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An empirical equation for polymer electrolyte fuel cell (PEFC) behaviour

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Abstract

A simple analytical expression to determine cell potential (E) against current density (i) behaviour in polymer electrolyte fuel cells (PEFCs) was derived. The equation describes experimental data over the whole range of current density taking into account possible mass transport limitations. The empirical equation was used to fit experimental data obtained in a 50 cm^2 single cell in H$_2$/air operation using electrodes with low Pt loading ($\sim$0.1 mg cm^{-2}). A good agreement between theoretical and experimental data was found.

List of symbols

b	Tafel slope (V dec^{-1})
E	cell potential (V)
E_r	cell reversible potential (V)
F	Faraday constant (96 487 C mol^{-1})
i	cell current density (mA cm^{-2} or A cm^{-2})
i_0	exchange current density (mA cm^{-2})
j_i, j_L	limiting current densities (A cm^{-2})
R	cell resistance (Ω cm^2)
$\mathscr{R}$	Gas constant
T	absolute temperature (K)
z	number of electrons transferred in the electrochemical reaction (g equiv mol^{-1})

1. Introduction

In a polymer electrolyte fuel cell (PEFC) the use of air as oxidant for the cathodic reaction causes several problems due to the mass transport overpotential which makes difficult the interpretation of the cell potential against current density behaviour, especially at medium and high current density. For this reason, there is interest in the development of models describing the cell performance and the current distribution in porous electrodes.

Several modelling studies [1–11] were carried out to elucidate the electrochemical behaviour of a PEFC, and for this purpose several analytical expressions were derived. However, theoretical models based on mechanistic approaches require the knowledge of not readily available parameters such as humidity levels, transfer coefficients, thickness of the membrane etc. [1, 2, 5, 8], because their values inside the cell are modified by gradients of temperature, pressure and humidity, by physical constraints and by current density [12–16]. On the other hand, empirical models are not generally able to cover the whole current range when activation, mass transport and ohmic overpotentials are simultaneously present; for this reason, they are not applicable over a wide range of conditions.

Srinivasan et al. [6] developed an equation that describes the relation between the cell potential and current density in the low and intermediate current density region, where electrode reactions are activation and ohmic controlled. Starting from this point, Kim et al. [17] introduced an additional term that allows fitting of the experimental curves over the whole range of current density. However, they did not find evidence of a link between the introduced parameters and the experimental variables related to mass transport.

In the present work, an equation derived from a semi-empirical approach is proposed. Through a mechanistic similarity, the basic electrochemical theory was used to introduce a simple equation that fits the experimental data over the whole range of current density with high accuracy. The resulting equation appears to be valid under several experimental conditions. On the basis of the experimental data obtained with a 50 cm^2 H$_2$/air single cell using low Pt loading electrodes ($\sim$0.1 Pt mg cm^{-2}), an attempt to offer an interpretation of the inserted parameters is described.

2. Experimental details

Several electrodes with the same type of catalyst layer and different backings were taken into consideration to validate the model.

The electrodes were manufactured by a spray method, as previously described [18, 19]. The catalyst layer was prepared by mixing a 20 wt% Pt on Vulcan XC-72 (E-TEK, Inc.) catalyst with ionomer Nafion® as a binder. The Pt loading was maintained constant at about 0.1 mg Pt cm^{-2}. The backings consisted of a PTFE-bonded carbon layer with 20 or 40% PTFE loading sprayed on different substrates. Carbon paper (Toray TGPH090 and Kureha E-75), and carbon cloth (type A, purchased from E-TEK) were used as support for the carbon layer.

The membrane and electrode assemblies (MEAs) were prepared by hot-pressing the electrodes to the membranes at 130 °C for 3 min with Nafion® 117, 115 and 112 membranes.

Experimental measurements were carried out in a 50 cm^2 H_2/air single cell (Globe Tech. Inc.) at 70 and 80 °C and different gas pressure (1/1, 1.5/1.5, 2.5/3 or 3/5 absolute bar for anode/cathode side). The fuel cell test station was equipped with a humidifying system of the reactant gases and temperature control of the cell [19]. The humidifying temperature for H_2/air was maintained at 85/75 °C and 95/85 °C for cell temperature of 70 and 80 °C, respectively. A constant flow configuration was used with gas fluxes of 1.5 and 3 times the stoichiometric value at 1 A cm^{-2} for H_2 and air, respectively. The gas flow rates were fixed and checked by electronic mass flow controllers (MKS Instruments). The cell potential against current density measurements were recorded using a computer interfaced with the fuel cell station.

