurements was used to ensure stability of the system.

The polarisation curves for a CSIC and a commercial ( $1 \text{ mg Pt cm}^{-2}$ , Electrochem) MEA were recorded at  $60^\circ\text{C}$ , with  $\text{H}_2$  in the anode and  $\text{O}_2$  in the cathode, both gases at the pressures of 2 bar in the electrodes.  $Q_a$ ,  $0.41 \text{ min}^{-1}$ ;  $Q_c$ ,  $0.41 \text{ min}^{-1}$  and 100% RH.

### 2.3. Electrode symmetrical mode tests using EIS measurements

The overall impedance can be measured directly in the frequency domain by applying a single-frequency voltage

to the PEMFC and recording the phase shift and amplitude (or real and imaginary parts) of the resulting current at that frequency. In this work, an impedance analyser (HP 4192 A LF) connected by a GPIB interface to the computer was used to measure complex impedance data. Equivalent circuit (Version 3.97) was the software chosen for the electrochemical ac impedance data system analysis [11].

The EIS measurement protocol in PEMFC performs the analysis of impedance magnitude  $|Z|$  and phase over a frequency range (10 Hz–1 MHz). A logarithmic decreasing frequency sweep was used because of problems in the membrane caused by its possible polarisation due to the deposit of ions in the electrodes. Measurement speed was set to ‘average’; ac voltage signal was set at 100 mV and the dc bias was set to 0 V. Due to the fact that the complete single fuel cell tested has thick collector plates (1 cm each side) it was necessary to use an ac signal amplitude larger than 25 mV.

The influence of the sort of gas injected in both electrodes ( $O_2$  or  $H_2$ ), the working temperature of the cell (40–70 °C), and the humidification conditions for  $H_2/H_2$  case: (45% RH/100% RH,) are also studied and characterised with the equivalent circuit modelled. The cell was conditioned through appropriate settings of temperature, pressure and humidification to reach a stable spectrum measurement (over 2 h) which implies the cell was in stationary or equilibrium condition.

The SM configurations of the electrochemical cell studied are described as follows:

- (anode part)  $H_2$ , Pt/C//Nafion membrane//Pt/C,  $H_2$  (cathode part)
- (anode part)  $O_2$ , Pt/C//Nafion membrane//Pt/C,  $O_2$  (cathode part)

### 3. Results and discussion

#### 3.1. Polarisation curve

The good state and the correct operation of the PEMFC were proved by working it at 100% RH with  $H_2/O_2$  at 70 °C and determining the polarisation curve (Fig. 2), which relates the cell voltage ( $V_{cell}$ ) to current density.

The CSIC MEA shows a behaviour similar to that of the commercial MEA. This result would indicate that the method developed for MEAs preparation leads to electrode–membrane assemblies with similar features to those of the commercial assemblies, and provides a MEA that is appropriate for subsequent SM operation.

#### 3.2. PEMFC working in SM by EIS-analysis of EC parameters

Fig. 3 the impedance plot ( $Z''$ , the imaginary part plotted against  $Z'$ , the real part of impedance  $Z$ ) for the cell measured,

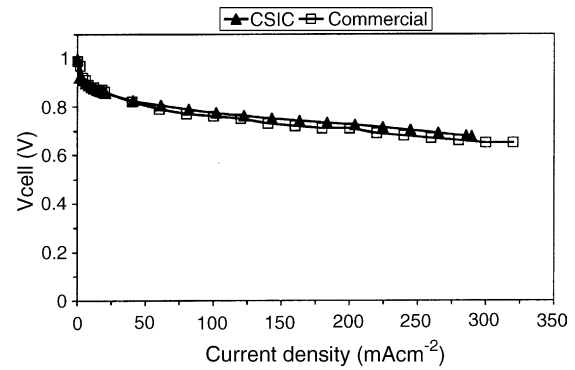


Fig. 2. Polarisation curve of the CSIC and commercial MEA, at 60 °C, with  $H_2/O_2$  at 2 bar in both electrodes.  $Q_a$ ,  $0.41 \text{ min}^{-1}$ ;  $Q_c$ ,  $0.41 \text{ min}^{-1}$ , and 100% RH.

working in SM with oxygen or hydrogen over the whole range of temperatures at  $45 \pm 5\%$  RH.

For the case of hydrogen injection (Fig. 3a), the impedance spectra consist of an approximate semicircle at intermediate frequency (if) range ( $10^5$  to  $10^3$  Hz), with a depression angle around  $10^\circ$ , which means that the interface corresponding to this approximate semicircle is almost homogeneous. At low-frequency (lf) range ( $10^3$  to 10 Hz), a smaller additional approximate semicircle appears which is more evident as temperature increases.

In the high-frequency (hf) range ( $10^5$  to  $10^6$  Hz), a pseudo-inductive impedance appears and the spectra pass through the real ( $Z$ ) or  $Z'$  axis. That plot can be associated with the pseudo-inductance part due to all the metallic components of the complete single fuel cell tested [9]. The equivalent circuit fitted is shown in Fig. 4a, and the values and interpretation of the parameters are given in Table 1.

For the case of oxygen injection (Fig. 3b), the impedance spectrum consists of an approximate semicircle at intermediate frequencies (if) similar to that of the hydrogen case, but at low frequencies (lf) they show a spike with an almost  $45^\circ$  angle associated with a Warburg impedance. The final equivalent circuit is illustrated in Fig. 4b.

The impedance data of a PEMFC is represented by an EC obtained using an EC program [11]. The structure of the EC is shown in Fig. 4.

The parameters of the equivalent circuit obtained from the fitting process are presented in Table 1.

- $L$  is the pseudo-inductance associated with the effects produced by the collector plates, plus all the metallic components of the single cell, as they create a signal that can be identified with a behaviour generally associated with metal.
- $R_m$  is the electrical resistance associated with the Nafion<sup>®</sup> membrane.
- $R_1$  is ascribed to the electrode resistance of the charge transfer at the electrode–membrane interfaces, and is associated with the presence of mixed conduction (protonic–electronic) at this interface.

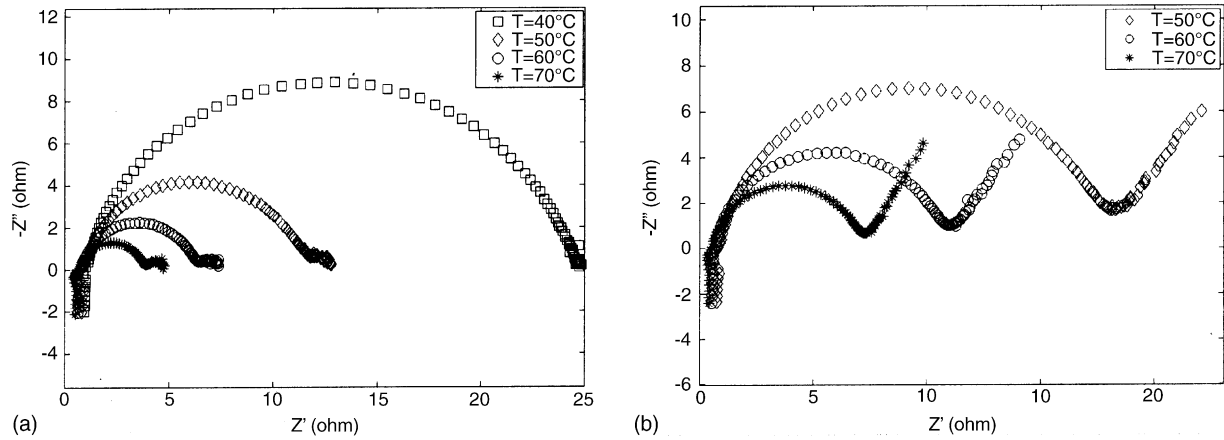


Fig. 3. Impedance plots for PEMFC working in “symmetrical mode” with (a) H<sub>2</sub>/H<sub>2</sub> and (b) O<sub>2</sub>/O<sub>2</sub> at 45 ± 5% RH.