3. Development and analysis

As previously reported [6], the cell voltage against current density behaviour, in the activation and ohmic controlled current density region, can be described by the following relationship:

$$E = E_0 - b \log i - Ri \tag{1}$$

where $E_0 = E_r + b \log i_0$ and E_r is the reversible potential of the cell, i_0 is the exchange current density, b is the Tafel slope for oxygen reduction and R represents the resistance which causes a linear variation of E with i. The predominant contribution to R is the ohmic resistance of the proton exchange membrane; the other contributions, due to mass transport and charge transfer, become important in the last part of the intermediate current density region.

To fit the cell potential against current density behaviour over the whole current density range, Equation 1 was modified by Kim et al. [17] by introducing an additional term as follows:

$$E = E_0 - b \log i - Ri - m \exp(ni) \tag{2}$$

where the parameters m and n were derived from mathematical and statistical considerations. Starting from the interesting results obtained with Equations 1 and 2, we have carried out an analysis of the different contributions to the mass transport limitation.

The measured resistance was found to vary with current density; with air, ohmic losses do not represent the major fraction of the measured loss at high current density [2]; to explain this behaviour different approaches were attempted [2, 4–5, 15, 20, 21]. In the present study, we considered two different contributions: an ohmic contribution, independent from current density, and a non ohmic one that varies with the current density; in Equation 1, R represents the ohmic resistance, then a term that takes into account the non ohmic contribution must to be included.

Operating conditions (cell temperature, gas pressure etc.), parameters correlated to the MEA morphology, and cell design influence in different ways the mass transport properties, the resulting effect being a depletion of the reactant species concentration at the reaction sites as the current density increases. This situation is quite similar to that of the concentration overpotential expressed by [22]:

$$\eta^C = (\mathscr{R}T/zF)\ln\{1 - (i/j_L)\} \tag{3}$$

where z is the ionic charge and the remaining symbols are listed at the outset of this paper.

Different MEA regions, diffusion and catalyst layers, electrolyte/catalyst interface, membrane may contribute to mass transport limitations in PEFC; they act simultaneously and are mutually correlated. Likewise, each contribution can be expressed by an equation similar to Equation 3, where j_L is the limiting current density associated to the considered contribution, and the prelogarithmic term depends on the various physical parameters related to the nature of the limitation. In particular, we expect that this term will depend on current density, whose effect on the fuel cell working conditions is prominent. Accordingly, it has been reported that MEA operation is not uniform at every point of its surface at different current densities [16].

On the basis of previous considerations, a linear combination of the different terms can not be used to account for the superposition of contributions. To a first approximation we can simply assume that the total mass transport overpotential is described by the following expression:

$$\eta = \alpha i^k \ln(1 - \beta i) \tag{4}$$

where αi^k accounts for the prelogarithmic terms associated to the different contributions and acts as an 'amplification term', expressed in potential units; k is a dimensionless number and β is the inverse of the limiting current density. The effect of the 'amplification term' on the logarithm is shown in Figure 1. The logarithm varies from 0 to $-\infty$ as βi increases from 0 to 1 (line), a constant prelogarithmic term changes the slope of the pseudolinear part in proximity of 0 (dotted line); the introduction of a power ($k \geqslant 1$) of the current density