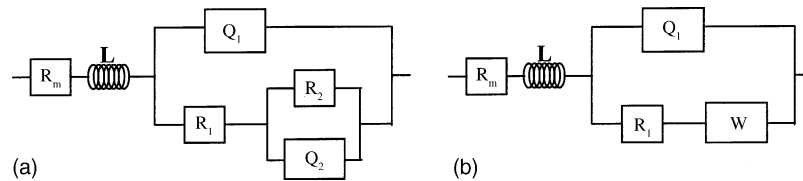


Fig. 4. Equivalent circuit fitted for a complete single PEMFC in SM at 45% RH, with electrode gases (a) H<sub>2</sub>/H<sub>2</sub> and (b) O<sub>2</sub>/O<sub>2</sub>.

- $Q_1$  is the pseudo-capacitance associated with the double electrochemical layer at the electrode–membrane interfaces. This double layer appears through all the electrode–electrolyte system, even if it is a solid or liquid. The existence of pseudo-capacitances instead of pure capacitances in the EC circuit produces the depression of the semicircles of the EIS data, and that effect is mainly associated with the presence of non-homogeneous electrodes. The high value ( $F$ ) of pseudo-capacitance demonstrates that this component exhibits typical characteristics of that mixed conductor.
- $R_2$  can be considered to be the so-called polarisation resistance of the zone of mass transport of the polarisation curve which can be ascribed to the gas–electrode interaction. It should be noted that this parameter only appears

when the gas injected is hydrogen, since in the case of the oxygen, the identification could produce unacceptable errors. This parameter can also be related to morphological properties of the electrodes during its fabrication (porosity and porous architecture).

- $Q_2$  is the pseudo-capacitance related to the adsorption phenomenon, resulting from the presence of adsorbed hydrogen species.
- $W$  is the pseudo-capacitance related to the diffusion. The parameter  $n = 0.5$ , is the value of the Warburg impedance, obtained from Fick’s second law equation of diffusion of a particle in one dimension in a semi-infinite space. This supports the fact that the branch  $R_2//Q_2$  of the circuit in Fig. 4b characterises the process of mass transference that happens in the cell.

Table 1  
Parameters evaluated from a fit of EIS for the equivalent circuit of Fig. 4

	$T^a$ (°C)	$R_m$ (Ω)	$L$ (H)	$R_1$ (Ω)	$Q_1$		$R_2$ (Ω)	$Q_2$		$W(F)^{0.5}$
					$Y_{O_2}(F)^{n_1}$	$n_1$		$Y_{O_2}(F)^{n_2}$	$n_2$	
H <sub>2</sub> /H <sub>2</sub> 45% RH	40	0.84	3.68E–07	23.66	3.68E–6	0.83	–	–	–	–
	50	0.77	3.61E–07	9.72	4.25E–6	0.87	3.27	3.58E–02	0.34	–
	60	0.60	3.63E–07	5.55	4.67E–6	0.88	1.58	2.07E–02	0.58	–
	70	0.48	3.65E–07	3.31	5.35E–6	0.88	1.08	1.04E–02	0.73	–
O <sub>2</sub> /O <sub>2</sub> 45% RH	50	0.72	4.19E–07	16.87	4.02E–06	0.88	–	–	–	1.23E–02
	60	0.47	4.25E–07	10.19	4.61E–06	0.88	–	–	–	1.44E–02
	70	0.35	4.19E–07	6.74	4.98E–06	0.88	–	–	–	1.33E–02
H <sub>2</sub> /H <sub>2</sub> 45% RH	40	0.17	4.96E–07	–	–	–	–	–	–	–
	50	0.13	5.30E–07	–	–	–	–	–	–	–
	60	0.11	4.96E–07	–	–	–	–	–	–	–

Thus,  $R_2$  and  $Q_2$  are parameters associated with mass transport phenomenon (diffusion and/or adsorption ( $H_2 = 2H_{ads}$ )) so it seems that analytical relations can be established between these parameters and the diffusion coefficients. For example, if the impedance of the  $R_2/Q_2$  branch were equal to  $Z_w$ , as in the oxygen case, then it would be given by Eq. (1):

$$Z_w \equiv R_{DO} \left[ \frac{\tanh \sqrt{j l_e^2 (\omega/D)}}{\sqrt{j l_e^2 (\omega/D)}} \right] \quad (1)$$

where  $l_e$  is the thickness of the electrode,  $D$  the coefficient of diffusion and  $R_{DO}$  the value of  $Z_w$  for frequency  $\omega = 0$  being  $j$  the complex number.

It should be noted that the EC obtained corresponds to the entire PEM. The EC for half-cell (single electrode and its interface under supported conditions), reported by MacDonal [1], is here generalised to a full-cell situation. One then obtains two contributions to the impedance, each one associated with an electrode. Since the electrodes are assumed to be identical, the two impedances are identical and may be combined to yield, theoretically, a result which is a combination of the individual impedances.

According to Ciureanu and Wang [8], it is suggested that the impedance pattern in SM conditions for  $H_2/H_2$  cells at 45% RH, shows evidence of two processes occurring at the interface. The first process (at intermediate frequencies) is associated with the charge transfer and the second (at low frequencies) is assigned to the pseudo-capacitance resulting from the presence of adsorbed hydrogen species. A similar effect was noted when  $O_2/O_2$  is injected, but in this case the constant phase element (CPE) is an almost Warburg impedance related to the diffusion mechanism which is, in this case, a kinetically slower process than that of  $H_2$  adsorption mechanism.

From the impedance plots, a significant depression of low frequency semicircles was noted (Fig. 3a), which suggests that the hydrogen adsorption mechanism is not a simple process. To verify this observation, the CPE model was used, in which the two capacitances are replaced by the corresponding CPE, defined in Eq. (2):

$$Z_{CPE} = Z_0(j\omega)^{-n} = \frac{1}{Y_0(j\omega)^{-n}} \quad (2)$$

where  $Z_{CPE}$  is the impedance of CPE,  $Y_0$  the pseudo-capacitance and  $\omega$  is the angular frequency.

Wagner et al. [9] reported the impedance response of a single PEMFC in a SM operation with  $H_2/H_2$  and  $O_2/O_2$  as injected gases. The impedance values extracted from the EC are higher for the case of oxygen injection in both compartments than for the hydrogen case. This seems to show that the high impedance in “normal mode operation” might be due mainly to the cathode process, as suggested by Romero-Castañón et al. [12].

This result was checked and the impedance responses recorded for the  $45 \pm 5\%$  RH in  $H_2/H_2$  and in  $O_2/O_2$  at  $70^\circ\text{C}$

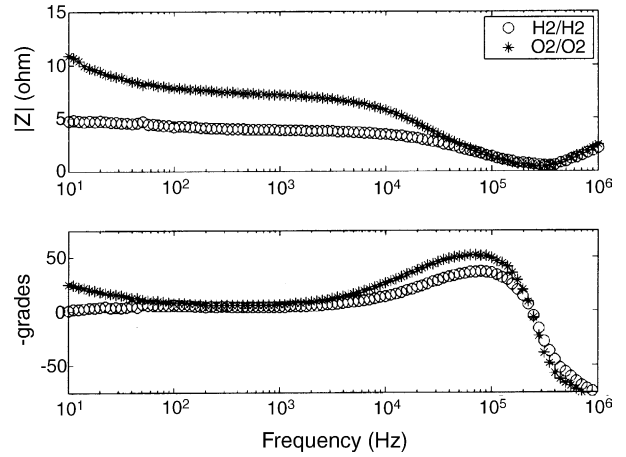


Fig. 5. Bode plots of the impedance  $Z$  of the PEMFC with  $H_2/H_2$  and  $O_2/O_2$  at  $45 \pm 5\%$  RH and at  $70^\circ\text{C}$ .

are shown in Fig. 5. The top plot shows  $|Z|$  while the bottom plot shows phase angle  $\theta$  as a function of frequency. Note that the minimum frequency is 10 Hz.

As can be seen from Fig. 5, in the frequency range studied, the impedance spectrum obtained shows that the  $H_2/H_2$  anode impedance is half of the  $O_2/O_2$  cathode impedance. As reported elsewhere [8], the SM has the advantage of studying a system made of the superposition of two identical sub-circuits (one for each interface).