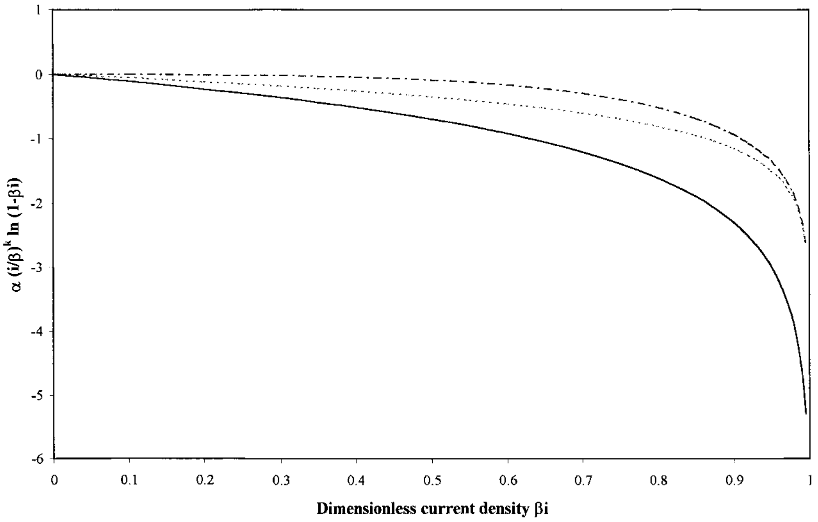


Fig. 1. Dimensionless plot of the analytical behaviour of Equation 4. Key: (– · –) $\alpha = 0.5$, $k = 2$; (· · · ·) $\alpha = 0.5$, $k = 0$; (——) $\alpha = 1.0$, $k = 0$.

reduces the slope and significantly extends the pseudo linear region (semidotted line). The addition of this term to Equation 1 gives the following equation, very similar to that reported by Kim et al. [17]:

$$E = E_0 - b \log i - Ri + \alpha i^k \ln(1 - \beta i) \tag{5}$$

using mA cm^{-2} as the unit for i.

On the basis of the above, Equation 5 is of general validity; its application appears to be extendible to other types of electrochemical cells.

The logarithmic term $\ln(1 - \beta i)$ in Equation 5 introduces a limit in the available current density: when the $(1 - \beta i)$ term approximates to zero, the logarithm changes to $-\infty$. For $k = 1$, α has the same dimension of R, and the term $\alpha \ln(1 - \beta i)$ can be interpreted as an additional resistance term due to the overall mass transport limitation.

A more careful analysis of Equation 5 can be made by varying α and k. Figures 2 and 3 show the behaviour of E against i when $k = 1$ and $k = 3$, respectively, α ranging from 0 to 0.6. E_0, b, R and β were fixed at values of 0.980 V, 0.060 V dec^{-1}, 0.285 Ω cm^2, 0.99 cm^2 A^{-1}, respectively, according to the literature and to our experimental data [4, 17–20, 23, 24]. By comparison of Figures 1 and 2, it can be seen that k and α affect the behaviour of the potential in the intermediate and high current density region; k mainly influences the point at which there is the departure from the linear behaviour of Equation 1, and α determines the shape of the curve at high current density (see above). Moreover, for each fixed k value, as α becomes smaller and smaller, the last term of Equation 5 approximates to zero and therefore Equation 5 changes to Equation 1.

4. Application to experimental data

To validate Equation 5 and find some correlation between the introduced parameters and the physico-

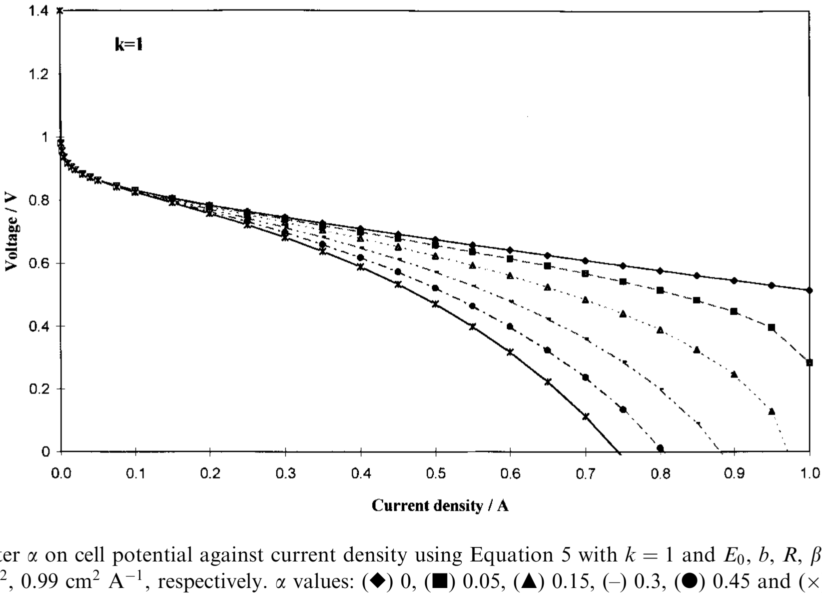


Fig. 2. Effects of parameter α on cell potential against current density using Equation 5 with $k = 1$ and E_0, b, R, β fixed at values of 0.980 V, 0.060 V dec^{-1}, 0.285 Ω cm^2, 0.99 cm^2 A^{-1}, respectively. α values: (◆) 0, (■) 0.05, (▲) 0.15, (–) 0.3, (●) 0.45 and (×) 0.6.