The impedance pattern for the case of hydrogen injected in both compartments shows a system with two different time constants at 1 kHz and 1 Hz. It was concluded that the electrical behaviour of the EC of an entire PEMFC working in SM with hydrogen can be described by a series combination of the resistance of the membrane and two identical circuits, one for each electrode–membrane interface.

### 3.3. Influence of the temperature–interaction with $R_m$ activation energies

The expression (3):

$$\sigma_1 = \sigma_{01} \exp \left( \frac{-E_a}{KT} \right) \quad (3)$$

is the Arrhenius law and it has been used to experimentally determine the energy of activation of the electrical conductivity of the membrane. The exponential factor of the Arrhenius law,  $\exp(-E_a/KT)$ , indicates the contribution of the activated molecules that have an energy not less than  $E_a$ . This parameter decreases at a higher  $E_a$ , that is, at the higher activation energy, which means difficulty for molecules to acquire that energy and which in turn corresponds to a reduction in the rate of reaction.

The plots of log of proton conductivity versus reciprocal temperature (Fig. 6) were used to calculate these activation energies. The proton conductivity data were obtained from the intersection of the impedance curve and the  $Z'$  axis in Fig. 3.

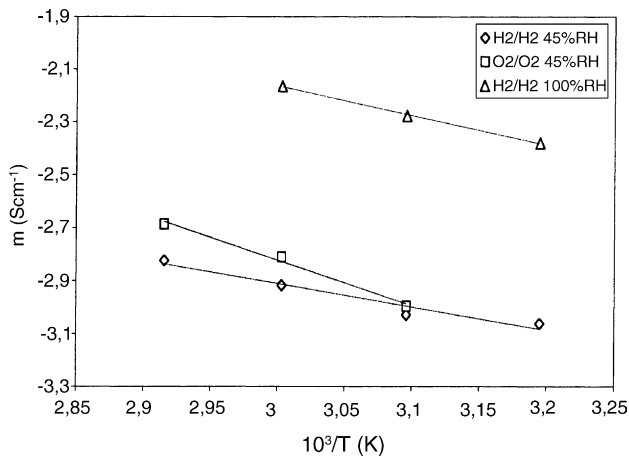


Fig. 6. Arrhenius plot of membrane conductivity.

The experimentally obtained activation energies ( $E_a$ ) and the proton conductivity ( $\sigma$ ) of the membrane Nafion<sup>®</sup> 117 are shown in Table 2.

Some authors [13,16] claim values of Nafion<sup>®</sup> conductivity of 0.15–0.20 S cm<sup>-1</sup> at 100 °C and at 100% RH. The values found in this work are recorded in Table 2. The value of  $1.58 \times 10^{-2}$  S cm<sup>-1</sup> at 100 °C and 100% RH is one order of magnitude lower than those above. However, other authors have also reported values similar to those in this work [17,18]. Therefore, the problem is still unresolved.

At present, our research efforts are focussed on enhancing the conductivity of Nafion or on the search for new materials, rather than on the proton conduction process. Therefore, very little attention has been paid to the proton activation energy and the literature on the topic is very scarce.

The value of Nafion<sup>®</sup> activation energy normally accepted in the literature is around 0.18–0.20 eV [16], which can be fitted to a typical ionic hopping transport. However, Sone et al. [14] reported, for 45–80 °C, an activation energy of 0.02 eV, which is much smaller than that reported by others. Sone et al. [14] pointed to two contradictory effects to explain the small value. At high-temperature, the membrane retains less water and hence the conductivity decreases, but simultaneously, according to the Arrhenius equation, the conductivity should increase with temperature.

The activation energies obtained in our investigation are shown in Table 2. For both values of RH, the activation energy is similar for H<sub>2</sub>/H<sub>2</sub> symmetrical mode, though the conductivity changes from  $1.21 \times 10^{-3}$  S cm<sup>-1</sup> at 60 °C and 45% RH, to  $6.84 \times 10^{-3}$  S cm<sup>-1</sup> at the same temperature but at