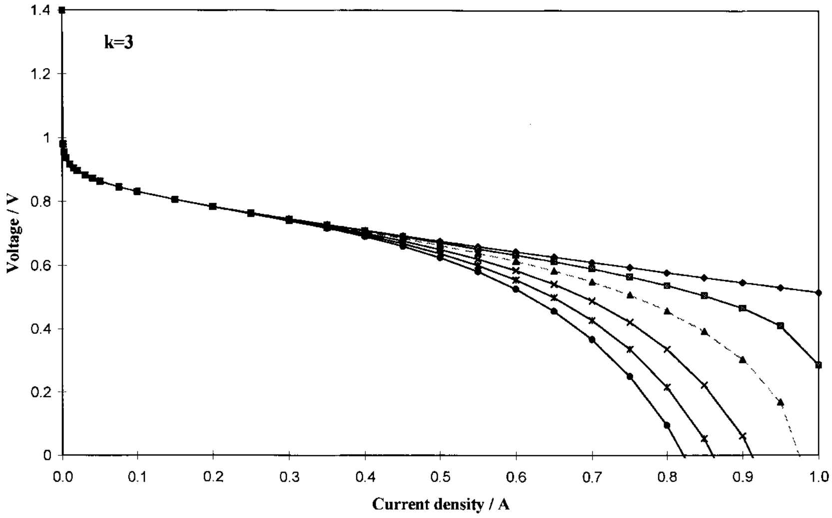


Fig. 3. Effects of parameter α on cell potential against current density curve using Equation 5 with $k = 3$ and E_0, b, R, β fixed at values of 0.980 V, 0.060 V dec^{-1}, 0.285 Ω cm^2, 0.99 cm^2 A^{-1}, respectively. α values: (◆) 0.00, (■) 0.05, (▲) 0.15, (×) 0.30, (∗) 0.45 and (●) 0.60.

Table 1. Calculated values of electrode kinetic parameters from some typical sets of PEFCs performance data using Equations 1 and 5

Sample	Substrate	PTFE in carbon layer/%	Equation	E_0 /V	b /V dec^{-1}	R /Ω cm^2	α /V(cm^2 A^{-1})^k	k	β /cm^2 A^{-1}	Correlation coefficient
A	C. Paper	40	1	0.966	0.060	0.3870				0.99956
	Kureha E-75		5	0.966	0.060	0.3884	0.0735	3.08	0.9365	0.99994
B	C. Cloth	40	1	0.937	0.050	0.570				0.99898
	E-Tek type A		5	0.937	0.051	0.559	1.865	2.66	1.010	0.99991
C	C. Paper	20	1	0.956	0.052	0.4953				0.99922
	Toray TGPH090		5	0.957	0.053	0.4864	0.309	3.26	0.9602	0.99994

chemical variables, the fitting of experimental data obtained on three electrodes with different structure under different operating conditions was performed, using software based on a nonlinear regression and applying Equation 1 for i up to 300 mA cm^{-2} and Equation 5 in the whole range of current density.

Representative results at 70 °C and gas pressure of 2.5/3 bar (absolute) for anode/cathode side are reported in Table 1. The correlation coefficient obtained with Equation 5 is in excess of 0.999, and the values for E_0, b and R are similar in the two cases. Values of the exponent k are in the range 2–4 in 90% of the performed fits (not reported).

Afterwards, a new series of fits was performed on the standard electrode (sample C) by locking the parameter k. To simplify calculations k values were considered as an integer in the range 1–5; results are reported in Table 2. As expected, by increasing k the parameter α increases and β decreases, in accordance with previous analysis. Moreover, the increase in k causes a decrease in Tafel slope (b) and E_0, while R increases to compensate the effect of the last term in Equation 5 at low and intermediate current densities. From these results, the experimental data of cell potential against current density will be analysed with Equation 5 by fixing $k = 3$.

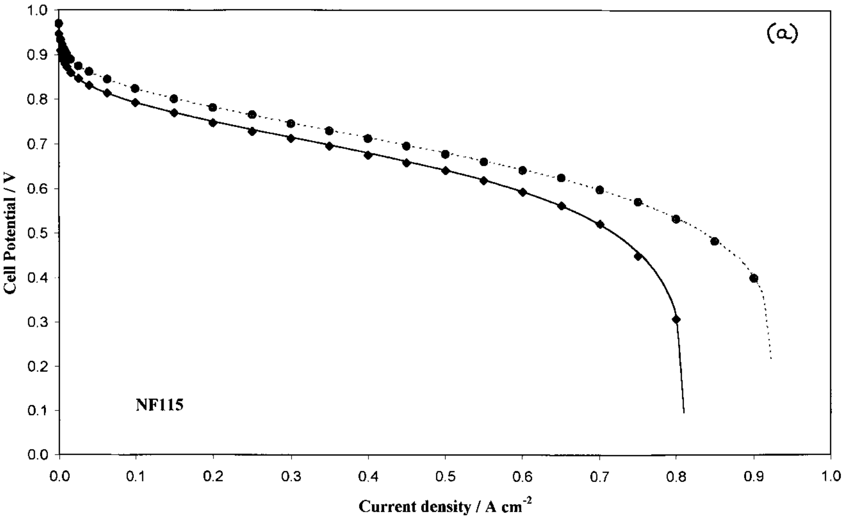
An attempt to find a correlation between the introduced parameters and the physicochemical variables was done by analysing experimental data from sample C as a function of the reactant gas pressure, cell temperature and different membranes.

In Figures 4 and 5, experimental data for cell potential against current density (symbols) are fitted with Equation 5 (lines); good agreement was found. The values of the electrode kinetic and mass transport parameters obtained by applying Equation 5 under different experimental conditions are reported in Table 3.

The increase in gas pressure produces an increase in E_0 and a decrease in β, for NF117 and NF115 membranes; this behaviour is a consequence of the increased reagent concentration in the cell. The Tafel slope b does not change, being independent of pressure.

Table 2. Values of electrode kinetic parameters calculated with Equation 5 for k = 1,2,3,4 and 5 on sample C at 70 °C and 1.5 bar (absolute) gas pressure

k	E_0 /V	b /V dec^{-1}	R /Ω cm^2	α /V(cm^2 A^{-1})^k	β /cm^2 A^{-1}	Correlation coefficient
1	0.938	0.065	0.193	0.106	1.148	0.99989
2	0.937	0.063	0.246	0.112	1.146	0.99995
3	0.936	0.061	0.275	0.132	1.137	0.99994
4	0.935	0.059	0.293	0.165	1.121	0.99985
5	0.934	0.058	0.305	0.222	1.088	0.99973



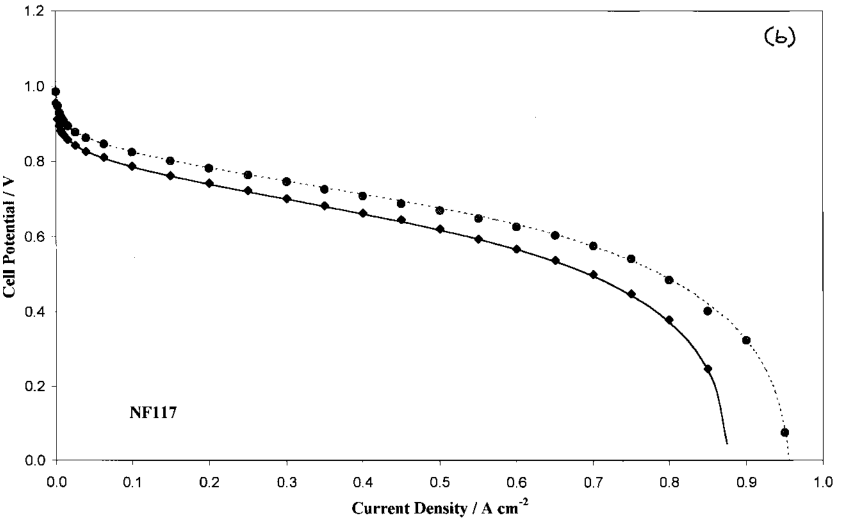


Fig. 4. Comparison between experimental (bullets) and theoretical (lines) data at 70 °C: (a) gas pressures of 1/1 (◆) and 2.5/3 (●) bar (absolute) for H_2/air, using Nafion 115 membrane; (b) gas pressures of 1.5/1.5 (◆) and 3/5 (●) bar (absolute) for H_2/air, using Nafion 117 membrane.