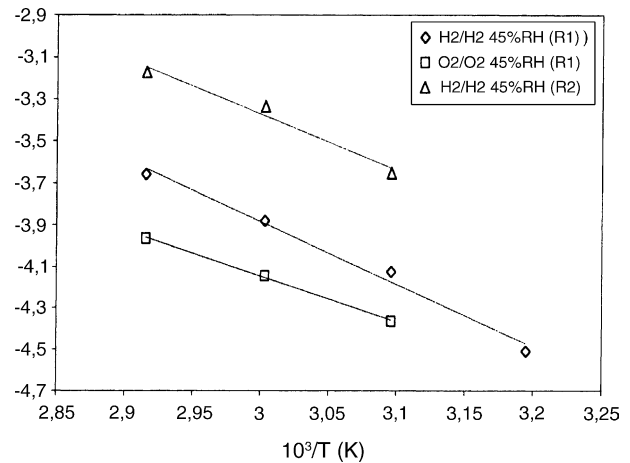
Table 2  
Experimental activation energies and electrical conductivities of membrane (Nafion 117) at 60 °C

Percentage RH gas injected	45% RH H <sub>2</sub> /H <sub>2</sub>	45% RH O <sub>2</sub> /O <sub>2</sub>	100% RH H <sub>2</sub> /H <sub>2</sub>
$E_a$ (eV)	0.17	0.32	0.21
$\sigma$ (S cm <sup>-1</sup> )	$1.21 \times 10^{-3}$	$1.55 \times 10^{-3}$	$6.84 \times 10^{-3}$

Table 3

Experimental activation energies and electrical conductivities for interface processes at 60 °C

	45% RH H <sub>2</sub> /H <sub>2</sub>		45% RH O <sub>2</sub> /O <sub>2</sub>	
	$E_a$ (eV)	$\sigma$ (S cm <sup>-1</sup> )	$E_a$ (eV)	$\sigma$ (S cm <sup>-1</sup> )
$R_1$	0.57	$1.32 \times 10^{-4}$	0.42	$7.18 \times 10^{-5}$
$R_2$	0.52	$4.63 \times 10^{-4}$	–	–

Fig. 7. Arrhenius plot of charge transfer process ( $R_1$ ) and H<sub>2</sub> adsorption process ( $R_2$ ).

100% RH as can be seen in Table 2. This fits the actual values of Nafion<sup>®</sup> conductivity, for which the activation energy is 0.21 eV, confirming the hopping-Grothaus mechanism expected.

The same study could be made from the fitted values ( $R_1$  or  $R_2$ ) for the equivalent sub-circuits obtaining the activation energies for the charge and the mass transport mechanisms in both interfaces. The values obtained are shown in Table 3.

The conductivity plots from which the activation energies were calculated are shown in Fig. 7. The activation energy values indicate the presence of electronic conductivity at the interface, which means that a mixed conduction (protonic–electronic) transport process with semiconductor behaviour is indicated. The conductivity value ( $4.63 \times 10^{-4}$  S cm<sup>-1</sup>) of the interface processes is more than one order of magnitude lower compared to membrane conductivity, which means that it is still important to reduce the blocking effect of the interface during MEA fabrication. This fact is generalised in all the PEMFCs and it was clearly noticed by using the SM operation. Therefore, the membrane–electrode assembly process is a significant challenge at present.

#### 4. Conclusions

From the results and discussion above, the following conclusions may be drawn.

- (1) Our investigation shows the equivalent circuit of a PEM-type fuel cell working in “symmetrical mode”, and at 45% RH, with the same gas injected in both electrodes. It demonstrates the potential of the EIS technique as a tool for researching processes that occur in the PEMFC and for characterising the influence of the operating conditions.
- (2) The analysis of this study shows that EIS permits us to distinguish between effects of the gases (oxygen and hydrogen) injected in the cell which are a substantial part of the real working components of the PEMFC. It is also possible to assess the effect of water content in the cell, and its effect on the conductivity of the Nafion® under known conditions.
- (3) The analysis of the activation energies provides an indication of the different electrical transport mechanisms that are present in the components and interfaces. Thus, it is clear that the EIS, using SM operation and low water partial-pressures, is an appropriate technique to model and characterise PEMFC using an equivalent electric circuit for achieving the double objective of gaining a quantitative/qualitative knowledge of the cell, and offering rules that allow us to improve the design and operation of the cell.

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