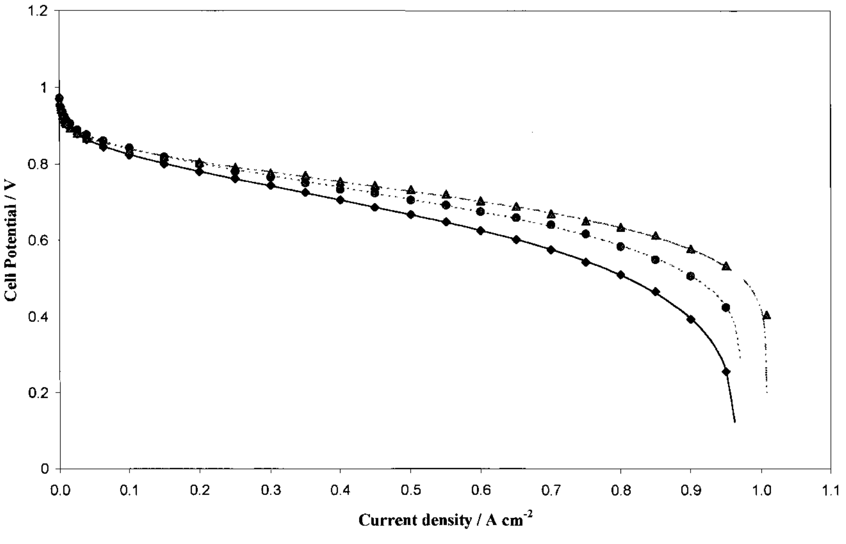


Fig. 5. Comparison between experimental (bullets) and theoretical (lines) data at 80 °C and gas pressures of 3/5 bar (absolute) for H_2/air, respectively, varying the Nafion membrane: NF112 (▲), NF115 (●), NF117 (◆).

Table 3. Calculated values of electrode kinetic parameters at 70 and 80 °C as function of hydrogen/air pressures and membrane thickness. Reported errors are the maximum statistical errors coming from the performed fits

Operating conditions			Fitting results					
Membrane	Temperature /°C	Gas Pressures H_2/air/ bar (abs.)	E_0 /V ± 2	b /V dec^{-1} ± 0.002	R /$\Omega\ \mathrm{cm}^2$ ± 0.01	α /mV$(\mathrm{cm}^2\ \mathrm{A}^{-1})^k$ ± 0.007	β /$\mathrm{cm}^2\ \mathrm{A}^{-1}$ ± 0.004	α/β /mV$(\mathrm{cm}^2\ \mathrm{A}^{-1})^{k-1}$
NF117	70	1/1	0.937	0.056	0.30	0.147	1.214	0.121
		1.5/1.5	0.936	0.061	0.28	0.132	1.137	0.116
		2.5/3	0.962	0.058	0.28	0.129	1.102	0.117
		3/5	0.970	0.060	0.24	0.126	1.040	0.121
NF115	70	1/1	0.933	0.058	0.24	0.116	1.234	0.094
		1.5/1.5	0.940	0.059	0.23	0.110	1.201	0.092
		2.5/3	0.956	0.053	0.25	0.064	1.083	0.059
NF112	70	2.5/3	0.946	0.050	0.19	0.038	0.994	0.038
NF117	80	3/5	0.961	0.054	0.28	0.078	1.036	0.075
NF115			0.966	0.051	0.23	0.052	1.029	0.051
NF112			0.955	0.049	0.18	0.043	0.992	0.043

The cell resistance (R) is clearly influenced by the membrane thickness; a decrease in R is observed passing from NF117 to NF115 and NF112, under the same cell conditions (70 °C, 2.5/3.0 bar; 80 °C, 3/5 bar). However, the expected resistance values, calculated for Nafion® conductivities of 0.17 and $0.12\,\Omega^{-1}\,\mathrm{cm}^{-1}$ at 80 and 70 °C, respectively [1], and thickness of 210, 160 and 60 μm for NF117, NF115, NF112, respectively, are about 0.12 to $0.14\,\Omega\,\mathrm{cm}^2$ lower than the values calculated using Equation 5. This difference may be attributed to the resistance of other cell components such as backings, flow plates and current collectors.

By increasing the gas pressure, the cell resistance appears to be constant, with the exception of NF117 at 70 °C and 3/5 bar, for which we obtained a decrease in R, even though at the same gas pressure conditions and 80 °C the resistance increases. The dependence of R on gas pressure was analysed by other authors using different models [1, 15]. Particularly, Bernardi et al. [1] found a decrease in resistance as pressure increased, but by applying their equation to NF117 at 70 °C we obtain a decrease in resistance of the order of $1 \times 10^{-3}\,\Omega\,\mathrm{cm}^2$ from 1/1 to 3/5 bar. This decrease is very small, even lower than the regression error. According to Eikerling et al. [15], the progressive dehydration of the membrane at the anode side, as current density increases, is a limiting factor that may be balanced by a small pressure increase at the cathode inlet to force the water towards the anode side (as in the case of 3/5 bar at 70 °C); consequently, the resistance decreases. A further increase in cell temperature up to 80 °C enhances the water management problems and the difference in gas pressure is not sufficient to balance the dehydration of the membrane. The observed behaviour seems to be in accordance with Eikerling's model. No further analysis at different gas pressures, in order to confirm the observed behaviour, was made. The parameter α with $k = 3$ has the dimension of $V(\mathrm{cm}^2\,\mathrm{A}^{-1})^3$. From a dimensional point of view this could result in the following equation:

$$\alpha = (\mathcal{R}T/zF)(m_1 j_1)^{-1}(m_2 j_2)^{-1}(m_3 j_3)^{-1} \qquad (7)$$

where the j_i are the limiting current densities associated to mass transport limitation from the different contributions; and m_i are dimensionless numbers. In this case, each limiting factor probably contributes to mass transport overpotential by the inverse of the associated limiting current density, or a power of it. Each j_i must be equal to or greater than the assymptotic current β^{-1}: *ab absurdo*, if $j_{\mathrm{i}^*} < \beta^{-1}$, we cannot reach β^{-1}, because the cell attains its limiting current density before reaching β^{-1}. This means that if there is a dominant effect in mass transport limitation, the limiting current density of the system coincides with the current density of the determining contribution. If α is a function of the limiting current density of all contributions, while β^{-1} depends on the limiting current density of the determining contribution, the comparison of the behaviour of α with $(\alpha\beta^{-1})$ may be useful to understand if the experimental variable influences the determining contribution or the other ones. In this case, taking into consideration the increase in gas pressure we can see that both the α and β parameters decrease, but the ratio α/β is almost constant; then the two parameters vary proportionally and we expect that the determining contribution will be influenced by the gas pressure. Indeed, by decreasing the membrane thickness α and α/β decrease in the similarly; then the determining contribution is not greatly influenced by the membrane thickness, and the variation of α is mainly due to the other contributions.

5. Conclusions

A new empirical equation to fit experimental data for a fuel cell in the whole range of current density was proposed. Equation 5 was obtained by introducing to the equation of Srinivasan [6] a term accounting for mass transport limitation. This term contains three parameters: the inverse of the limiting current, β; a coefficient, α; and an exponent, k. In spite of its simplicity the proposed equation is able to fit experimental data with great accuracy.

By applying Equation 5 the influence of some variables, gas pressure and membrane thickness on the cell resistance was evaluated. As a result of this analysis, Equation 5 appears to be able to separate the ohmic contribution from the others. For a fixed value of α and β, the choice of exponent k defines the current density at which the mass transport term becomes significant. A first attempt at correlating α to the cell and electrode properties was proposed through dimensional analysis. The fit of experimental data agrees with the assumptions, but is not sufficient to define the correct mathematical correlation between this parameter and the physical properties of the system.

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